Laboratory Research in Environmental Engineering

Laboratory Manual

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Preface

Continued leadership in environmental protection requires efficient transfer of innovative environmental technologies to the next generation of engineers. Responding to this challenge, the Cornell Environmental Engineering faculty redesigned the undergraduate environmental engineering curriculum and created a new senior-level laboratory course. This laboratory manual is one of the products of the course development. Our goal is to disseminate this information to help expose undergraduates at Cornell and at other institutions to current environmental engineering problems and innovative solutions.

A major goal of the undergraduate laboratory course is to develop an atmosphere where student understanding will emerge for the physical, chemical, and biological processes that control material fate and transport in environmental and engineered systems. Student interest is piqued by laboratory exercises that present modern environmental problems to investigate and solve.

The experiments were designed to encourage the process of “learning around the edges.” The manifest purpose of an experiment may be a current environmental problem, but it is expected that students will become familiar with analytical methods in the course of the laboratory experiment (without transforming the laboratory into an exercise in analytical techniques). It is our goal that students employ the theoretical principles that underpin the environmental field in analysis of their observations without transforming the laboratories into exercises in process theory. As a result, students can experience the excitement of addressing a current problem while coincidentally becoming cognizant of relevant physical, chemical, and biological principles.

At Cornell, student teams of two or three carry out the exercises, maximizing the opportunity for a hands-on experience. Each team is equipped with modern instrumentation as well as experimental reactor apparatus designed to facilitate the study of each topic.

Computerized data acquisition and instrument control are used extensively to make it easier for students to learn how to use new instruments and to eliminate the drudgery of manual data acquisition. Software was developed at Cornell to use computers as virtual instruments that interface with a pH meter/ion (Accumet 50), gas chromatograph (HP 5890A), UV-Vis Spectrophotometer (HP 8452). This code is available at the course web site.

The development of this manual and the accompanying course would not have been possible without funds from the National Science Foundation, the DeFrees Family Foundation, the Procter and Gamble Fund, the School of Civil and Environmental Engineering and the College of Engineering at Cornell University.

Monroe L. Weber-Shirk
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James J. Bisogni, Jr.

Ithaca, NY
January 15, 2002
Laboratory Safety

Introduction

Safety is a collective responsibility that requires the full cooperation of everyone in the laboratory. However, the ultimate responsibility for safety rests with the person carrying out a given procedure. In the case of an academic laboratory, that person is usually the student. Accidents often result from an indifferent attitude, failure to use common sense, or failure to follow instructions. Each student should be aware of what the other students are doing because all can be victims of one individual's mistake. Do not hesitate to point out to other students that they are engaging in unsafe practices or operations. If necessary, report it to the instructor. In the final assessment, students have the greatest responsibility to ensure their own personal safety.

This guide provides a list of do's and don'ts to minimize safety and health problems associated with experimental laboratory work. It also provides, where possible, the ideas and concepts that underlie the practical suggestions. However, the reader is expected to become involved and to contribute to the overall solutions. The following are general guidelines for all laboratory workers:

1) Follow all safety instructions carefully.
2) Become thoroughly acquainted with the location and use of safety facilities such as safety showers, exits and eyewash fountains.
3) Become familiar with the hazards of the chemicals being used, and know the safety precautions and emergency procedures before undertaking any work.
4) Become familiar with the chemical operations and the hazards involved before beginning an operation.

Personal Protection

Eye Protection

All people in the laboratory including visitors must wear eye protection at all times, even when not performing a chemical operation. Wearing of contact lenses in the laboratory is normally forbidden because contact lenses can hold foreign materials against the cornea. Furthermore, they may be difficult to remove in the case of a splash. Soft contact lenses present a particular hazard because they can absorb and retain chemical vapors. If the use of contact lenses is required for therapeutic reasons fitted goggles must also be worn. In addition, approved standing shields and face shields that protect the neck and ears as well as the face should be used when appropriate for work at reduced pressure or where there is a potential for explosions, implosions or splashing. Normal prescription eyeglasses, though meeting the Food and Drug Administration's standards for shatter resistance, do not provide appropriate laboratory eye protection.

Clothing

Clothing worn in the laboratory should offer protection from splashes and spills, should be easily removable in case of accident, and should be at least fire resistant.
Nonflammable, nonporous aprons offer the most satisfactory and the least expensive protection. Lab jackets or coats should have snap fasteners rather than buttons so that they can be readily removed.

High-heeled or open-toed shoes, sandals, or shoes made of woven material should not be worn in the laboratory. Shorts, cutoffs and miniskirts are also inappropriate. Long hair and loose clothing should be constrained. Jewelry such as rings, bracelets, and watches should not be worn in order to prevent chemical seepage under the jewelry, contact with electrical sources, catching on equipment, and damage to the jewelry.

**Gloves**

Gloves can serve as an important part of personal protection when they are used correctly. Check to ensure the absence of cracks or small holes in the gloves before each use. In order to prevent the unintentional spread of chemicals, gloves should be removed before leaving the work area and before handling such things as telephones, doorknobs, writing instruments, computers, and laboratory notebooks. Gloves may be reused, cleaned, or discarded, consistent with their use and contamination.

A wide variety of gloves is available to protect against chemical exposure. Because the permeability of gloves of the same or similar material varies from manufacturer to manufacturer, no specific recommendations are given here. Be aware that if a chemical diffuses through a glove, that chemical is held against the worker's hand and the individual may then be more exposed to the chemical than if the glove had not been worn.

**Personal Hygiene**

Everyone working in a chemistry laboratory should be aware of the dangers of ingesting chemicals. These common sense precautions will minimize the possibility of such exposure:

1) Do not prepare, store (even temporarily), or consume food or beverages in any chemical laboratory.

2) Do not smoke in any chemical laboratory. Additionally, be aware that tobacco products in opened packages can absorb chemical vapors.

3) Do not apply cosmetics in a laboratory.

4) Wash hands and arms thoroughly before leaving the laboratory, even if gloves have been worn.

5) Wash separately from personal laundry, lab coats or jackets on which chemicals have been spilled.

6) Never wear or bring lab coats or jackets into areas where food is consumed.

7) Never pipette by mouth. Always use a pipette aid or suction bulb.

**Laboratory Protocol**

The chemistry laboratory is a place for serious learning and working. Horseplay cannot be tolerated. Variations in procedures including changes in quantities or
reagents may be dangerous. Such alterations may only be made with the knowledge and approval of the instructor.

**Housekeeping**

In the laboratory and elsewhere, keeping things clean and neat generally leads to a safer environment. Avoid unnecessary hazards by keeping drawers and cabinets closed while working. Never store materials, especially chemicals, on the floor, even temporarily. Work spaces and storage areas should be kept clear of broken glassware, leftover chemicals and scraps of paper. Keep aisles free of obstructions such as chairs, boxes and waste receptacles. Avoid slipping hazards by keeping the floor clear of ice, stoppers, glass beads or rods, other small items, and spilled liquids. Use the required procedure for the proper disposal of chemical wastes and solvents.

**Cleaning Glassware**

Clean glassware at the laboratory sink or in laboratory dishwashers. Use hot water, if available, and soap or other detergent. If necessary, use a mild scouring powder. Wear appropriate gloves that have been checked to ensure that no holes are present. Use brushes of suitable stiffness and size. Avoid accumulating too many articles in the cleanup area. Usually work space around a sink is limited and piling up dirty or cleaned glassware leads to breakage. Remember that the turbid water in a sink may hide a jagged edge on a piece of broken glassware that was intact when put into the water. A pair of heavy gloves may be useful for removing broken glass, but care must be exercised to prevent glove contamination. To minimize breakage of glassware, sink bottoms should have rubber or plastic mats that do not block the drains.

Avoid the use of strong cleaning agents such as nitric acid, chromic acid, sulfuric acid, strong oxidizers, or any chemical with a "per" in its name (such as perchloric acid, ammonium persulfate, etc.) unless specifically instructed to use them, and then only when wearing proper protective equipment. A number of explosions involving strong oxidizing cleaning solutions, such as chromic sulfuric acid mixtures, have been reported. The use of flammable solvents should be minimized and, when they are used, appropriate precautions must be observed.

**Unattended Operation of Equipment**

Reactions that are left to run unattended overnight or at other times are prime sources for fires, floods and explosions. Do not let equipment such as power stirrers, hot plates, heating mantles, and water condensers run overnight without fail-safe provisions and the instructor's consent. Check unattended reactions periodically. Always leave a note plainly posted with a phone number where you and the instructor can be reached in case of emergency. Remember that in the middle of the night, emergency personnel are entirely dependent on accurate instructions and information.

**Fume Hoods and Ventilation**

A large number of common substances present acute respiratory hazards and should not be used in a confined area in large amounts. They should be dispensed and handled only where there is adequate ventilation, such as in a hood. Adequate
ventilation is defined as ventilation that is sufficient to keep the concentration of a
chemical below the threshold limit value or permissible exposure limit.

If you smell a chemical, it is obvious that you are inhaling it. However, odor does
not necessarily indicate that a dangerous concentration has been reached. By contrast,
many chemicals can be present at hazardous concentrations without any noticeable
odor.

Refrigerators

Chemicals stored in refrigerators should be sealed, double packaged if possible,
and labeled with the name of the material, the date placed in the refrigerator, and the
name of the person who stored the material. A current inventory should be maintained.
Old chemicals should be disposed of after a specified storage period. Household
refrigerators should not be used for chemical storage.

If used for storage of radioactive materials, a refrigerator should be plainly marked
with the standard radioactivity symbol and lettering, and routine surveys should be
made to ensure that the radioactive material has not contaminated the refrigerator.

Food should never be stored in a refrigerator used for chemical storage. These
refrigerators should be clearly labeled "No Food". Conversely food refrigerators,
which must be always outside of, and away from, the chemical work area, should be
labeled "Food Only—No Chemicals".

Radioactive Materials

Radioactive materials are used in the Environmental Engineering laboratories.
Doors of rooms containing radioactive materials are clearly labeled. Areas where
radioactive materials are used are clearly delineated with labeling tape and signs. All
equipment within areas labeled radioactive are potentially contaminated and should
not be touched or removed. Do not place anything into or take anything from an area
labeled radioactive.

Working Alone

Avoid working alone in a building or in a laboratory.

Use of Chemicals

Before using any chemical you need to know how to safely handle it. The safety
precautions taken are dependent on the exposure routes and the potential harmful
effects.

