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Global Change Teaching Unit

Target grade & Subject: Gr. 11; Chemistry

Unit Overview:
As our earth “shrinks,” understanding global issues in economics, politics, culture, and in science become an important prerequisite for students graduating high school. Global changes can be difficult for young minds to comprehend because of the intense complexity associated with them. This unit seeks to take one issue, acid precipitation, and apply it first to local implications, then expand students’ understanding of the global process and impact on other societies. Topics to be covered in this unit include 1) the formation of acid precipitation, both natural and man-made, 2) how acid precipitation can benefit or harm society and the earth, 3) critiquing arguments about personal or societal issues based on scientific evidence, and 4) presenting the information in a way that is meaningful to them personally and to the larger society. Students will accomplish these goals by simulating the production of acid precipitation in the laboratory, by evaluating maps of various pollutant sources and by writing a web report to be posted to the school’s website (High School Content Expectations Documents 2007).

Goals:
- Explain what acid precipitation is and where it forms
- Explain the formation of acid precipitation, both natural and man-made
- Describe how acid precipitation is harmful to humans and to the earth
- Evaluate a piece of legislation that increases use of renewable resources in light of acid rain formation
- Write a web report on acid rain from a variety of perspectives

Sources Consulted:
- High School Science Content Expectations Companion Document 2007
- High School Social Studies Content Expectations Companion Document 2007
- High School English Language Arts Content Expectations Companion Document 2007
- Information found on the Global Change CD 2008
- Variety of websites – all URLs are found in each section

Learning Objectives:
Students will be able to:
1. Explain the formation of acid precipitation, both natural and man-made
2. Write balanced chemical equations for the formation of acid precipitation
3. Describe and conduct tests to determine the formation of an acid or base
4. Explain why areas with limestone beds are less adversely affected by acid precipitation
5. Use their knowledge of acid precipitation and its affects on society and the earth to write a web report on acid rain from a variety of perspectives
Michigan Content Curriculum Addressed [E=Earth Science, C=Chemistry, CG=Contemporary Global Issues (Social Studies), ELA = English Language Arts]:

C1.2B Identify and critique arguments about personal or societal issues based on scientific evidence
C5.7C Describe tests that can be used to distinguish an acid from a base
C5.7D Classify various solutions as acidic or basic, given their pH
C5.7E Explain why lakes with limestone or calcium carbonate beds experience less adverse effects from acid rain than lakes with granite beds
C5.7h Explain why sulfur oxides and nitrogen oxides contribute to acid rain

E2.1B Analyze the interactions between the major systems that make up the earth
E2.1C Explain how a change in one system affects other earth systems
E2.3A Explain how carbon exists in different forms within earth systems and how those forms affect humans
E2.3d Explain how carbon moves through the earth system and how it may benefit or harm society

CG2 Explain the changes over the past 50 years in the use, distribution, and importance of natural resources (including land, water, energy, food, renewable, non-renewable, and flow resources) on human life, settlement, and interactions by describing and evaluating social, political, economic, and environmental consequences of the development, distribution, and use of natural resources

ELA 1.2 Use writing, speaking, and visual expression for personal understanding and growth.
ELA 1.3 Communicate in speech, writing, and multimedia using content, form, voice, and style appropriate to the audience and purpose.

5 Blocks (80 minutes each) of Classroom or Lab Activities:

Block 1: FORMATION OF ACID RAIN AND ITS EFFECTS

Learning Objectives 1 & 2

10 minutes
Warm-up:
Let the students know that marble is a rock that is derived from limestone (chalk), whose formula is CaCO$_3$. In front of the students, place several drops of an acid (vinegar, HCl, etc.) onto a piece of chalk that has been placed in a beaker or test tube.

Have the students write what they see happening to the chalk and try to predict what composes the bubbles. If students have a background in chemical reactions already, they should write a balanced chemical equation (make sure you tell them the name of the acid). Show a picture of a defaced marble statue and have them write about what may have caused the statue to become defaced.
35 minutes TOTAL (broken into two segments, 25 and 10 minutes)
Lecture:
Using the notes modified by Burton, go over the information on acid rain with the students. Note-taking has been broken up by a lab activity.

25 minute Lecture:
To show students how a cloud is formed you can take a 2-L bottle (remove label) and replace its cap with a Fizz keeper. Place a few drops of water in the bottle and swish it around for a minute (you need water vapor to make clouds!). Take a lit match, blow it out and waft a few particles of smoke into the bottle (all cloud droplets must form on a condensation nuclei like smoke or dust – or even a bacterium!). Screw on the Fizz keeper and start pumping (to really get a good idea of what is happening, take a temperature strip and tape it to the inside of the bottle – temperature will rise as pressure increases – just like in our atmosphere!). When the bottle is pressurized, unscrew the Fizz keeper and a cloud should appear!

To help illustrate pH, you may want to give students pH test strips (not litmus paper – this only tells you if it is an acid or a base, not HOW acidic or basic it is) and several household items to test such as distilled water, lemonade, orange juice, milk, milk of magnesia, vinegar, an apple or orange, ammonia, bleach (don’t put near ammonia!), Works®, spit, apple juice, pop, sugar water, rain water, etc.

10 minute Lecture:
Finish the notes on who monitors the acid deposition and associated pollutants. Visit the websites listed and look for monitoring in your area.

25 minutes
Activity:
See note sheet – “Acid Rain in a Bag”
You may need to go over surface area-to-volume ratios with students before they complete the assessment.

10 minutes
Assessment:
Lab questions

Block 2: ACID RAIN IN A MICRO-ENVIRONMENT

Learning Objective 3 & 4

5 minutes
Warm-up
Print the crossword puzzle on Acid Rain from the EPA’s website at www.epa.gov/acidrain/education/site_students/crossword.html

If you have a student who finishes early, they can be asked to poke small holes into the roasting pan or help set-up the aquarium
10 minutes
Review of yesterday’s lecture
Take a few minutes to review yesterday’s lecture. Students will be using FLINN SCIENTIFIC’S lab called “Acid Rain in a Micro-Environment” which contains some additional background about the industrial revolution’s impact on acid rain development, how terrestrial and aquatic systems are impacted by acid rain, and other reactions that take place besides acid rain formation.