Routes of Exposure

1) ingestion
2) inhalation
3) absorbed through skin
4) eye contact

Each potential exposure route requires different precautions. Chemical exposure
may have acute (immediate, short term) or chronic (long term potentially cumulative)
affects. Information on health hazards can be found on chemical labels and in Material Safety Data Sheets.

Material Safety Data Sheets

MSDS sheets for most chemicals used in the laboratory are located on the bookshelf in the entrance hallway of the Environmental Laboratory. Electronic versions (potentially more current) can be found using the world wide web at: [http://www.cee.cornell.edu/safety/](http://www.cee.cornell.edu/safety/)

MSDS provide extensive information on safe handling, first aid, toxicity, etc.

Following is a list of terms used in MSDS:

TLV—Threshold Limit Value—are values for airborne toxic materials that are to be used as guides in control of health hazards. They represent concentrations to which nearly all workers (workers without special sensitivities) can be exposed for long periods of time without harmful effect. TLV’s are usually expressed as parts per million (ppm). TLV’s are also expressed as mg of dust or vapor/m$^3$ of air.

TDLo—Toxic Dose Low—the lowest dose of a substance introduced by any route, other than inhalation, over any given period of time and reported to produce any toxic effect in humans or to produce carcinogenic, neoplastic, or teratogenic effects in animals or humans.

TCLo—Toxic Concentration Low—the lowest concentration of a substance in air to which humans or animals have been exposed for any given period of time and reported to produce any toxic effect in humans or to produce carcinogenic, neoplastic, or teratogenic effects in animals or humans.

TDLo—Lethal Dose Low—the lowest dose (other than LD50) of a substance introduced by any route, other than inhalation, over any given period of time in one or more divided portions and reported to have caused death in humans or animals.

LD50—Lethal Dose Fifty—a calculated dose of a substance that is expected to cause the death of 50% of an entire defined experimental animal population. It is determined from the exposure to the substance by any route other than inhalation of a significant number from that population.
LCLo—Lethal Concentration Low—the lowest concentration of a substance in air, other than LC50, that has been reported to have caused death in humans or animals. The reported concentrations may be entered for periods of exposure that are less than 24 hours (acute) or greater than 24 hours (subacute and chronic).

LC50—Lethal Concentration Fifty—a calculated concentration of a substance in air, exposure to which for a specified length of time is expected to cause the death of 50% of an entire defined experimental animal population. It is determined from the exposure to the substance of a significant number from that population.

### Chemical Labels

All chemicals must be labeled. Unlabeled containers of mystery chemicals or chemical solutions are a nightmare for disposal as well as a potential safety hazard. The OSHA Hazard Communication Standard and the OSHA Lab Standard have specific requirements for the labeling of chemicals. In a laboratory covered under the Lab Standard, if a chemical is designated as a hazardous material, that is having the characteristics of corrosivity, ignitability, toxicity (generally meaning a highly toxic material with an LD50 of 50 mg/kg or less), reactivity, etc., and if it is made into a solution or repackaged as a solid or liquid in a concentration greater than 1% (0.1% for a carcinogen) it needs to have a so called Right-To-Know (RTK) label that duplicates the hazard warnings, precautions and first aid steps found on the original label. All other chemicals must have at minimum a label with chemical name, concentration, and date prepared. "Right to Know Labels" will be made available for your use when necessary.

### Table 1-1. NFPA hazard code ratings.

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<th>Code</th>
<th>Health</th>
<th>Fire</th>
<th>Reactivity</th>
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<tr>
<td>4</td>
<td>Very short exposure can cause death or major residual injury</td>
<td>Will rapidly or completely vaporize at normal pressure and temperature</td>
<td>Capable of detonation or explosive reaction at normal temperatures and pressures</td>
</tr>
<tr>
<td>3</td>
<td>Short exposure can cause serious temporary or residual injury</td>
<td>Can be ignited under almost all ambient temperatures</td>
<td>Capable of detonation or explosive reaction buy requires a strong initiating source or must be heated under confinement before initiation</td>
</tr>
<tr>
<td>2</td>
<td>Intense or continued exposure can cause temporary incapacitation or possible residual injury</td>
<td>Must be moderately heated or exposed to high temperature before ignition</td>
<td>Undergoes violent chemical change at elevated temperatures and pressures or reacts violently with water.</td>
</tr>
<tr>
<td>1</td>
<td>Can cause irritation but only minor residual injury</td>
<td>Must be preheated before ignition</td>
<td>Normally stable but can become unstable at elevated temperatures and pressures.</td>
</tr>
<tr>
<td>0</td>
<td>During a fire offers no hazard beyond combustion</td>
<td>Will not burn</td>
<td>Stable even under fire conditions.</td>
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National Fire Protection Association (NFPA) ratings are included to indicate the types and severity of the hazards. The NFPA ratings are on a scale of 0-4 with 0 being nonhazardous and 4 being most hazardous. The ratings are described in Table [-1.]

Chemical Storage

There has been much concern, and some confusion, about the proper storage of laboratory chemicals. Here “proper” means the storage of chemicals in such a manner as to prevent incompatible materials from being accidentally mixed together in the event of the breakage of one or more containers in the storage area or to prevent the formation of reactive vapors that may require vented chemical storage areas. Below is a concise guide to the storage of common laboratory chemicals.

1) Perchloric acid is separated from all other materials.
2) Hydrofluoric acid is separated from all other materials.
3) Concentrated nitric acid is separated from all other materials.
4) Highly toxic materials (LD$_{50}$ of 50 mg/kg or less) are stored separately.
5) Carcinogenic chemicals are stored separately.
6) Inorganic acids (except for 1, 2, 3 above) are stored separately.
7) Bases are stored separately.
8) Strong oxidizing agents are stored separately.
9) Strong reducing agents are stored separately.
10) Water reactive, pyrophoric and explosive materials are stored separately.
11) Flammable organic materials (solvents, organic acids, organic reagents) are stored separately.

Guidelines for separating incompatible chemicals:

1) Place the chemicals to be stored separately in a heavy gauge Nalgene (or similar plastic) tub. Plastic secondary containers must be compatible with the material being stored.
2) Strong acids, especially perchloric, nitric and hydrofluoric are best stored in plastic containers designed to store strong mineral acids. These are available from lab equipment supply houses.
3) Bottle-in-a-can type of containers are also acceptable as secondary containment. Small containers of compatible chemicals may be stored in a dessicator or other secure container. Secondary containment is especially useful for highly toxic materials and carcinogens.
4) Dry chemicals stored in approved cabinets with doors may be grouped together by compatibility type on separate shelves or areas of shelves separated by taping off sections of shelving to designate where chemicals of one type are stored. Physically separated cabinets may be used to provide a barrier between groups of

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Prepared by Tom Shelley (Chemical Hygiene Officer) 7/96. For additional information or questions you may have, please contact Tom Shelley at 5-4288.
stored incompatible chemicals. Strong mineral acids may be stored in one cabinet and strong bases stored in a second cabinet, for example. Flammable solvents should be stored in a rated flammable storage cabinet if available.

If you are uncertain of the hazardous characteristics of a particular chemical refer to the MSDS for that material. A good MSDS will not only describe the hazardous characteristics of the chemical, it will also list incompatible materials.

**Transporting Chemicals**

Transport all chemicals using the container-within-a-container concept to shield chemicals from shock during any sudden change of movement. Large containers of corrosives should be transported from central storage in a chemically resistant bucket or other container designed for this purpose. Stairs must be negotiated carefully. Elevators, unless specifically indicated and so designated, should not be used for carrying chemicals. Smoking is never allowed around chemicals and apparatus in transit or in the work area itself.

When moving in the laboratory, anticipate sudden backing up or changes in direction from others. If you stumble or fall while carrying glassware or chemicals, try to project them away from yourself and others.

When a flammable liquid is withdrawn from a drum, or when a drum is filled, both the drum and the other equipment must be electrically wired to each other and to the ground in order to avoid the possible buildup of a static charge. Only small quantities should be transferred to glass containers. If transferring from a metal container to glass, the metal container should be grounded.

**Chemical Disposal**

The Environmental Protection Agency (EPA) classifies wastes by their reaction characteristics. A summary of the major classifications and some general treatment guidelines are listed below. Specific information may be found in the book, Prudent Practices for Disposal of Chemicals from Laboratories, as well as other reference materials.

**Ignitability:** These substances generally include flammable solvents and certain solids. Flammable solvents must never be poured down the drain. They should be collected for disposal in approved flammable solvent containers. In some cases it may be feasible to recover and reuse solvents by distillation. Such solvent recovery must include appropriate safety precautions and attention to potentially dangerous contamination such as that due to peroxide formation.

**Corrosivity:** This classification includes common acids and bases. They must be collected in waste containers that will not ultimately corrode and leak, such as plastic containers. It often may be appropriate to neutralize waste acids with waste bases and where allowed by local regulations, dispose of the neutral materials via the sanitary sewer system. Again, the nature of the neutralized material must be considered to ensure that it does not involve an environmental hazard such as chromium salts from chromic acid neutralization.

**Reactivity:** These substances include reactive metals such as sodium and various water reactive reagents. Compounds such as cyanides or sulfides are included in this
Laboratory Safety

class if they can readily evolve toxic gases such as hydrogen cyanide. Their collection for disposal must be carried out with particular care. When present in small quantities, it is advisable to deactivate reactive metals by careful reaction with appropriate alcohols and to deactivate certain oxygen or sulfur containing compounds through oxidation. Specific procedures should be consulted.

Toxicity: Although the EPA has specific procedures for determining toxicity, all chemicals may be toxic in certain concentrations. Appropriate procedures should be established in each laboratory for collection and disposal of these materials.

The handling of reaction byproducts, surplus and waste chemicals, and contaminated materials is an important part of laboratory safety procedures. Each laboratory worker is responsible for ensuring that wastes are handled in a manner that minimizes personal hazard and recognizes the potential for environmental contamination.

Most instructional laboratories will have clear procedures for students to follow in order to minimize the generation of waste materials. Typically reaction byproducts and surplus chemicals will be neutralized or deactivated as part of the experimental procedure. Waste materials must be handled in specific ways as designated by federal and local regulations. University guidelines for waste disposal can be found in chapter 7 of the Chemical Hygiene Plan (available at [http://www.cee.cornell.edu/safety/](http://www.cee.cornell.edu/safety/)).