50 minutes
Activity/Lecture
Use FLINN SCIENTIFIC’s lab called “Acid Rain in a Micro-Environment” to simulate acid rain production and the effects limestone has on the acidity of lake water.

After limestone is added, there is a 30 minute wait for the reaction to go to completion. Take this time to complete the note sheet on the effects of acid rain on the environment.

15 minutes
Assessment
Lab questions and analysis

Blocks 3 – 5 ACID RAIN FORUM

BLOCK 3

Learning Objectives 5

10 minutes
Instruction
Explain how the Acid Rain Forum will work.

10 minutes
Student organization
Students should take about 10 minutes to delegate roles and outline their approach and time allotment to research.

60 minutes
Internet Research
Students should take the remaining hour of class to look up information, related to their perspective, and record pertinent information – they also need to site their sources!

BLOCK 4

10 minutes
Review
You should take this time review the forum process, essential questions, clarify any issues and encourage students to work together on the report.

70 minutes
Web report
  Students should work on the web report for the rest of the block. They may need to do additional research as new questions or issues are raised.

  Students should present a rough draft copy to you to review – make suggestions and have students make a final copy for their presentation and posting to the web.

**BLOCK 5**

10 minutes
Instruction
  Give basic instructions on how to be polite listeners, set out guidelines for transitions between groups, time limits, how to post their web report, etc.

60 minutes
Web report presentations
  Students, as a group, should present their web report and post it to the website.

10 minutes
Peer evaluation
  Students should complete peer evaluations on each other.

Unit Assessment:
  Lab questions
  Web report
ACID PRECIPITATION

(Modified from Burton document on Global Change CD, 2008)

I. What is acid precipitation?
   a. Definitions
      i. Cloud or rain droplets combine with gaseous pollutants, such as oxides of sulfur and nitrogen, to make falling rain or snow acidic.
      ii. Rain that has become acidic after contact with certain atmospheric gases (primarily sulfur dioxide, carbon dioxide, and nitrogen oxides).
         www.dmh.gov.mm/glossary.cfm
      iii. Rain containing acids that form in the atmosphere when industrial gas emissions (especially sulfur dioxide and nitrogen oxides) combine with water wordnet.princeton.edu/perl/webwn
      iv. Precipitation whose pH is below 5
   b. pH scale (pH = power of the hydrogen) hydrogen referring to the H^+ ion
      1. 0-14 logarithmic scale
         1. pH of 4 is 100 times more alkaline or basic than a pH of 2
         2. How are a pH of 4 and 8 related? [pH 8 is 10^4 or 10,000 times more basic than a pH of 4]
      2. pH 7 is neutral
         1. Equal concentrations of H^+ and OH^- ions [water is H_2O or HOH and consists of H^+ and OH^- ions; when these ions are in equal concentrations, as in pure water, the pH is neutral or 7; adding an acid adds more H^+ ions to the solution and adding a base typically adds more OH^- ions to the solution. Hence adding a base to an acid neutralizes or equals out the ion concentrations]
      3. lower pH is more acidic
         1. Based on the diagram below, which is more acidic, an apple or milk? Ammonia or milk? [apple; milk]
         2. If rainwater has a pH of 5.2, which substance(s) show in the diagram below are more basic than the rainwater? [milk and ammonia]

(source: http://www.epa.gov/acidrain/ph.html)
c. “Natural rain” has a pH of 5.0 to 5.6
   i. CO₂ in atmosphere forms carbonic acid (H₂CO₃) - pH = 5.6
   ii. Other natural organic acids can lower pH to about 5.0

d. “Acid” rain has a pH of <5.0
   i. Due to man’s activities
      1. Automobile exhaust
      2. Power plants burning coal or oil
   ii. HNO₃ (nitric acid) and H₂SO₄ (sulfuric acid) are the two principle substances that make rain acidic
   iii. In 2006, much of the rain in northeastern US had a pH of around 4.4 to 4.6

II. Formation of acid precipitation

(source: [http://www.epa.gov/acidrain/index.html#what](http://www.epa.gov/acidrain/index.html#what))

VOC = Volatile Organic Compounds

A. Chemical Reactions

1. Formation of sulfur dioxide (SO₂) and nitrogen oxides (NO & NOx) (a.k.a. acid forming precursors):
   
   S (in fuel) + O₂ → SO₂
   N₂ + O₂ → 2NO
   2NO + O₂ → 2NO₂
   NO₂ + UV energy → NO + O
   O + O₂ → O₃
2. Formation of acids:
   \[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]
   \[ \text{SO}_2 + \text{H}_2\text{O}_2 \text{ and O}_3 \text{ (in clouds)} \rightarrow \text{H}_2\text{SO}_4 \]
   \[ \text{SO}_2 + \text{OH}^- + \text{O}_2 \text{ (in air)} \rightarrow \text{H}_2\text{SO}_4 \]
   \[ \text{SO}_2 + \text{Oxidants (from wet surfaces)} \rightarrow \text{H}_2\text{SO}_4 \]
   \[ \text{NO}_x + \text{sunlight} + \text{OH}^- \text{ (in air)} \rightarrow \text{HNO}_3 \]

B. Sources of acid forming precursors:

<table>
<thead>
<tr>
<th></th>
<th>Natural</th>
<th>Anthropogenic (man-made)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NOx</strong></td>
<td>Lightning, biological denitrification</td>
<td>Transportation, electric utilities, industry, biomass burning</td>
</tr>
<tr>
<td></td>
<td>About 40% of total</td>
<td>About 60% of total</td>
</tr>
<tr>
<td><strong>SO2</strong></td>
<td>Biological, volcanoes, sea spray</td>
<td>Electric utilities (especially coal burning), industry, oil refining, ore smelting</td>
</tr>
<tr>
<td></td>
<td>&gt; 60 % of total</td>
<td>&lt; 40% of total</td>
</tr>
</tbody>
</table>

1. Currently about 43% of anthropogenic NOx in US comes from motor vehicles (60% in Canada)
2. 70% of anthropogenic SO2 in US comes from power plants
3. Problem – man-made sources are concentrated
1998 National Nitrogen Oxide (NOx) Emissions by Principal Source Category (source U.S. EPA)

Vehicles and other engines 53%
Fuel-combustion electric utility 25%
Fuel-combustion industrial 12%
Fuel-combustion other 5%
All other 5%

Density Map of Sulfur Dioxide Emissions 2001
(Source: Environmental Protection Agency: http://www.epa.gov/air/data/geosel.html)
III. Deposition patterns

Deposition Patterns

A. $\text{NO}_3^-$ (nitrate) (NADP/NTN maps available at http://nadp.sws.uiuc.edu/isopleths/)

**Nitrate ion wet deposition, 2006**

B. $\text{SO}_4^{2-}$ (sulfate)

**Sulfate ion wet deposition, 1994**
C. \( \text{H}^+ \) (hydrogen)

D. Forms of acid deposition

1. wet deposition (rain, fog, snow)
2. dry deposition (acid gases and particles)
   - contribute up to 50% of total anthropogenic deposition
   - leaves and needles can filter from air and concentrate
   - more important near source – Go to lab page – “Acid Rain in a Bag”

Wet and Dry Deposition in Southwestern Pennsylvania - 1989-1999
(source: http://www.epa.gov/castnet/overview.html)
E. Monitoring of acid deposition: Acid rain's pH, and the chemicals that cause acid rain, are monitored by two networks, both supported by EPA.

1. The National Atmospheric Deposition Program (NADP) measures wet deposition, and its Web site features maps of rainfall pH and other important precipitation chemistry measurements. ([http://nadp.sws.uiuc.edu/](http://nadp.sws.uiuc.edu/))

2. The Clean Air Status and Trends Network (CASTNET) measures dry deposition. Its Web site features information about the data it collects, the measuring sites, and the kinds of equipment it uses. ([http://www.epa.gov/castnet/](http://www.epa.gov/castnet/))

F. Associated pollutants (same geographic regions and many of the same sources)

1. ozone ([http://www.msc-smc.ec.gc.ca/aq_smog/chronos_e.cfm](http://www.msc-smc.ec.gc.ca/aq_smog/chronos_e.cfm))
2. heavy metals (Pb in the past, Hg from coal and metals from smelting today)
3. ammonium (NH₄⁺)
4. CO₂

II. Effects of acid precipitation

A. Forests

1. Direct foliar injury from SO₂
   - can reduce photosynthesis and growth
   - most likely to occur near SO₂ sources and/or at high elevations

2. Soil cation depletion
   - Ca²⁺, Mg²⁺ and K⁺ are displaced by H⁺ and leave the site in soil water
     (they pair with SO₄²⁻ and NO₃⁻)
   - many soils have large cation reserves
   - weathering of minerals can replace cations
   - some soils have very low cation reserves and mineral weathering, so long-term cation loss can lead to nutrient deficiencies or imbalances (for example, thin soils derived from granite and gneiss, typically at high elevation)

3. Aluminum and other metal toxicity due to soil acidification
   - as nutrient cations are lost and soil acidifies, Al³⁺ becomes more soluble
   - can damage roots and microbes
   - soil acidification can also mobilize mercury (Hg), although direct Hg deposition from burning coal is a much larger source
   - water leaving the ecosystem can lead to high Al concentrations and acidification in surrounding lakes and steams

4. Forests where damage has been attributed, at least in part, to acid rain
a. Black Forest in Germany and other forests in high deposition areas of Europe
b. forested sites in southern California and the Colorado Front Range and high-elevation spruce-fir forests in the Northeast and southern Appalachians
   - acid rain is one of several contributing stressors to these problems
c. Sugar maple in New Hampshire (Juice et al. 2006)
   - Reduced growth, crown dieback and increased mortality during last 15 years
   - Acidic spodosol soils (pH 3.4 to 3.8 in O horizon), with very low base saturation, due in part to acid deposition
   - Foliage was deficient in Ca deficiency and had potentially toxic Mn levels
   - Foliar nutrient status, crown condition and tree survival improved markedly after helicopter Ca additions to the watershed

5. Difficulty in attributing effects to acid rain or N saturation
   - acid rain co-occurs with many other pollutants
   - one of several stressing agents forests are experiencing (pollution, insects, disease, drought)
   - only a few clear cases documented
   - many ecosystems may be undergoing cation depletion and approaching N saturation
B. Aquatic Systems

1. Lakes and streams in areas where soils have little acid-neutralizing capacity can become acidified

- at low pH, many fish and aquatic species are affected

(sources: http://www.epa.gov/airmarkets/acidrain/effects/surfacewater.html)

- water in some lakes in NE US and Canada has pH < 5, many have lost their brook trout and other fish (normal pH would be 6 to 8)

- Norway’s major rivers have become acidified, likely contributing to reduced salmon and trout populations
2. Waterbodies, such as estuaries, can undergo eutrophication
   - excessive nutrient inputs (N) lead to increased growth of N limited plants, especially algae
   - when they die and decompose, they deplete dissolved oxygen levels
   - fish, shellfish, plants and other organisms needing oxygen can be affected

C. Man-made structures
   - can damage buildings, statues and other structures made of stone (especially limestone), metal or other susceptible materials exposed to the weather for a long period of time
   - In 1856, Robert Angus Smith - the scientist who first used the term acid rain - wrote: "it has often been observed that the stones and bricks of buildings crumble more readily in large towns where much coal is burnt.... I was led to attribute this effect to the slow but constant action of acid rain."