Some general guidelines are:

1) Dispose of waste materials promptly. When disposing of chemicals one basic principle applies: Keep each different class of chemical in a separate clearly labeled disposal container.

2) Never put chemicals into a sink or down the drain unless they are deactivated or neutralized and they are allowed by local regulation in the sanitary sewer system. [See Chemical Hygiene Plan for list of chemicals that can be safely disposed of in the sanitary sewer.]

3) Put ordinary waste paper in a wastepaper basket separate from the chemical wastes. If a piece of paper is contaminated, such as paper toweling used to clean up a spill, put the contaminated paper in the special container that is marked for this use. It must be treated as a chemical waste.

4) Broken glass belongs in its own marked waste container. Broken thermometers may contain mercury in the fragments and these belong in their own special sealed "broken thermometer" container.

5) Peroxides, because of their reactivity, and the unpredictable nature of their formation in laboratory chemicals, have attracted considerable attention. The disposal of large quantities (25 g or more) of peroxides requires expert assistance. Consider each case individually for handling and disposal.

A complete list of compounds considered safe for drain disposal can be found in Chapter 7 of the Chemical Hygiene Plan ([http://www.cee.cornell.edu/safety/](http://www.cee.cornell.edu/safety/)). Disposal techniques for chemicals not found in this list must be disposed of using techniques approved of by Cornell Environmental Health and Safety. When possible,
hazardous chemicals can be neutralized and then disposed. When chemicals are produced that cannot be disposed of using the sanitary sewer, techniques to decrease the volume of the waste should be considered.

References


OSHA Laboratory Standard

One of the best books to get started with regulatory compliance is a publication from the American Chemical Society entitled, "Laboratory Waste Management. A Guidebook."

Questions

1) Why are contact lenses hazardous in the laboratory?
2) What is the minimum information needed on the label for each chemical? When are right to know labels required?
3) Why is it important to label a bottle even if it only contains distilled water?
4) Find an MSDS for sodium nitrate.
   a) Who created the MSDS?
   b) What is the solubility of sodium nitrate in water?
   c) Is sodium nitrate carcinogenic?
   d) What is the LD50 oral rat?
   e) How much sodium nitrate would you have to ingest to give a 50% chance of death (estimate from available LD50 data).
   f) How much of a 1 M solution would you have to ingest to give a 50% chance of death?
   g) Are there any chronic effects of exposure to sodium nitrate?
5) You are in the laboratory preparing chemical solutions for an experiment and it is lunchtime. You decide to go to the student lounge to eat. What must you do before leaving the laboratory?
6) Where are the eyewash station, the shower, and the fire extinguishers located in the laboratory?
Laboratory Measurements and Procedures

Introduction

Measurements of masses, volumes, and preparation of chemical solutions of known composition are essential laboratory skills. The goal of this exercise is to gain familiarity with these laboratory procedures. You will use these skills repeatedly throughout the semester.

Theory

Many laboratory procedures require preparation of chemical solutions. Most chemical solutions are prepared on the basis of mass of solute per volume of solution (grams per liter or Moles per liter). Preparation of these chemical solutions requires the ability to accurately measure both mass and volume.

Preparation of dilutions is also frequently required. Many analytical techniques require the preparation of known standards. Standards are generally prepared with concentrations similar to that of the samples being analyzed. In environmental work many of the analyses are for hazardous substances at very low concentrations (mg/L or µg/L levels). It is difficult to weigh accurately a few milligrams of a chemical with an analytical balance. Often dry chemicals are in crystalline or granular form with each crystal weighing several milligrams making it difficult to get close to the desired weight. Thus it is often easier to prepare a low concentration standard by diluting a higher concentration stock solution. For example, 100 mL of a 10 mg/L solution of NaCl could be obtained by first preparing a 1 g/L NaCl solution (100 mg in 100 mL). One mL of the 1 g/L stock solution would then be diluted to 100 mL to obtain a 10 mg/L solution.

Absorption spectroscopy is one analytical technique that can be used to measure the concentration of a compound. Solutions that are colored absorb light in the visible range. The resulting color of the solution is from the light that is transmitted. According to Beer's law the attenuation of light in a chemical solution is related to the concentration and the length of the path that the light passes through.

$$\log \left( \frac{P_o}{P} \right) = \varepsilon bc$$  
\[ 2.1 \]

where \(c\) is the concentration of the chemical species, \(b\) is the distance the light travels through the solution, \(\varepsilon\) is a constant \(P_o\) is the intensity of the incident light, and \(P\) is the intensity of the transmitted light. Absorption, \(A\), is defined as:

$$A = \log \left( \frac{P_o}{P} \right)$$  
\[ 2.2 \]

In practice \(P_o\) is the intensity of light through a reference sample (such as deionized water) and thus accounts for any losses in the walls of the sample chamber. From equation \[ 2.1 \] and \[ 2.2 \] it may be seen that absorption is directly proportional to the concentration of the chemical species.

$$A = \varepsilon bc$$  
\[ 2.3 \]
The instrument you will use to measure absorbance is a Hewlett Packard (HP) model 8452A diode array spectrophotometer. The diode array spectrophotometer uses a broad-spectrum source of incident light from a deuterium lamp. The light passes through the sample and is split by a grating into a spectrum of light that is measured by an array of diodes. Each diode measures a bandwidth of 2 nm with 316 diodes covering the range from 190 nm to 820 nm. The wavelengths of light and their colors are given in Table 2-1. The light path for the diode array spectrophotometer is shown in Figure 2-1.

The HP 8452A spectrophotometer has a photometric range of 0.002 - 3.3 absorbance units. In practice absorbance measurements greater than 2.5 are not very meaningful as they indicate that 99.7% of the incident light at that wavelength was absorbed. Conversely, an absorbance of 0.002 means that 0.5% of the incident light at that wavelength was absorbed.

When measuring samples of known concentration the Spectrophotometer software [http://ceeserver.cee.cornell.edu/mw24/Software/Spectrophotometer.htm](http://ceeserver.cee.cornell.edu/mw24/Software/Spectrophotometer.htm) calculates the relationship between absorbance and concentration at a selected wavelength. The slope (m), intercept (b) and correlation coefficient (r) are calculated using equations 2.6 through 2.8.

The slope of the best fit line is

\[
m = \frac{\sum xy - \frac{\Sigma x \Sigma y}{n}}{\sum x^2 - \frac{(\Sigma x)^2}{n}}
\]

2.6

The intercept of the line is

\[
b = \bar{y} - m \bar{x}
\]

2.7

The correlation coefficient is defined as

<table>
<thead>
<tr>
<th>color</th>
<th>wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ultra violet</td>
<td>190-380</td>
</tr>
<tr>
<td>violet</td>
<td>380-450</td>
</tr>
<tr>
<td>blue</td>
<td>450-490</td>
</tr>
<tr>
<td>green</td>
<td>490-560</td>
</tr>
<tr>
<td>yellow</td>
<td>560-590</td>
</tr>
<tr>
<td>orange</td>
<td>590-630</td>
</tr>
<tr>
<td>red</td>
<td>630-760</td>
</tr>
</tbody>
</table>

Table 2-1. Wavelengths of light

![Figure 2-1. Diagram of light path in diode array spectrophotometer.](image)
\[ r = \frac{\sum xy - \frac{\sum x \sum y}{n}}{\sqrt{\left( \sum x^2 - \frac{(\sum x)^2}{n} \right) \left( \sum y^2 - \frac{(\sum y)^2}{n} \right)}} \]

where \( x \) is the concentration of the solute (methylene blue in this exercise), \( y \) is the absorbance, and \( n \) is the number of samples.

**Experimental Objectives**

To gain proficiency in:

1) Calibrating and using electronic balances
2) Digital pipetting
3) Preparing a solution of known concentration
4) Preparing dilutions
5) Measuring concentrations using a UV-Vis spectrophotometer

**Experimental Methods**

**Mass Measurements**

Mass can be accurately measured with an electronic analytical balance. Perhaps because balances are so easy to use it is easy to forget that they should be calibrated on a regular basis. It is recommended that balances be calibrated once a week, after the balance has been moved, or if excessive temperature variations have occurred. In order for balances to operate correctly they also need to be level. Most balances come with a bubble level and adjustable feet. Before calibrating a balance verify that the balance is level.

The environmental laboratory is equipped with balances manufactured by Denver Instruments. To calibrate the Denver Instrument balances:

1) **Zero the balance** by pressing the tare button.
2) Press the **MENU** key until "MENU #1" is displayed.
3) Press the **1** key to select Calibrate.
4) Note the preset calibration masses that can be used for calibration on the bottom of the display.
5) Place a calibration mass on the pan (handle the calibration mass using a cotton glove or tissue paper).
6) The balance will automatically calibrate. A short beep will occur and the display will read CALIBRATED for three seconds, and then return to the measurement screen.

Dry chemicals can be weighed in disposable plastic "weighing boats" or other suitable containers. It is often desirable to subtract the weight of the container in which the chemical is being weighed. The weight of the chemical can be obtained
either by weighing the container first and then subtracting, or by "zeroing" the balance with the container on the balance.

**Temperature Measurement**

Use a thermistor to measure the temperature of distilled water. The thermistor is stored in the knee-space drawer and has a 4-mm diameter metallic probe. Plug the probe into one of the ports on the top row of the bench top data acquisition panel. Monitor the thermistor using Signal Monitor software. See [http://ceeserver.cee.cornell.edu/mw24/Software/signal_monitor.htm](http://ceeserver.cee.cornell.edu/mw24/Software/signal_monitor.htm) for information on sensor calibration. Place the probe in a 100-mL plastic beaker full of distilled water. Wait at least 15 seconds to allow the probe to equilibrate with the solution.

**Pipette Technique**

1) Use Figure 2-2 to estimate the mass of 990 µL of distilled water (at the measured temperature).

2) Use a 100-1000 µL digital pipette to transfer 990 µL of distilled water to a tared weighing boat on the 100 g scale. Record the mass of the water and compare with the expected value (Figure 2-2). Repeat this step if necessary until your pipetting error is less than 2%, then measure the mass of 5 replicate 990 µL pipette samples. Calculate the mean (\( \bar{x} \) defined in equation 2.9), standard deviation (\( s \) defined in equation 2.10), and coefficient of variation, \( s/\bar{x} \), for your measurements. The coefficient of variation (c.v.) is a good measure of the precision of your technique. For this test a c.v. < 1% should be achievable.

\[
\bar{x} = \frac{\sum x}{n} \quad 2.9
\]

\[
s = \sqrt{\frac{\sum x^2 - (\sum x)^2}{n}} \quad 2.10
\]

Note that these functions are available on most calculators and in Excel.
Measure Density

1) Weigh a 100 mL volumetric flask with its cap (use the 400 g or 800 g balance).
2) Prepare 100 mL of a 1 M solution of sodium chloride in the weighed flask. Make sure to mix the solution and then verify that you have exactly 100 mL of solution. Note that the volume decreases as the salt dissolves.
3) Weigh the flask (with its cap) plus the sodium chloride solution and calculate the density of the 1 M NaCl solution.