D. Air quality and human health
   1. SO₂ and NOx can contribute to haze
      - EPA estimated reduced haze in eastern National Parks due to emission reductions could be worth several billion $ in tourism
   2. SO₂ and NOx both can affect respiratory system, although damaging concentrations are extremely rare reached
   3. NOx contributes to the production of O₃

IV. Control of acid precipitation
   A. Clean Air Act of 1970 and amendments of 1990
      1. In 1990, national SO₂ emissions were targeted for a 40% reduction (from 1980 levels) by 2010 (Title IV of the 1990 Clean Air Act Amendments)
      2. Polluters are allowed to buy or sell emission reductions
         - if a power plant reduced emissions below their allowed level, they can sell their excess allowance to another emitter
      3. No national target for NOx, but stationary sources (power plants) were required to reduce NOx emissions 10% by 2010
         - catalytic converters on automobiles also reduce NOx emissions, required since 1980
   B. Additional regulations for northeastern states place NOx emissions caps on these states
- Ozone Transport Commission memorandum of understanding (1999)
- NOx SIP Call (EPA, 1998) (SIP = state implementation plan)
- Section 126 (EPA, 2003) - reduces emissions to downwind states
- Mobile source emission limits (regulations for your tailpipe, started in 1996)

C. Clean Air Interstate Rule (EPA, March 2005)
   1. CAIR will permanently cap power plant emissions of sulfur dioxide (SO\textsubscript{2}) and nitrogen oxides (NO\textsubscript{x}) in the eastern United States
   2. CAIR achieves large reductions of SO\textsubscript{2} and/or NO\textsubscript{x} emissions across 28 eastern states and the District of Columbia
   3. When fully implemented, CAIR will reduce power plant SO\textsubscript{2} emissions in these states by over 70 percent and NO\textsubscript{x} emissions by over 60 percent from 2003 levels

http://www.epa.gov/interstateairquality/index.html

On July 11, 2008, the D.C. Circuit vacated EPA's Clean Air Interstate Rule. EPA is reviewing the Court's decisions and evaluating its impacts.

States covered by CAIR

D. Clean Air Mercury Rule (EPA, March 2005)
   - permanently cap and reduce mercury emissions from coal-fired power plants for the first time ever

http://www.epa.gov/oar/mercuryrule/
E. Western Europe and Canada have also legislated strong emission reductions
   - In 1994 in Oslo, 12 European nations agreed to reduce SO$_2$ emissions by as much as 87% by 2010

F. Clear Skies Legislation (proposed)
   
   http://www.epa.gov/air/clearskies/

E. Responses to control efforts
   1. SO$_4^{2-}$ deposition has decreased significantly
   2. N deposition has been affected only slightly
      - increase in number of power plants and vehicles has offset gains by reducing emissions from individual sources
      - emissions caps going into effect now in portions of the NE US should help
   3. Precipitation pH has improved (gotten higher)
   4. Lake water quality has improved slightly (in NE US lakes there is now less sulfate, unchanged nitrate, recovery of alkalinity in New England but not the Adirondacks)

Lab – “Acid Rain in a Bag” [lab taken from Glencoe Chemistry ©2002, textbook pg. 848]

Background:
Acid precipitation often falls to Earth hundreds of kilometers away from where the pollutant gasses enter the atmosphere because the gases diffuse through the air and are carried by the wind. In this lab, you will model the information of acid rain to observe how the damage caused by acid varies with the distance from the source of pollution. You also will observe another factor that affects the amount of damage caused by acid rain.

Purpose:
1. To model acid rain formation and
2. Analyze how damage by the acid rain varies with the distance from the source of the air pollutants

Hypothesis: Write a hypothesis in the space below. See purpose #2 for help.
Possible hypothesis: Acid rain damage is greater near the source of pollution.

Materials:
- Plastic petri dish bottom
- 1-gallon, zipper close plastic bag
- White paper
- droppers
- 0.5 M KNO₂
- 0.04% bromocresol green indicator
- 1.0 M H₂SO₄
- stopwatch or clock

Procedures:
1. Place 25 drops of 0.04% bromocresol green indicator of varying sizes in the bottom half of a plastic petri dish so that they are about 1 cm apart. Be sure that there are both large and small drops at any given distance from the center. Leave the center of the petri dish empty.
2. Place a zipper-close plastic bag on a piece of white paper.
3. Carefully slide the petri dish containing the drops of indicator inside the plastic bag.
4. In the center of the petri dish, place on large drop of 0.5 M KNO₂. To this KNO₂ drop, add two drops of 1.0 M H₂SO₄. CAUTION: KNO₂ and H₂SO₄ are both skin irritants! Carefully seal the bag. Observe whether the mixing of these two chemicals produces any bubbles of gas. This is the pollution source.
5. Observe and compare the color changes that take place in the drops of indicator of different sizes and distance from the pollution source. Record your observations every 15 seconds.
6. To clean up, carefully remove the petri dish from the bag, rinse it with water, then dry it.

Data: Make a data table to record your observations every 15 seconds.
Analysis:

1. As the gas reacts with water in the drops, two acids form. Using the equation below, 1) balance the reaction and 2) name the two acids.

\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3 \]

nitrous and nitric acid, respectively

2. Did the small or large drops change color first? WHY?
   The small drops changed color first. The surface area-to-volume ratio is greater.

3. Did the distance of the indicator drops from the pollution source have an effect on how quickly the reaction occurred? Explain.
   The drops that were closer to the pollution source reacted faster because diffusion of the pollution occurred over a shorter distance.

4. State two hypotheses that will explain your observations, and incorporate the answers from questions 2 and 3 in your hypotheses.
   a. The gas diffuses and dissolves faster in water drops that are smaller.
   b. The gas diffuses and dissolves faster in water drops that are closer to the source.

5. Based on your hypotheses in question 4, what can you infer about the damage done to plants by acid fog as compared with acid rain?
   Acid fog would do more damage to plants than acid rain in the same area because the surface-to-volume ratio is greater.

6. Based on the information given to you in your notes about acid formation, how could we generate SO\(_2\) ? What substance could be reacted with H\(_2\)SO\(_4\) to produce SO\(_2\) (and water)? [Hint: use solubility rules] Write a balanced chemical equation for this substance with H\(_2\)SO\(_4\) (don't forget to predict the products).
   Na\(_2\)SO\(_3\) crystals – placed into petri dish with a drop of H\(_2\)SO\(_4\) added to it. (other possibilities may exist)

\[ \text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2 \]

7. What is the anthropogenic source of the sulfur that contributes to the formation of acid rain?
   Burning high-sulfur coal and oil in power plants
I. What is acid precipitation?
   a. Definitions
      i. Cloud or ___________ droplets combine with gaseous pollutants, such as __________ of sulfur and nitrogen, to make falling rain or __________ acidic.
         [www.kcbd.com/Global/story.asp]
      ii. Rain that has become ___________ after contact with certain atmospheric gases (primarily ___________ dioxide, carbon dioxide, and ___________ oxides).
         [www.dmh.gov.mm/glossary.cfm]
      iii. Rain containing acids that form in the atmosphere when ___________ gas emissions (especially sulfur dioxide and nitrogen oxides) combine with ___________ wordnet.princeton.edu/perl/webwn
      iv. Precipitation whose pH is below 5
   b. pH scale (pH = power of the ___________)
      i. 0-14 logarithmic scale
         1. pH of 4 is ___________ times more alkaline or basic than a pH of 2
         2. How are a pH of 4 and 8 related? ___________
      ii. pH 7 is neutral
         1. Equal concentrations of ___________ & ___________ ions
      iii. lower pH is more acidic
         1. Based on the diagram below, which is more acidic, an apple or milk? ___________ Ammonia or milk? ___________
         2. If rainwater has a pH of 5.2, which substance(s) show in the diagram below are more basic than the rainwater?

(source: [http://www.epa.gov/acidrain/ph.html](http://www.epa.gov/acidrain/ph.html))
c. “____________ rain” has a pH of 5.0 to 5.6
   i. CO₂ in atmosphere forms ____________ acid (H₂CO₃) - pH = 5.6
   ii. Other natural ____________ acids can lower pH to about 5.0

d. “Acid” rain has a pH of <5.0
   i. Due to man’s ______________
      1. ____________ exhaust
      2. ____________ plants burning ____________ or oil
   ii. HNO₃ (____________ acid) and H₂SO₄ (____________ acid) are the two principle substances that make rain acidic
   iii. In 2006, much of the rain in northeastern US had a pH of around ______________

II. Formation of acid precipitation

(source: http://www.epa.gov/acidrain/index.html#what)

A. Chemical Reactions
   1. Formation of sulfur dioxide (SO₂) and nitrogen oxides (NO & NOx) (a.k.a. acid forming precursors):
      S (in fuel) + O₂ → ____________
      N₂ + O₂ → ____________
      2NO + O₂ → ____________
      NO₂ + ____________ → NO + O
      O + O₂ → ____________
2. Formation of acids:

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{________}
\]

\[ \text{SO}_2 + \text{H}_2\text{O}_2 \text{ and O}_3 \text{ (in clouds)} \rightarrow \text{________}
\]

\[ \text{SO}_2 + \text{OH}^- + \text{O}_2 \text{ (in air)} \rightarrow \text{________}
\]

\[ \text{SO}_2 + \text{Oxidants (from wet surfaces)} \rightarrow \text{________}
\]

\[ \text{NOx + sunlight + OH}^- \text{ (in air)} \rightarrow \text{________}
\]

B. Sources of acid forming precursors:

<table>
<thead>
<tr>
<th></th>
<th>Natural</th>
<th>Anthropogenic (man-made)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NOx</strong></td>
<td>Lightning, biological denitrification</td>
<td>Transportation, electric utilities, industry, biomass burning</td>
</tr>
<tr>
<td></td>
<td>About 40% of total</td>
<td>About 60% of total</td>
</tr>
<tr>
<td><strong>SO\textsubscript{2}</strong></td>
<td>Biological, volcanoes, sea spray</td>
<td>Electric utilities (especially coal burning), industry, oil refining, ore smelting</td>
</tr>
<tr>
<td></td>
<td>&gt; 60% of total</td>
<td>&lt; 40% of total</td>
</tr>
</tbody>
</table>

1. Currently about 43% of anthropogenic NOx in US comes from ____________ (60% in Canada)
2. 70% of anthropogenic SO\textsubscript{2} in US comes from ____________________________
3. Problem – man-made sources are ____________________________
1998 National Nitrogen Oxide (Nox) Emissions by Principal Source Category (source U.S. EPA)

Density Map of Sulfur Dioxide Emissions 2001
(Source: Environmental Protection Agency: http://www.epa.gov/air/data/geosel.html)
III. Deposition patterns

Deposition Patterns

A. $\text{NO}_3^-$ (nitrate)  (NADP/NTN maps available at http://nadp.sws.uiuc.edu/isopleths/)

B. $\text{SO}_4^{2-}$ (sulfate)
C. H⁺ (hydrogen)

D. Forms of acid deposition
- ____________deposition (rain, fog, snow)
- ____________deposition (acid gases and particles)
  - leaves and needles can ____________ from air and concentrate
  - contribute up to ______% of total anthropogenic deposition
  - more important near source – Go to lab page – “Acid Rain in a Bag”

Wet and Dry Deposition in Southwestern Pennsylvania - 1989-1999
(source: http://www.epa.gov/castnet/overview.html)
E. Monitoring of acid deposition: Acid rain's pH, and the chemicals that cause acid rain, are monitored by two networks, both supported by EPA.

1. The ____________________________ (NADP) measures wet deposition, and its Web site features maps of rainfall pH and other important precipitation chemistry measurements. (http://nadp.sws.uiuc.edu/)

2. The ____________________________ (CASTNET) measures dry deposition. Its Web site features information about the data it collects, the measuring sites, and the kinds of equipment it uses. (http://www.epa.gov/castnet/)

F. Associated pollutants (same geographic regions and many of the same sources)

1. ____________ (http://www.msc-smc.ec.gc.ca/aq_smog/chronos_e.cfm)

2. ____________metals (Pb in the past, Hg from coal & metals from smelting today)

3. ____________ (NH$_4^+$)

4. ______________

III. Effects of acid precipitation

A. Forests

1. Direct foliar injury from SO$_2$
   - can reduce ____________________________ and growth
   - most likely to occur ______________ SO$_2$ sources and/or at high elevations

2. ____________ cation depletion
   1. Ca$^{2+}$, Mg$^{2+}$ and K$^+$ are displaced by H$^+$ and leave the site in soil water (they pair with SO$_4^{2-}$ and NO$_3^-$)
   2. many soils have large cation ____________
   3. ____________________________ of minerals can replace cations
   4. some soils have very low cation reserves and mineral weathering, so long-term cation loss can lead to nutrient ____________________________ or imbalances (for example, thin soils derived from granite and gneiss, typically at high elevation)