Prepare methylene blue standards of several concentrations

1) A methylene blue stock solution of 1 g/L has been prepared. Use it to prepare 100 mL of each of the following concentrations: 1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L, and 5 mg/L.
2) Note any errors in transfer of mass as you prepare these dilutions (the color will make it easy to see).

Prepare a standard curve and measure an unknown

1) See [http://ceeserver.cee.cornell.edu/mw24/Software/Spectrophotometer.htm](http://ceeserver.cee.cornell.edu/mw24/Software/Spectrophotometer.htm) for instructions on using the UV-Vis Spectrophotometer software.
2) Measure the absorbance of the methylene blue solutions using a UV-Vis spectrophotometer. Analyze the 5 methylene blue samples plus a distilled water sample (0 mg/L methylene blue) as standards. Select Measure Standards from the computer control palette. Fill in the information for the six samples (starting with distilled water and ending with the highest concentration of methylene blue) and follow instructions as you are prompted.
3) Save the data as \enviro\Courses\453\fundamentals\netid_blue.
4) Record the absorbance at 660 nm for each of the solutions. You can drag the blue cursor on the “standard graph” to the wavelength of choice and read the exact absorbance (and wavelength) in the digital display to the right of the graph. Note that you can do this after you have analyzed all of the standards.
5) Record the correlation coefficient (equation 2.8), slope (equation 2.6), and intercept (equation 2.7) for the absorbance at 660 nm vs. methylene blue concentration. These values are shown next to the “calibration graph” and correspond to the wavelength selected using the blue cursor on the “standard graph.”
6) Measure the absorbance of a methylene blue solution of unknown concentration. Select Measure Samples from the control palette. Save the data as...
Laboratory Measurements and Procedures

Record its absorbance at 660 nm and the calculated concentration. These values are given in the digital displays in the bottom left of the window.

7) Export your standards spectra to the enviro\Courses\453\fundamentals folder.

8) Turn on the pump and place the sipper tube in distilled water to clean out the sample cell by selecting Run Pump from the control palette.

Prelab Questions

1) You need 100 mL of a 1 µM solution of zinc that you will use as a standard to calibrate an atomic adsorption spectrophotometer. Find a source of zinc ions combined either with chloride or nitrate (you can use the world wide web or any other source of information). What is the molecular formula of the compound that you found? Zinc disposal down the sanitary sewer is restricted at Cornell. How does the disposal restriction for zinc influence how you prepare the zinc standard? How would you prepare this standard using techniques readily available in the environmental laboratory? Note that we have pipettes that can dispense volumes between 10 µL and 1 mL and that we have 100 mL and 1 L volumetric flasks. Include enough information so that you could prepare the standard without doing any additional calculations. Consider your ability to accurately weigh small masses. Explain your procedure for any dilutions.

2) The density of sodium chloride solutions as a function of concentration is approximately 0.6985C + 998.29 (kg/m³) (C is kg of salt/m³). What is the density of a 1 M solution of sodium chloride?

Data Analysis and Questions

Submit one spreadsheet containing the data sheet, exported absorbance data, graphs and answers to the questions.


2) Create a graph of absorbance at 660 nm vs concentration of methylene blue in Excel using the exported data file. Does absorbance at 660 nm increase linearly with concentration of methylene blue?

3) Plot ε as a function of wavelength for each of the standards on a single graph. Make sure you include units and axis labels on your graph. If Beer’s law is obeyed what should the graph look like?

4) Did you use interpolation or extrapolation to get the concentration of the unknown?

5) What colors of light are most strongly absorbed by methylene blue?

6) What measurement controls the accuracy of the density measurement? What should the accuracy be?
## Data Sheet

### Balance Calibration

<table>
<thead>
<tr>
<th>Balance ID</th>
<th>Mass of calibration mass</th>
<th>2nd mass used to verify calibration</th>
<th>Measured mass of 2nd mass</th>
</tr>
</thead>
</table>

### Temperature Measurement

<table>
<thead>
<tr>
<th>Distilled water temperature</th>
</tr>
</thead>
</table>

### Pipette Technique (use DI-100 balance)

<table>
<thead>
<tr>
<th>Density of water at that temperature</th>
<th>Actual mass of 990 µL of pure water</th>
<th>Mass of 990 µL of water (rep 1)</th>
<th>Mass of 990 µL of water (rep 2)</th>
<th>Mass of 990 µL of water (rep 3)</th>
<th>Mass of 990 µL of water (rep 4)</th>
<th>Mass of 990 µL of water (rep 5)</th>
<th>Average of the 5 measurements</th>
<th>Standard deviation of the 5 measurements</th>
</tr>
</thead>
</table>

### Precision

<table>
<thead>
<tr>
<th>Percent coefficient of variation of the 5 measurements</th>
</tr>
</thead>
</table>

### Accuracy

<table>
<thead>
<tr>
<th>average percent error for pipetting</th>
</tr>
</thead>
</table>

### Measure Density (use DI-800 balance)

<table>
<thead>
<tr>
<th>Molecular weight of NaCl</th>
<th>Mass of NaCl in 100 mL of a 1-M solution</th>
<th>Measured mass of NaCl used</th>
<th>Measured mass of empty 100 mL flask</th>
<th>Measured mass of flask + 1M solution</th>
<th>Mass of 100 mL of 1 M NaCl solution</th>
<th>Density of 1 M NaCl solution</th>
<th>Literature value for density of 1 M NaCl solution</th>
<th>percent error for density measurement</th>
</tr>
</thead>
</table>

### Prepare methylene blue standards of several concentrations

Volume of 1 g/L MB diluted to 100 mL to obtain:
- 1 mg/L MB
- 2 mg/L MB
- 3 mg/L MB
- 4 mg/L MB
- 5 mg/L MB

### Measure absorbance at 660 nm using a spectrophotometer.

<table>
<thead>
<tr>
<th>Absorbance of distilled water</th>
<th>Absorbance of 1 mg/L methylene blue</th>
<th>Absorbance of 2 mg/L methylene blue</th>
<th>Absorbance of 3 mg/L methylene blue</th>
<th>Absorbance of 4 mg/L methylene blue</th>
<th>Absorbance of 5 mg/L methylene blue</th>
<th>Slope at 660 nm (m)</th>
<th>Intercept at 660 nm (b)</th>
<th>Correlation coefficient at 660 nm (r)</th>
<th>Absorbance of unknown at 660 nm</th>
<th>Calculated concentration of unknown</th>
</tr>
</thead>
</table>

Lab Prep Notes

Table 2-2. Reagent list.

<table>
<thead>
<tr>
<th>Description</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Fisher Scientific</td>
<td>BP358-1</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Fisher Scientific</td>
<td>M291-25</td>
</tr>
</tbody>
</table>

Table 2-3. Equipment list

<table>
<thead>
<tr>
<th>Description</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibra 100-1095 µL</td>
<td>Fisher Scientific</td>
<td>13-707-5</td>
</tr>
<tr>
<td>Calibra 10-109.5 µL</td>
<td>Fisher Scientific</td>
<td>13-707-3</td>
</tr>
<tr>
<td>DI 100 analytical toploader</td>
<td>Fisher Scientific</td>
<td>01-913-1A</td>
</tr>
<tr>
<td>DI-800 Toploader 100 mL volumetric</td>
<td>Fisher Scientific</td>
<td>01-913-1C</td>
</tr>
<tr>
<td>UV-Vis spectrophotometer</td>
<td>Hewlett-Packard Company</td>
<td>8452A</td>
</tr>
</tbody>
</table>

Table 2-4. Methylene Blue Stock Solution

<table>
<thead>
<tr>
<th>Description</th>
<th>MW (g/M)</th>
<th>conc. (g/L)</th>
<th>100 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₆H₁₈N₃SCl</td>
<td>319.87</td>
<td>1</td>
<td>100.0 mg</td>
</tr>
</tbody>
</table>

Setup

1) Prepare stock methylene blue solution and distribute to student workstations in 15 mL vials.
2) Prepare 100 mL of unknown in concentration range of standards. Divide into two bottles (one for each spectrophotometer).
3) Verify that spectrophotometers are working (prepare a calibration curve as a test).
4) Verify that balances calibrate easily.
5) Disassemble, clean and lubricate all pipettes.
Acid Precipitation and Remediation of Acid Lakes

Introduction

Acid precipitation has been a serious environmental problem in many areas of the world for the last few decades. Acid precipitation results from the combustion of fossil fuels, that produces oxides of sulfur and nitrogen that react in the earth's atmosphere to form sulfuric and nitric acid. One of the most significant impacts of acid rain is the acidification of lakes and streams. In some watersheds the soil doesn’t provide ample acid neutralizing capacity to mitigate the effect of incident acid precipitation. These susceptible regions are usually high elevation lakes, with small watersheds and shallow non-calcareous soils. The underlying bedrock of acid-sensitive lakes tends to be granite or quartz. These minerals are slow to weather and therefore have little capacity to neutralize acids. The relatively short contact time between the acid precipitation and the watershed soil system exacerbates the problem. Lakes most susceptible to acidification: 1) are located downwind, sometimes hundreds of miles downwind, from major pollution sources–electricity generation, metal refining operations, heavy industry, large population centers; 2) are surrounded by hard, insoluble bedrock with thin, sandy, infertile soil; 3) have a high runoff to infiltration ratio; 4) have a low watershed to lake surface area. Isopleths of precipitation pH are depicted in Figure 3-1.