3. Aluminum and other metal toxicity due to soil acidification
   - as nutrient cations are lost and soil acidifies, ________ becomes more soluble
   - can damage __________________ and __________________
   - soil acidification can also mobilize mercury (Hg), although direct Hg deposition from ____________________________ is a much larger source
   - water leaving the ecosystem can lead to high Al concentrations and acidification in surrounding lakes and steams
IV. Forests where damage has been attributed, at least in part, to acid rain

a. ________________________ in Germany and other forests in high deposition areas of Europe  

b. forested sites in southern ____________ and the Colorado Front Range and high-elevation spruce-fir forests in the Northeast and southern Appalachians  

- acid rain is one of several contributing stressors to these problems  

c. Sugar maple in New Hampshire (Juice et al. 2006)  

- ____________ growth, crown dieback and increased mortality during last 15 years  

- Acidic spodosol soils (pH 3.4 to 3.8 in O horizon), with very low base saturation, due in part to acid deposition  

- Foliage was deficient in ____________ deficiency and had potentially toxic Mn levels  

- Foliar nutrient status, crown condition and tree survival improved markedly after helicopter Ca additions to the ________________________

V. Difficulty in attributing effects to acid rain or N saturation

- acid rain ____________ with many other pollutants  

- one of several stressing agents forests are experiencing (pollution, insects, disease, drought)
only a few clear cases documented

- many ecosystems may be undergoing cation depletion and approaching N saturation

VI. Aquatic Systems
1. Lakes and streams in areas where soils have little acid-neutralizing capacity can become ______________________

- at low pH, many fish and aquatic species are affected

(source: http://www.epa.gov/airmarkets/acidrain/effects/surfacewater.html)
- water in some lakes in NE US and Canada has pH < 5, many have lost their brook trout and other fish (normal pH would be 6 to 8)
- Norway’s major rivers have become acidified, likely contributing to reduced salmon and trout populations

2. Waterbodies, such as estuaries, can undergo eutrophication
- excessive nutrient inputs (N) lead to __________________________ growth of N limited plants, especially algae
- when they die and __________________________, they deplete dissolved oxygen levels
- ____________, shellfish, plants and other organisms needing oxygen can be affected

VII. Man-made structures
- can damage buildings, statues and other structures made of stone (especially limestone), metal or other susceptible materials exposed to the weather for a long period of time
- In 1856, Robert Angus ____________ - the scientist who first used the term acid rain - wrote: "it has often been observed that the stones and bricks of buildings crumble more readily in large towns where much coal is burnt.... I was led to attribute this effect to the slow but constant action of acid rain."

VIII. Air quality and human health
1. SO₂ and NOₓ can contribute to __________
   - EPA estimated reduced haze in eastern National Parks due to emission reductions could be worth several __________ in tourism
2. SO₂ and NOₓ both can affect __________ system, although damaging concentrations are extremely rare reached
3. NOₓ contributes to the production of ______

IX. Control of acid precipitation
A. Clean Air Act of 1970 and amendments of 1990
1. In 1990, national SO₂ emissions were targeted for a _____% reduction (from 1980 levels) by 2010 (Title IV of the 1990 Clean Air Act Amendments)
2. Polluters are allowed to __________________________ emission reductions
   a. if a power plant reduced emissions below their allowed level, they can sell their excess allowance to another emitter
3. No national target for NOₓ, but stationary sources (power plants) were required to reduce NOₓ emissions _____% by 2010
- catalytic converters on automobiles also reduce NOx emissions, required since 1980

B. Additional regulations for __________ states place NOx emissions caps on these states
   2. NOx SIP Call (EPA, 1998) (SIP = state implementation plan)
   3. Section 126 (EPA, 2003) - reduces emissions to downwind states
   4. Mobile source emission limits (regulations for your tailpipe, started in 1996)

C. Clean Air Interstate Rule (EPA, March 2005)
   1. CAIR will permanently _______ power plant emissions of sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) in the eastern United States
   2. CAIR achieves __________ reductions of SO₂ and/or NOₓ emissions across 28 eastern states and the District of Columbia
   3. When fully implemented, CAIR will reduce power plant SO₂ emissions in these states by over _____% and NOₓ emissions by over _____% from 2003 levels

http://www.epa.gov/interstateairquality/index.html

On July 11, 2008, the D.C. Circuit vacated EPA’s Clean Air Interstate Rule. EPA is reviewing the Court’s decisions and evaluating its impacts.

States covered by CAIR

Clean Air Mercury Rule (EPA, March 2005)
1. permanently cap and reduce ____________ emissions from coal-fired power plants for the first time ever

   http://www.epa.gov/oar/mercuryrule/

D. ___________________ & ____________ have also legislated strong emission reductions
   - In 1994 in Oslo, 12 European nations agreed to reduce SO$_2$ emissions by as much as 87% by 2010

E. Clear Skies Legislation (proposed)
   http://www.epa.gov/air/clearskies/

X. Responses to control efforts
1. SO$_4^{2-}$ deposition has _______________ significantly
2. N deposition has been affected only slightly
   - increase in number of power plants and vehicles has offset gains by reducing emissions from individual sources
   - emissions caps going into effect now in portions of the NE US should help
3. Precipitation pH has improved (gotten ____________)
4. Lake water quality has improved _______________ (in NE US lakes there is now less sulfate, unchanged nitrate, recovery of alkalinity in New England but not the Adirondacks)

Lab – “Acid Rain in a Bag” [lab taken from Glencoe Chemistry ©2002, textbook pg. 848]

Background:
Acid precipitation often falls to Earth hundreds of kilometers away from where the pollutant gasses enter the atmosphere because the gases diffuse through the air and are carried by the wind. In this lab, you will model the information of acid rain to observe how the damage caused by acid varies with the distance from the source of pollution. You also will observe another factor that affects the amount of damage caused by acid rain.

Purpose:
1. To model acid rain formation and
2. Analyze how damage by the acid rain varies with the distance from the source of the air pollutants

Hypothesis: Write a hypothesis in the space below. See purpose #2 for help.

Materials:
- Plastic petri dish bottom
- 1-gallon, zipper close plastic bag
- White paper
- Droppers
- 0.5 M KNO₂
- 0.04% bromocresol green indicator
- 1.0 M H₂SO₄
- Stopwatch or clock

Procedures:
1. Place 25 drops of 0.04% bromocresol green indicator of varying sizes in the bottom half of a plastic petri dish so that they are about 1 cm apart. Be sure that there are both large and small drops at any given distance from the center. Leave the center of the petri dish empty.
2. Place a zipper-close plastic bag on a piece of white paper.
3. Carefully slide the petri dish containing the drops of indicator inside the plastic bag.
4. In the center of the petri dish, place on large drop of 0.5 M KNO₂. To this KNO₂ drop, add two drops of 1.0 M H₂SO₄. CAUTION: KNO₂ and H₂SO₄ are both skin irritants! Carefully seal the bag. Observe whether the mixing of these two chemicals produces any bubbles of gas. This is the pollution source.
5. Observe and compare the color changes that take place in the drops of indicator of different sizes and distance from the pollution source. Record your observations every 15 seconds.
6. To clean up, carefully remove the petri dish from the bag, rinse it with water, then dry it.

Data: Make a data table to record your observations every 15 seconds.
Analysis:

1. As the gas reacts with water in the drops, two acids form. Using the equation below, 1) balance the reaction and 2) name the two acids formed.

   \[ \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3 \]

2. Did the small or large drops change color first? WHY?

3. Did the distance of the indicator drops from the pollution source have an effect on how quickly the reaction occurred? Explain.

4. State two hypotheses that will explain your observations, and incorporate the answers from questions 2 and 3 in your hypotheses.

5. Based on your hypotheses in question 4, what can you infer about the damage done to plants by acid fog as compared with acid rain?

6. Based on the information given to you in your notes about acid formation, how could we generate SO\(_2\)? What substance could be reacted with H\(_2\)SO\(_4\) to produce SO\(_2\) (and water)? [Hint: use solubility rules for help] Write a balanced chemical equation for this substance with H\(_2\)SO\(_4\) (don’t forget to predict the products).

7. What is the anthropogenic source of the sulfur that contributes to the formation of acid rain?
1. What is an indicator solution? What color is it?

2. What color does universal indicator solution turn when a base is present?

3. What color does universal indicator solution turn when an acid is present?

4. What do you think would happen to the color of the universal indicator solution if the acid and base test tubes were mixed together?

5. What do you think happens to an acid when a base is added to it?

6. Describe the pond water.

7. Why must the penny used in the experiment be pre-1982?

8. Describe the sulfur powder.
9. Write your observations as the teacher places the nitric acid on the penny and ignites the sulfur.

10. When sulfur burns, it is combining with the oxygen in the air (a combustion reaction). Write a balanced chemical equation for the production of sulfur dioxide from the combustion of sulfur.

11. This sulfur dioxide can continue to react with oxygen in the atmosphere to produce sulfur trioxide. Write a balanced chemical equation for this reaction.

12. The nitric acid is reacting with copper to produce nitrogen dioxide. Write a balanced chemical equation for this reaction.

13. What is the pH of the “rain water” before it “falls” through the atmosphere?
14. When “rain” combines with the gases of the atmosphere, acids can be produced.
   a. Write the balanced chemical equation for the production of sulfuric and sulfurous acid.

   b. Write the balanced chemical equation for the production of nitric acid – note that nitrogen monoxide is also a product of this reaction

15. What is the pH of the pond water? Note any other observed changes to the pond water.

16. What acid(s) are present in the pond water?

17. Describe the marble (limestone or calcium carbonate) chips.

18. What happened, if anything, to the pH of the pond water after the marble chips were added? Note any other observed changes to the pond water and to the marble chips.

19. Write out a balanced chemical equation for the neutralization of acidic lake water by limestone. Be sure to write a neutralization reaction for each acid present in the pond water. Note that carbonic acid quickly decomposes into water and carbon dioxide.
20. Why are areas with limestone beds less adversely affected by acid precipitation?

21. Explain how a change in one earth system affects another earth system (earth systems include the biosphere, hydrosphere, lithosphere, and atmosphere)

22. Explain how carbon exists in different forms (at least 2) within earth systems and how those forms affect humans

23. Explain how carbon moves through the earth systems and how it may benefit or harm society (describe both)
1. What is an indicator solution? What color is it?

   Chemical dye whose color is affected by acidic and basic solutions
   Clear and colorless

2. What color does universal indicator solution turn when a base is present?

   Blue to violet (violet most basic)

3. What color does universal indicator solution turn when an acid is present?

   Red to orange to yellow (red most acidic)

4. What do you think would happen to the color of the universal indicator solution if
   the acid and base test tubes were mixed together?

   Turn green (neutral)

5. What do you think happens to an acid when a base is added to it?

   It is neutralized; it's pH increases

6. Describe the pond water.

   Clear and colorless

7. Why must the penny used in the experiment be pre-1982?

   Pre-1982 pennies are made mostly of copper. Today's pennies are made of
   zinc which will not produce NOx gases.

8. Describe the sulfur powder.

   Yellow powder.

9. Write your observations as the teacher places the nitric acid on the penny and
   ignites the sulfur.

10. When sulfur burns, it is combining with the oxygen in the air (a combustion
    reaction). Write a balanced chemical equation for the production of sulfur dioxide
    from the combustion of sulfur.

    \[ S (s) + O_2 (g) \rightarrow SO_2 (g) \]

11. This sulfur dioxide can continue to react with oxygen in the atmosphere to produce
    sulfur trioxide. Write a balanced chemical equation for this reaction.
2SO₂ (g) + O₂ → 2SO₃ (g)

12. The nitric acid is reacting with copper to produce nitrogen dioxide. Write a balanced chemical equation for this reaction.

Cu (s) + 4HNO₃ → Cu(NO₃)₂ (aq) + 2NO₂ (g) + 2H₂O (g)

13. What is the pH of the “rain water” before it “falls” through the atmosphere?

Should be between 5.0 and 7.0

14. When “rain” combines with the gases of the atmosphere, acids can be produced.

a. Write the balanced chemical equation for the production of sulfuric and sulfurous acid.