![Figure 3-1. The pH of precipitation in 2000.](image)

In acid-sensitive lakes the major parameter of concern is pH (pH = -log{H⁺}, where {H⁺} is the hydrogen ion activity, and activity is approximately equal to concentration in moles/L). In a healthy lake, ecosystem pH should be in the range of
6.5 to 8.5. In most natural freshwater systems, the dominant pH buffering (controlling) system is the carbonate system. The carbonate buffering system is composed of four components: dissolved carbon dioxide (CO\textsubscript{2,aq}), carbonic acid (H\textsubscript{2}CO\textsubscript{3}), bicarbonate (HCO\textsubscript{3}\textsuperscript{-}), and carbonate (CO\textsubscript{3}\textsuperscript{2-}). Carbonic acid exists only at very low levels in aqueous systems and for purposes of acid neutralization is indistinguishable from dissolved carbon dioxide. Thus to simplify things we define

\[
\left[\text{H}_2\text{CO}_3\right] = [\text{CO}_2\text{aq}] + [\text{H}_2\text{CO}_3] \quad \text{3.2}
\]

The \([\text{CO}_2\text{aq}] \gg [\text{H}_2\text{CO}_3]\) and thus \([\text{H}_2\text{CO}_3^+] \equiv [\text{CO}_2\text{aq}]\) (all terms enclosed in [] are in units of moles/L).

The sum of all the molar concentration of the components of the carbonate system is designated as C\textsubscript{T} as shown in equation 3.3.

\[
C_T = \left[\text{H}_2\text{CO}_3^+\right] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad \text{3.3}
\]

The carbonate system can be considered to be a "volatile" system or a "non-volatile" system depending on whether or not aqueous carbon dioxide is allowed to exchange and equilibrate with atmospheric carbon dioxide. Mixing conditions and hydraulic residence time determine whether an aquatic system is volatile or non-volatile relative to atmospheric carbon dioxide equilibrium. First, consider the "non-volatile" system.

**Non-volatile System**

For a fixed C\textsubscript{T}, the molar concentration of each species of the carbonate system is determined by pH. Equations 3.4-3.9 show these functional relationships.

\[
\left[\text{H}_2\text{CO}_3\right] = \frac{C_T}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}} = \alpha_0 C_T \quad \text{3.4}
\]

where

\[
\alpha_0 = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}} \quad \text{3.5}
\]

\[
\left[\text{HCO}_3^-\right] = \frac{C_T}{[H^+] + \frac{K_2}{K_1} [H^+] + \frac{K_2}{K_1} [H^+]^2} = \alpha_1 C_T \quad \text{3.6}
\]

where

\[
\alpha_1 = \frac{1}{[H^+] + \frac{K_2}{K_1} [H^+] + \frac{K_2}{K_1} [H^+]^2} \quad \text{3.7}
\]
\[
\left[ \text{CO}_3^{2-} \right] = \frac{C_T}{K_1 K_2 + [H^+]^2} = \alpha_2 C_T
\]

where

\[
\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1}
\]

K_1 and K_2 are the first and second dissociation constants for carbonic acid and \(\alpha_0, \alpha_1,\) and \(\alpha_2\) are the fraction of \(C_T\) in the form \(\text{H}_2\text{CO}_3,\ \text{HCO}_3,\) and \(\text{CO}_3^{2-}\) respectively. Because K_1 and K_2 are constants (K_1 = 10^{-6.3} and K_2 = 10^{-10.3}), \(\alpha_0, \alpha_1,\) and \(\alpha_2\) are only functions of pH.

A measure of the susceptibility of lakes to acidification is the acid neutralizing capacity (ANC) of the lake water. In the case of the carbonate system, the ANC is exhausted when enough acid has been added to convert the carbonate species \(\text{HCO}_3^-\) and \(\text{CO}_3^{2-}\) to \(\text{H}_2\text{CO}_3^*\). A formal definition of total acid neutralizing capacity is given by equation 3.10.

\[
\text{ANC} = \left[ \text{HCO}_3^- \right] + 2 \left[ \text{CO}_3^{2-} \right] + \left[ \text{OH}^- \right] - \left[ H^+ \right]
\]

ANC has units of equivalents per liter. The hydroxide ion concentration can be obtained from the hydrogen ion concentration and the dissociation constant for water \(K_w\).

\[
\left[ \text{OH}^- \right] = \frac{K_w}{[H^+]}
\]

Substituting equations 3.6, 3.8, and 3.11 into equation 3.10 we obtain

\[
\text{ANC} = C_T (\alpha_0 + 2\alpha_1) + \frac{K_w}{[H^+] - [H^+]} - [H^+]
\]

For the carbonate system, ANC is usually referred to as alkalinity.²

Volatile Systems:

Now consider the case where aqueous \(\text{CO}_2\) is volatile and in equilibrium with atmospheric carbon dioxide. Henry's Law can be used to describe the equilibrium relationship between atmospheric and dissolved carbon dioxide.

\[
\left[ \text{CO}_2\text{aq} \right] = P_{\text{CO}_2} K_H
\]

² Alkalinity can be expressed as equivalents/L or as mg/L (ppm) of CaCO_3. 50,000 mg/L CaCO_3 = 1 equivalent/L.
where $K_H$ is Henry's constant for CO$_2$ in moles/L-atm and $P_{CO_2}$ is partial pressure of CO$_2$ in the atmosphere ($K_H = 10^{-1.5}$ and $P_{CO_2} = 10^{-3.5}$). Because $[CO_{2aq}]$ is approximately equal to $[H_2CO_3]$ and from equations 3.2 and 3.4

$$P_{CO_2}K_H = \alpha_0 C_T$$  \hspace{1cm} 3.14

$$C_T = \frac{P_{CO_2}K_H}{\alpha_0}$$  \hspace{1cm} 3.15

Equation 3.15 gives the equilibrium concentration of carbonate species as a function of pH and the partial pressure of carbon dioxide.

The acid neutralizing capacity expression for a volatile system can be obtained by combining equations 3.15 and 3.12.

$$ANC = \frac{P_{CO_2}K_H}{\alpha_0}\left(\alpha_1 + 2\alpha_2\right) + \frac{K_w}{[H^+]} - [H^+] + \left[A^-_{org}\right]$$  \hspace{1cm} 3.16

In both non-volatile and volatile systems, equilibrium pH is controlled by system ANC. Addition or depletion of any ANC component in equation 3.12 or 3.16 will result in a pH change. Natural bodies of water are most likely to approach equilibrium with the atmosphere (volatile system) if the hydraulic residence time is long and the body of water is shallow.

Lake ANC is a direct reflection of the mineral composition of the watershed. Lake watersheds with hard, insoluble minerals yield lakes with low ANC. Typically watersheds with soluble, calcareous minerals yield lakes with high ANC. ANC of freshwater lakes is generally composed of bicarbonate, carbonate, and sometimes organic matter ($A^-_{org}$). Organic matter derives from decaying plant matter in the watershed. When organic matter is significant, the ANC becomes (from equations 3.12 and 3.16)

$$ANC = C_T\left(\alpha_1 + 2\alpha_2\right) + \frac{K_w}{[H^+]} - [H^+] + \left[A^-_{org}\right]$$  \hspace{1cm} 3.17

$$ANC = \frac{P_{CO_2}K_H}{\alpha_0}\left(\alpha_1 + 2\alpha_2\right) + \frac{K_w}{[H^+]} - [H^+] + \left[A^-_{org}\right]$$  \hspace{1cm} 3.18

where equation 3.17 is for a non-volatile system and equation 3.18 is for a volatile system.

During chemical neutralization of acid, the components of ANC associate with added acid to form protonated molecules. For example:

$$[H^+] + [HCO_3^-] \rightarrow [H_2CO_3]$$  \hspace{1cm} 3.19

or
In essence, the ANC of a system is a result of the reaction of acid inputs to form associated acids from basic anions that were dissolved in the lake water. The ANC (equation 3.10) is consumed as the basic anions are converted to associated acids. This conversion is near completion at low pH (approximately pH 4.5 for the bicarbonate and carbonate components of ANC). Neutralizing capacity to another (probably higher) pH may be more useful for natural aquatic systems. Determination of ANC to a particular pH is fundamentally easy — simply add and measure the amount of acid required to lower the sample pH from its initial value to the pH of interest. Techniques to measure ANC are described under the procedures section of this lab.

Neutralization of acid precipitation can occur in the watershed or directly in the lake. How much neutralization occurs in the watershed versus the lake is a function of the watershed to lake surface area. Generally, watershed neutralization is dominant. Recently engineered remediation of acid lakes has been accomplished by adding bases such as limestone, lime, or sodium bicarbonate to the watershed or directly to the lakes.

**Reactor theory applied to Acid Lake Remediation**

In this experiment sodium bicarbonate will be added to a lake to mitigate the deleterious effect of acid rain. Usually sodium bicarbonate is added in batch doses (as opposed to metering in). The quantity of sodium bicarbonate added depends on how long a treatment is desired, the acceptable pH range and the quantity and pH of the incident rainfall. For purposes of this experiment, a 15-minute design period will be used. That is, we would like to add enough sodium bicarbonate to keep the lake at or above its original pH and alkalinity for a period of 15 minutes (i.e. for one hydraulic residence time).

By dealing with ANC instead of pH as a design parameter, we avoid the issue of whether the system is at equilibrium with atmospheric carbon dioxide. Keep in mind that eventually the lake will come to equilibrium with the atmosphere. In practice, neutralizing agent dosages may have to be adjusted to take into account non-equilibrium conditions.

We must add enough sodium bicarbonate to equal the negative ANC from the acid precipitation input plus the amount of ANC lost by outflow from the lake during the 15-minute design period. Initially (following the dosing of sodium bicarbonate) the pH and ANC will rise, but over the course of 15 minutes, both parameters will drop. Calculation of required sodium bicarbonate dosage requires performing a mass balance on ANC around the lake. This mass balance will assume a completely mixed lake and conservation of ANC. Chemical equilibrium can also be assumed so that the sodium bicarbonate is assumed to react immediately with the incoming acid precipitation. Mass balance on the reactor yields:

\[
Q \left( ANC_{in} - ANC_{out} \right) = V \frac{d(ANC)}{dt}
\]

where:

\[
\left[ H^+ \right] + \left[ A_{org} \right] \rightarrow \left[ HA_{org} \right]
\] 3.20
\[ \text{ANC}_{\text{out}} = \text{ANC in \ lake \ outflow \ at \ any \ time \ t} \text{ (for \ a \ completely \ mixed \ lake \ the \ effluent \ ANC \ is \ the \ same \ as \ the \ ANC \ in \ the \ lake)} \]

\[ \text{ANC}_{\text{in}} = \text{ANC of \ acid \ rain \ input} \]

\[ V = \text{volume \ of \ reactor} \]

\[ Q = \text{acid \ rain \ input \ flow \ rate}. \]

If the initial ANC in the lake is designated as \( \text{ANC}_0 \), then the solution to the mass balance differential equation is:

\[
\text{ANC}_{\text{out}} = \text{ANC}_{\text{in}} \cdot \left(1 - e^{-\theta} \right) + \text{ANC}_0 \cdot e^{-\theta} \quad 3.22
\]

where:

\[ \theta = \frac{V}{Q} \]

We want to find \( \text{ANC}_0 \) such that \( \text{ANC}_{\text{out}} = 50 \, \mu\text{eq/L} \) when \( t \) is equal to \( \theta \). Solving for \( \text{ANC}_0 \) we get

\[
\text{ANC}_0 = \left[ \text{ANC}_{\text{out}} - \text{ANC}_{\text{in}} \cdot \left(1 - e^{-\theta} \right) \right] e^{\theta} \quad 3.23
\]

The ANC of the acid rain (\( \text{ANC}_{\text{in}} \)) can be estimated from its pH. Below pH 6.3 most of the carbonates will be in the form \( \text{H}_2\text{CO}_3^- \) and thus for pH below about 4.3 equation 3.10 simplifies to

\[
\text{ANC} \cong -\left[\text{H}^+ \right] \quad 3.24
\]

An influent pH of 3.0 implies the \( \text{ANC}_{\text{in}} = -\left[\text{H}^+ \right] = -0.001 \)

Substituting into equation 3.23

\[
\text{ANC}_0 = \left[ -0.000050 + 0.001 \cdot \left(1 - e^{-1} \right) \right] e^1 = 1.854 \, \text{meq/L} \]

The quantity of sodium bicarbonate required can be calculated from:

\[
[\text{NaHCO}_3]_0 = \text{ANC}_0 \quad 3.25
\]

where \([\text{NaHCO}_3]_0 = \text{moles \ of \ sodium \ bicarbonate \ required \ per \ liter \ of \ lake \ water}\)

\[
\frac{1.854 \, \text{mmole \ NaHCO}_3}{\text{liter}} \times \frac{84 \, \text{mg \ NaHCO}_3}{\text{mmole \ NaHCO}_3} \times 5 \, \text{Liters} = 779 \, \text{mg \ NaHCO}_3 \quad 3.26
\]

**Experimental Objectives**

Remediation of acid lakes involves addition of ANC so that the pH is raised to an acceptable level and maintained at or above this level for some design period. In this experiment sodium bicarbonate (\( \text{NaHCO}_3 \)) will be used as the ANC supplement. Since ANC addition usually occurs as a batch addition, the design pH is initially exceeded. ANC dosage is selected so that at the end of the design period pH is at the acceptable level. Care must be taken to avoid excessive initial pH — high pH can be as deleterious as low pH.
The most common remediation procedure is to apply the neutralizing agent directly to the lake surface, instead of on the watershed. We will follow that practice in this lab experiment. Sodium bicarbonate will be added directly to the surface of the lake that has an initial ANC of 0 µeq/L and is receiving acid rain with a pH of 3. After the sodium bicarbonate is applied, the lake pH and ANC will be monitored for approximately one hour.

**Experimental Apparatus**

The experimental apparatus consists of an acid rain storage reservoir, peristaltic pump, and lake (Figure 3-2). The pH of the lake will be monitored using a pH probes connected to a pH meter.

**Experimental Procedures**

**Calibration of pH Meter**

Calibrate the pH probes attached to the pH meter. To calibrate the probe attached to channel A toggle the display by pressing **Channel** until only the pH from channel A is in the display. (The display toggles between channel A, channel B, and both channels.) Then follow the calibration procedure outlined at [http://ceeserver.cee.cornell.edu/mw24/Labdocumentation/pH/calibration.htm](http://ceeserver.cee.cornell.edu/mw24/Labdocumentation/pH/calibration.htm).

1) Verify that the system is plumbed so that the “acid rain” is pumped directly into the lake.

2) Take a 50-mL sample from the acid rain container. Collect the sample in a 125-mL bottle.

3) Preset pump to give desired flow rate of 334 mL/min (5 L/15 minutes).

4) Fill lake with distilled water.

5) Set stirrer speed to 8.

6) Add 1 mL of bromocresol green indicator solution to the lake.

7) Weigh out 779 mg (not grams!) NaHCO₃.

8) Add NaHCO₃ to the lake.

9) After the lake is well stirred take a 100 mL sample from the lake.

10) Prepare to monitor the pH of one probe using the Compumet™ software. Set the method for automatic sampling of the pH probe on channel A every 10 seconds. See [http://ceeserver.cee.cornell.edu/mw24/Software/Compumet.htm](http://ceeserver.cee.cornell.edu/mw24/Software/Compumet.htm) for information on using the computer to monitor pH.

11) Place the probe attached to channel A to monitor the pH of the lake.

12) Label sample bottles (see step 14).

13) At time equal zero start the pump and begin monitoring the lake pH.
14) Take 100-mL grab samples from the lake effluent at 5, 10, 15, and 20 minutes. The sample volumes do not need to be measured. Collect the samples in 125-mL bottles.

15) Measure the flow rate.

16) After the 20-minute sample turn off the pump and stop sampling pH.

17) Save the pH data to \Enviro\enviro\Courses\453\acid\netid_remediate by selecting Save data from the control palette. The data will be saved in a file (tab delimited format) that can be opened by any spreadsheet program.

18) Measure the lake volume.

**Analytical Procedures**

**pH.** pH (-log{H⁺}) is usually measured electrometrically with a pH meter. The pH meter is a null-point potentiometer that measures the potential difference between an indicator electrode and a reference electrode. The two electrodes commonly used for pH measurement are the glass electrode and a reference electrode. The glass electrode is an indicator electrode that develops a potential across a glass membrane as a function of the activity, ~ molarity, of H⁺. Combination pH electrodes, in which the H⁺-sensitive and reference electrodes are combined within a single electrode body will be used in this lab. The reference electrode portion of a combination pH electrode is a [Ag/AgCl/4M KCl] reference. The response (output voltage) of the electrode follows a "Nernstian" behavior with respect to H⁺ ion activity.

\[
E = E^0 + \frac{RT}{nF} \ln \left( \frac{[H^+]}{[H^+^0]} \right)
\]

where \( R \) is the universal gas constant, \( T \) is temperature in Kelvin, \( n \) is the charge of the hydrogen ion, and \( F \) is the Faraday constant. \( E^0 \) is the calibration potential (Volts), and \( E \) is the potential (Volts) measured by the pH meter between glass and reference electrode. The slope of the response curve is dependent on the temperature of the sample and this effect is normally accounted for with simultaneous temperature measurements.

The electrical potential that is developed between the glass electrode and the reference electrode needs to be correlated with the actual pH of the sample. The pH meter is calibrated with a series of buffer solutions whose pH values encompass the range of intended use. The pH meter is used to adjust the response of the electrode system to ensure a Nernstian response is achieved over the range of the calibration standards.

See [http://ceeserver.cee.cornell.edu/mw24/Labdocumentation/pH/calibration.htm](http://ceeserver.cee.cornell.edu/mw24/Labdocumentation/pH/calibration.htm) for specific procedures. To measure pH the electrode(s) are submersed in at least 50 mL of a sample. It is important that the porous frit on the side of the probe be submerged in the sample. Samples are generally stirred during pH reading to establish homogeneity, to prevent local accumulation of reference electrode filling solution at the interface near the electrode, and to ensure the diffusive boundary layer thickness at the electrode surface is uniform and small.
ANC. The most common method to determine ANC for aqueous samples is titration with a strong acid to an endpoint pH. A pH meter is usually used to determine the endpoint or "equivalence point" of an ANC titration. Determination of the endpoint pH is difficult because it is dependent on the magnitude the sample ANC. Theoretically this endpoint pH should be the pH where all of the ANC of the system is consumed, but since the ANC is not known a-priori, a true endpoint cannot be predetermined. However, if most of the ANC is composed of carbonate and bicarbonate this endpoint is approximately pH = 4.5 for a wide range of ANC values.

A 50 to 100-mL sample is usually titrated while slowly stirred by a magnetic stirrer. pH electrodes are ordinarily used to record pH as a function of the volume of strong acid titrant added. The volume of strong acid required to reach the ANC endpoint (pH 4.5) is called the "equivalent volume" and is used in the following equation to compute ANC.

\[
\text{ANC} = \frac{(\text{equivalent vol.})(\text{normality of titrant})}{(\text{vol. of sample})}
\]  

A more accurate technique to measure ANC is the Gran plot analysis. This is the subject of a subsequent experiment. All ANC samples should be labeled and stored for subsequent Gran analysis.

Prelab Questions

1) How many grams of NaHCO₃ would be required to keep the ANC levels in a lake above 50 µeq/L for 3 hydraulic residence times given an influent pH of 3.0 a lake volume of 5 L, if the current lake ANC is 0 µeq/L?

Data Analysis

\[K_1 = 10^{-6.3}, K_2 = 10^{-10.3}, K_H = 10^{-1.5} \text{ mol/atm L}, P_{CO_2} = 10^{-3.5} \text{ atm}, \text{ and } K_w = 10^{-14}.\]

1) Plot measured pH of the lake versus time.
2) Given that ANC is a conservative parameter and that the lake is essentially in a completely mixed flow regime equation \[3.22\] applies. Graph the predicted ANC based on the completely mixed flow reactor equation with the plot labeled (in the legend) as “conservative ANC”.
3) Derive an equation for \( C_T \) (the concentration of carbonate species) as a function of time based on the input of NaHCO₃ and its dilution in the completely mixed lake assuming a non-volatile system (the equation will be the same form as equation \[3.22\]).
4) Combine your equation for \( C_T \) with equation \[3.12\] and plot the predicted ANC of the lake vs. time for a non-volatile system based on the measured pH (plot on the same graph as \#2with plot labeled as “non-volatile model”).
5) Plot the predicted ANC of the lake vs. time for a volatile system using equation \[3.16\] based on the measured pH (plot on the same graph as \#4with plot labeled as “volatile model”).
6) Compare the plots and determine whether the lake is best modeled as a volatile or non-volatile system. What changes could be made to the lake to bring the lake into equilibrium with atmospheric CO₂?

Questions

1) What do you think would happen if enough NaHCO₃ were added to the lake to maintain an ANC greater than 50 µeq/L for 3 residence times with the stirrer turned off?