SO₂ + H₂O → H₂SO₃ (sulfurous acid)
SO₃ + H₂O → H₂SO₄ (sulfuric acid)

b. Write the balanced chemical equation for the production of nitric acid – note that nitrogen monoxide is also a product of this reaction

3NO₂ + H₂O → 2HNO₃ + NO

15. What is the pH of the pond water? Note any other observed changes to the pond water.

16. What acid(s) are present in the pond water?

Sulfurous, sulfuric and nitric acids

17. Describe the marble (limestone or calcium carbonate) chips.

18. What happened, if anything, to the pH of the pond water after the marble chips were added? Note any other observed changes to the pond water and to the marble chips.

pH should have increased (become more alkaline or basic)
19. Write out a balanced chemical equation for the neutralization of acidic lake water by limestone. Be sure to write a neutralization reaction for each acid present in the pond water. Note that carbonic acid quickly decomposes into water and carbon dioxide.

\[
\begin{align*}
\text{H}_2\text{SO}_3 + \text{CaCO}_3 & \rightarrow \text{CaSO}_3 + \text{H}_2\text{O} + \text{CO}_2 \\
\text{H}_2\text{SO}_4 + \text{CaCO}_3 & \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \\
2\text{HNO}_3 + \text{CaCO}_3 & \rightarrow \text{Ca(NO)}_3_2 + \text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]

20. Why are areas with limestone beds less adversely affected by acid precipitation?

The calcium carbonate combines with the nitrate producing water and carbon dioxide, so the acid is “removed” from the environment.

21. Explain how a change in one earth system affects another earth system (earth systems include the biosphere, hydrosphere, lithosphere, and atmosphere)

22. Explain how carbon exists in different forms (at least 2) within earth systems and how those forms affect humans

23. Explain how carbon moves through the earth systems and how it may benefit or harm society (describe both)
Acid Rain Forum Teacher Page
[modified from the website
www.geocities.com/ResearchTriangle/1896/Acid_Rain_Lesson_Plans.htm]

This type of lesson is based on identifying bias in a website. Students will be searching websites to gather information to report back to small groups in an effort to come to consensus on the issue of acid rain solutions. These arguments will be given as a methodology to solving the problem of acid rain in our communities.

Essential questions to be answered:
1. What are the problems concerning acid rain?
2. Who is to blame?
3. Who has contributed to the decline of air quality?
4. What are the economic impacts of acid rain?
5. Which solution(s) will clearly make an impact?

Objectives:
1. Exposing students to various points of view regarding the acid rain debate.
2. Helping students to analyze a website for literal meaning and for bias.
3. Creating an atmosphere where students can voice different opinions about a controversial topic.
4. Developing consensus building and teamwork skills.

Procedures and Activities:
THE TASK:
A local citizen's group has hired you, and a group of other researchers, to investigate acid rain. In a group of four, you will take on the role of high school chemistry teacher, business economist, environmentalist, and elected government official. You will examine the issue from that perspective. Working within a team, you will create a web report detailing the problems caused by acid rain and recommend ways that these problems can be alleviated.

Within your group, decide who is going to assume the roles listed above. Use the questions appearing under each role to assist you in your research. While you are responsible for completing your section of the report, you will also be responsible for drawing up a series of recommendations, along with the other members of your team, on how to combat this serious issue. While you are investigating the solution strategies from your individual perspective, remember that eh web report should be a consensus of opinions.

While you are researching your particular area of concern, look for solutions to the problems caused by acid rain. While the final section of your report, the recommendations, will be drawn up by the entire group, you must be prepared to offer solutions in your specific area of concern.

1. As a group to divide the roles between members and brainstorm an outline of your approach to and time consideration for the 1 hour of in-class internet information gathering (you may need to spend additional time outside of class doing research).
2. As individuals, research your topic from your perspective. Keep detailed notes to put into your web report.
3. After you have finished your individual research, draft a first copy of your report. Come to a consensus as to what the solutions will be to the problem of acid.
4. Complete the final draft.
5. Present the web report to the class and post the data to the web

Decide, as a group, what is your position on acid rain. Determine the recommendations and conclusions that your report will present. Determine which members of the group will be responsible for writing this section, and which members of the group will put all the pieces of the report together.

Assessment
Web report = 40 points
Class presentation and web posting = 20 points
Group cooperation = 20 points
Individual participation = 20 points
(To be determined by the group as peer evaluation)
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1. What are the problems concerning acid rain?
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Within your group, decide who is going to assume the roles listed above. Use the questions appearing under each role to assist you in your research. While you are responsible for completing your section of the report, you will also be responsible for drawing up a series of recommendations, along with the other members of your team, on how to combat this serious issue. While you are investigating the solution strategies from your individual perspective, remember that the web report should be a consensus of opinions.

While you are researching your particular area of concern, look for solutions to all the problems caused by acid rain. While the final section of your report, the recommendations, will be drawn up by the entire group, you must be prepared to offer solutions in your specific area of concern.

1. As a group to divide the roles between members and brainstorm an outline of your approach to and time consideration for the 1 hour of in-class internet information gathering (you may need to spend additional time outside of class doing research).
2. As individuals, research your topic from your perspective. Keep detailed notes to put into your web report.
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Assessment

Web report = 40 points
Class presentation and web posting = 20 points
Group cooperation = 20 points
(To be determined by the teacher)
Individual participation = 20 points
(To be determined by the group as peer evaluation)

Web Report
1. Your web report must answer the 5 essential questions from the perspective of each assigned role. Any information taken from other sources (websites) must be cited.
   a. Each person should write their section of the web report.
2. Your web report must include a consensus opinion to the 5 essential questions. Again, site your sources.

Class presentation and web posting
1. The spokesperson for the group should present the consensus opinion for each of the 5 essential questions.
2. Those roles that oppose the consensus should speak about their dissenting opinion.
3. Posting the report to the website should be completed before the end of class by the spokesperson or another previously designated person.

Peer evaluation of individual participation
1. Each person will rate the other members on their participation within the group on a scale of 0 to 10. The average score will be used to calculate participation.
2. Not turning in a peer evaluation will result in a deduction of your score.