2) What are some of the complicating factors you might find in attempting to remediate a lake using CaCO₃? Below is a list of issues to consider.

- extent of mixing
- solubility of CaCO₃ (find the solubility and compare with NaHCO₃)
- density of CaCO₃ slurry (find the density of CaCO₃)

References


Lab Prep Notes

Bromocresol Green Indicating Solution

Prepare solution of 400 mg Bromocresol green/100 mL ethanol. Add 0.2 mL of indicator solution per liter of acid rain or lake.

Acid rain

Acid rain is at pH 3.0. Prepare from distilled water. Add 1 meq H$_2$SO$_4$/L ([H$^+$] at pH 3.0) to obtain a pH of 3.0. To acidify 20 liters of distilled water using 5 N H$_2$SO$_4$:

\[
20 \text{ L} \cdot \frac{1 \text{ meq H}_2\text{SO}_4}{5 \text{ N H}_2\text{SO}_4} \cdot \frac{1 \text{ N L}}{1000 \text{ meq}} = 4 \text{ mL of 5 N H}_2\text{SO}_4
\]

Add 4 mL of bromocresol green indicating solution to 20 L of acid rain solution.

Flow Rate

The residence time of the lake should be 15 minutes. The lake volume is 5 L. Thus the flow rate is 334 mL/min. Use # 18 PharMed tubing.

Setup

1) Prepare 20-L acid rain for each group.
2) Prepare bromocresol green solution if necessary.
3) Attach one Easy-Load pump head to the pump drives and plumb with #18 tubing.
4) Plumb Jerrican to pump to lake using quick connectors (see Figure 3-2).
5) Verify that pH probes are operational, stable, and can be calibrated.
6) Verify that buffers (pH = 4, 7, 10) are distributed to each student group.
7) Provide a mount for the pH probe in the lake.
8) Set up some lakes with aeration!

Table 3-1. Reagents

<table>
<thead>
<tr>
<th>Description</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 5.0 N</td>
<td>Fisher Scientific</td>
<td>LC15360-2</td>
</tr>
<tr>
<td>H$_2$SO$_4$ 5N</td>
<td>Fisher Scientific</td>
<td>LC25840-2</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>Fisher Scientific</td>
<td>C63-3</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>Fisher Scientific</td>
<td>S263-500</td>
</tr>
<tr>
<td>Buffer-Pac</td>
<td>Fisher Scientific</td>
<td>SB105</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>Fisher Scientific</td>
<td>S233-500</td>
</tr>
<tr>
<td>Bromocresol Green</td>
<td>Fisher Scientific</td>
<td>B383-5</td>
</tr>
<tr>
<td>ethanol</td>
<td>Fisher Scientific</td>
<td>A962P-4</td>
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</table>

Table 3-2. Equipment list

<table>
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<tr>
<th>Description</th>
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<th>Catalog number</th>
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</thead>
<tbody>
<tr>
<td>magnetic stirrer</td>
<td>Fisher Scientific</td>
<td>11-500-7S</td>
</tr>
<tr>
<td>floating stir bar</td>
<td>Fisher Scientific</td>
<td>14-511-99A</td>
</tr>
<tr>
<td>Accumet™ 50 pH meter</td>
<td>Fisher Scientific</td>
<td>13-635-50</td>
</tr>
<tr>
<td>100-1095 µL pipette</td>
<td>Fisher Scientific</td>
<td>13-707-5</td>
</tr>
<tr>
<td>10-109.5 µL pipette</td>
<td>Fisher Scientific</td>
<td>13-707-3</td>
</tr>
<tr>
<td>pH electrode</td>
<td>Fisher Scientific</td>
<td>13-620-108</td>
</tr>
<tr>
<td>6 L container (lake)</td>
<td>Fisher Scientific</td>
<td>03-484-22</td>
</tr>
<tr>
<td>Easy load pump head</td>
<td>Cole Parmer</td>
<td>H-07518-00</td>
</tr>
<tr>
<td>digital pump drive</td>
<td>Cole Parmer</td>
<td>H-07523-30</td>
</tr>
<tr>
<td>PharMed tubing size 18</td>
<td>Cole Parmer</td>
<td>H-06485-17</td>
</tr>
<tr>
<td>20 liter HDPE Jerrican</td>
<td>Fisher Scientific</td>
<td>02-961-50C</td>
</tr>
</tbody>
</table>

CEE 453: Laboratory Research in Environmental Engineering

Spring 2002
Measurement of Acid Neutralizing Capacity

Introduction

Acid neutralizing capacity (ANC) is a measure of the ability of water to neutralize acid inputs. Lakes with high ANC (such as Cayuga Lake) can maintain a neutral pH even with some acid rain input whereas lakes with an ANC less than the acid input will not maintain a neutral pH. In the Adirondack region of New York State, lakes typically receive large inputs of acids during the spring thaw when the accumulated winter snow melts and runs off into the lakes. The ANC of Adirondack lakes is not always sufficient to neutralize these inputs.

Theory

The ANC for a typical carbonate-containing sample is defined as:

\[
ANC = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \tag{4.1}
\]

This equation can be derived from a charge balance if ANC is considered to be the cation contributed by a strong base titrant and if other ions present do not contribute significantly.

Determination of ANC or Alkalinity involves determination of an equivalence point. The equivalence point is defined as the point in the titration where titrant volume that has been added equals the "equivalent" volume (\(V_e\)). The equivalent volume is defined as:

\[
V_e = \frac{V_s \cdot N_s}{N_t} \tag{4.2}
\]

where:
- \(N_s\) = normality (in this case Alkalinity or ANC) of sample, equivalents/L
- \(V_s\) = volume of sample, liters
- \(N_t\) = normality of titrant, equivalents/L.

The titration procedure involves incrementally adding known volumes of standardized normality strong acid (or base) to a known volume of unknown normality base (or acid). When enough acid (or base) has been added to equal the amount of base (or acid) in the unknown solution we are at the "equivalence" point. (Note: the point at which we add exactly an equivalent or stoichiometric amount of titrant is the equivalence point. Experimentally, the point at which we estimate to be the equivalence point is called the titration endpoint).

There are several methods for determining \(V_e\) (or the equivalence point pH) from titration data (titrant volume versus pH). The shape of the titration curve (\(V_t\) versus pH) can reveal \(V_e\). It can be shown that one inflection point occurs at \(V_t = V_e\). In the case of monoprotic acids, there is only one inflection in the pH range of interest. Therefore, an effective method to find the equivalence volume is to plot the titration curve and find the inflection point. Alternately, plot the first derivative of the titration plot and look for a maximum.
Gran Plot

Another method to find the ANC of an unknown solution is the Gran plot technique. When an ANC determination is being made, titration with a strong acid is used to "cancel" the initial ANC so that at the equivalence point the sample ANC is zero. The Gran plot technique is based on the fact that further titration will result in an increase in the number of moles of H⁺ equal to the number of moles of H⁺ added. Thus after the equivalence point has been reached the number of moles of H⁺ added equals the number of moles of H⁺ in solution.

\[
N_i (V_t - V_e) = (V_s + V_t)[H^+] \tag{4.3}
\]

Solving for the hydrogen ion concentration:

\[
[H^+] = \frac{N_i (V_t - V_e)}{(V_s + V_t)} \tag{4.4}
\]

Equation 4.4 can be solved directly for the equivalent volume.

\[
V_e = V_t - \frac{[H^+](V_s + V_t)}{N_i} \tag{4.5}
\]

Equation 4.5 is valid if enough titrant has been added to neutralize the ANC. A better measure of the equivalent volume can be obtained by rearranging equation 4.4 so that linear regression on multiple titrant volume - pH data pairs can be used.

\[
\left(\frac{V_s + V_t}{V_s}\right)[H^+] = \frac{N_i V_t}{V_s} - \frac{N_i V_e}{V_s} \tag{4.6}
\]

We define \( F_1 \) (First Gran function) as:

\[
F_1 = \frac{V_s + V_t}{V_s}[H^+] \tag{4.8}
\]

If \( F_1 \) is plotted as a function of \( V_t \) the result is a straight line with slope = \( \frac{N_i}{V_s} \) and abscissa intercept of \( V_e \) (Figure 4-1).

The ANC is readily obtained given the equivalent volume. At the equivalence pt:

\[
V_s \text{ ANC} = V_e N_i \tag{4.9}
\]

Equation 4.9 can be rearranged to obtain ANC as a function of the equivalent volume.

---

Figure 4-1. Gran plot from titration of a weak base with 0.05 N acid. \( C_i = 0.001 \) moles of carbonate and sample volume is 48 mL. The equivalent volume is 4.8 mL. From equation 4.10 the ANC is 5 meq/L.
ANC = \frac{V_c N_i}{V_s} \quad 4.10

**pH Measurements**

The pH can be measured either as activity ([H+] as measured approximately by pH meter) or molar concentration ([H+]). The choice only affects the slope of \( F_i \) since \([H^+] = \{H^+\}/\gamma\).

\[
F_i = \frac{V_s + V_t}{V_s} [H^+] = \frac{V_s + V_t}{V_s} \cdot \frac{\{H^+\}}{\gamma} = N_i \frac{V_t - V_c}{V_s} \quad 4.11
\]

where \( \gamma \) is the activity correction factor and the slope is \( N_t/V_0 \). If H+ concentration is used then

\[
F_i = \frac{V_s + V_t}{V_s} \cdot \{H^+\} = \gamma N_t \frac{V_t - V_c}{V_s} \quad 4.12
\]

where the slope is \( \gamma \cdot N_t \).

*This analysis assumes that the activity correction factor doesn’t change appreciably during the titration.*

There are many other Gran functions that can be derived. For example, one can be derived for Acidity or the concentration of a single weak or strong acid or base.

To facilitate data generation and subsequent Gran plot construction and analysis pH versus titrant volume can be read directly into a computer, that can be programmed to analyze the data using the Gran, plot theory. The program generates the Gran function for all data and then systematically eliminates data until the Gran function (plot) is as linear as possible. The line is then extrapolated to the abscissa to find the equivalent volume.

**ANC Determination for Samples with pH < 4**

After the equivalence point has been reached (adding more acid than ANC = 0) the only significant terms in equation 4.1 are [H+] and ANC.

\[
[H^+] >> [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad 4.13
\]

When the pH is 2 pH units or more below the pKs of the bases in the system the only species contributing significantly to ANC is the hydrogen ion (equation 4.13) and thus the ANC is simply

\[
ANC = -[H^+] \quad 4.14
\]

For a sample containing only carbonates, if the pH is below 4 the ANC is approximately equal to -[H+] and no titration is necessary.
Titration Techniques

Operationally, the first few titrant volumes can be relatively large increments since the important data lies at pH values less than that of the equivalence point (approximately pH = 4.5 for an Alkalinity titration). As the pH is lowered by addition of acid the ionic strength of the solution increases and the activity of the hydrogen ion deviates from the hydrogen ion concentration. This effect is significant below pH 3 and thus the effective linear range is generally between pH 4.5 and pH 3.0. The maximum incremental titrant volume (ΔVₙ) that will yield n points in this linear region is obtained as follows.

If Vₙ ≫ Vᵣ then equation 4.3 reduces to

\[
\frac{N_t}{V_s} \frac{(V_r - V_e)}{V_r} \equiv [H^+]_e
\]

Let [H⁺]ₑ be the concentration of hydrogen ions at the equivalence point and [H⁺]ᵣ be the final concentration of hydrogen ions at the end of the titration.

\[
\frac{N_t}{V_s} \frac{(V_e - V_c) - (V_f - V_e)}{V_r} = [H^+]_e - [H^+]_f
\]

Thus the volume of acid added to go from [H⁺]ₑ to [H⁺]ᵣ is

\[
V_f - V_e = \frac{V_s (\text{[H⁺]}_f - \text{[H⁺]}_e)}{N_t}
\]

To obtain n data points between [H⁺]ₑ - [H⁺]ᵣ requires the incremental titrant volume (ΔVᵣ) be 1/n times the volume of acid added between the equivalence point and the final titrant volume. Thus by substituting nΔVᵣ, and typical hydrogen ion concentrations of [H⁺]ₑ = 10⁻⁴.⁵ and [H⁺]ᵣ = 10⁻³.₀ into equation 4.17 the maximum incremental titrant volume is obtained.

\[
\Delta V_r \equiv \frac{(0.001 - 0.00003)V_s}{n N_t} \equiv \frac{0.001V_s}{n N_t}
\]

Procedure

Calibrate the pH Meter

Calibrate the pH meter using a pH probe connected to channel A. Use 3 standards (pH = 4, 7, and 10).

Determine ANC of a Known Standard

1) Weigh a 100 mL plastic beaker.
2) Add approximately 50 mL of a 2.5 mM solution of Na₂CO₃ to the beaker.
3) Weigh the beaker again to determine the exact volume of Na₂CO₃ solution.
4) Place the beaker on the magnetic stirrer, add a stir bar and stir slowly.

5) Place both the pH electrode and the temperature probe in the Na₂CO₃ solution using the probe holding arm attached to the Accumet™ meter.

6) Analyze the sample using Gran plot analysis as detailed at [http://www.cee.cornell.edu/mws/Software/Compumet.htm](http://www.cee.cornell.edu/mws/Software/Compumet.htm) Add 0.05 N HCl (the titrant) using a digital pipette in increments of 0.25 mL.

1) Save the pH data to `\Enviro\enviro\Courses\453\acid\netid_gran` by selecting `Save data` from the control palette. The data will be saved in a file (tab delimited format) that can be opened by any spreadsheet program. You will use this data to plot a titration curve and to verify that the Gran technique accurately measures the ANC of a sample.

7) Record the ANC and the equivalent volume.

**Determine ANC of Acid Rain Samples**

Determine ANC for all samples collected from the previous week's lab. Use the same technique as outlined above (Determine ANC of known standard) except substitute the samples collected last week and use titrant increment of 0.1 mL in the linear region. For samples that have a high ANC you can reduce the analysis time by adding titrant in larger volumes initially until the pH approaches 5. If the initial pH is less than 4.5 no titration is necessary and equation 4.14 can be used to calculate the ANC.

Record the initial pH (prior to adding any titrant) and initial sample volume. After the Gran plot analysis record the alkalinity (ANC) and equivalent volume for each sample. There is no need to save the data to disk.

**Prelab Questions**

1) Compare the ability of Cayuga lake and Wolf pond (an Adirondack lake) to withstand an acid rain runoff event (from snow melt) that results in 20% of the original lake water being replaced by acid rain. The acid rain has a pH of 3.5 and is in equilibrium with the atmosphere. The ANC of Cayuga lake is 1.6 meq/L and the ANC of Wolf Pond is 70 µeq/L. Assume that carbonate species are the primary component of ANC in both lakes, and that they are in equilibrium with the atmosphere. What is the pH of both bodies of water after the acid rain input? Remember that ANC is the conservative parameter (not pH!).

2) What is the ANC of a water sample containing only carbonates and a strong acid that is at pH 3.2?

3) Why is [H⁺] not a conserved species?

**Questions**

1) Plot the titration curve of 2.5 mM Na₂CO₃ with 0.05 N HCl (plot pH as a function of titrant volume). Label the equivalent volume of titrant. Label the 2 regions of the graph where pH changes slowly with the dominant reaction that is occurring. Note that in a third region of slow pH change no significant reactions are occurring (added hydrogen ions contribute directly to change in pH).
2) Prepare a Gran plot using the data from the titration curve of the 2.5 mM Na₂CO₃. Use linear regression on the linear region or simply draw a straight line through the linear region of the curve to identify the equivalent volume. Compare your calculation of Vₑ with that calculated by the Compumet™ computer program.

3) Compare the measured ANC with the theoretical value for the 2.5 mM Na₂CO₃ solution. Note that ANC can be defined as the excess of positive charges over the anions of strong acids.

4) Plot the ANC of the influent and the lake from phase I of the previous lab.

5) Plot the ANC of the lake from phase II of the previous lab on the same graph as was used to plot the conservative ANC model (see questions 2) to 5) on page 36). Did the measured ANC values agree with the conservative ANC model?

References


Table 4-1. Reagent list.

<table>
<thead>
<tr>
<th>Description</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 5.0 N</td>
<td>Fisher Scientific</td>
<td>LC15360-2</td>
</tr>
<tr>
<td>Buffer-Pac</td>
<td>Fisher Scientific</td>
<td>SB105</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>Fisher Scientific</td>
<td>BP357-1</td>
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</table>

Table 4-2. Equipment list

<table>
<thead>
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<th>Description</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accumet™ 50 pH meter</td>
<td>Fisher Scientific</td>
<td>13-635-50</td>
</tr>
<tr>
<td>pH electrode</td>
<td>Fisher Scientific</td>
<td>13-620-108</td>
</tr>
<tr>
<td>7x7 stirrer</td>
<td>Fisher Scientific</td>
<td>11-500-7S</td>
</tr>
<tr>
<td>stirbar 1/2&quot; long</td>
<td>Fisher Scientific</td>
<td>14-511-62</td>
</tr>
<tr>
<td>100 mL beaker</td>
<td>Fisher Scientific</td>
<td>02-593-50B</td>
</tr>
</tbody>
</table>

Setup

1) Prepare 1 L of the known standard (2.5 mM solution of Na₂CO₃). The MW is 105.99 g/mole.

\[
\frac{2.5 mM}{L} \cdot \frac{105.99 mg}{mM} = 265 mg Na₂CO₃/L
\]

2) Prepare 1 L of the titrant (0.05 N HCl from 5.0 N HCl). Dilute 10 mL of 5.0 N HCl to 1 L. Distribute 100 mL titrant to each student group.

3) Verify that the pH probes are operational, stable, and can be calibrated.

4) Verify that buffers (pH = 4, 7, 10) are distributed to each student group.
Methane Production from Municipal Solid Waste

Introduction

Archaeological investigations of landfills have revealed that biodegradable wastes can be found — virtually intact — 25 years after burial. We know that landfills contain bacteria with the metabolic capability to degrade many of the materials that are common components of municipal refuse. The persistence for decades of degradable materials in the presence of such organisms appears somewhat paradoxical. In this experiment students will explore the factors that influence biodegradation of waste materials in landfills. Although recycling has significantly reduced the amount of landfill space dedicated to paper and other lignocellulosics, paper products are still a significant fraction of the solid waste stream. In this laboratory students will measure the rate and extent of anaerobic degradation of newsprint, Kraft paper, coated paper, and food scraps.

Theory

Over 150 million tons of municipal solid waste (MSW) are generated every year in the United States, and more than 70% of the MSW is deposited in landfills (Gurijala and Sufliita 1993). Paper constitutes the major weight fraction of MSW, and this laboratory will focus on the biodegradation of that component. Anaerobic biodegradation of paper produces methane and carbon dioxide. Methane is a fuel and is the major component of natural gas. Methane produced in sanitary landfills represents a usable but underutilized source of energy. Energy recovery projects are frequently rejected because the onset of methane production is unpredictable and methane yields vary from 1-30% of potential yields based on refuse biodegradability data (Barlaz, Ham et al. 1992). The low methane yields are the result of several factors that conspire to inhibit anaerobic biodegradation including low moisture levels, resistance to biodegradation, conditions that favor bacterial degradation pathways that do not result in methane as an end product, and poor contact between bacteria and the organic matter.

Characteristics of municipal solid waste

The physical composition of residential municipal solid waste (MSW) in the United States is given in Table 5-1. The fractional

<table>
<thead>
<tr>
<th>Component</th>
<th>Range (% by weight)</th>
<th>Typical (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>food wastes</td>
<td>6-18</td>
<td>9.0</td>
</tr>
<tr>
<td>paper</td>
<td>25-40</td>
<td>34.0</td>
</tr>
<tr>
<td>cardboard</td>
<td>3-10</td>
<td>6.0</td>
</tr>
<tr>
<td>plastics</td>
<td>4-10</td>
<td>7.0</td>
</tr>
<tr>
<td>textiles</td>
<td>0-4</td>
<td>2.0</td>
</tr>
<tr>
<td>rubber</td>
<td>0-2</td>
<td>0.5</td>
</tr>
<tr>
<td>leather</td>
<td>0-2</td>
<td>0.5</td>
</tr>
<tr>
<td>yard wastes</td>
<td>5-20</td>
<td>18.5</td>
</tr>
<tr>
<td>wood</td>
<td>1-4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Organic total    79.5

<table>
<thead>
<tr>
<th>Component</th>
<th>Range (% by weight)</th>
<th>Typical (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>glass</td>
<td>4-12</td>
<td>8.0</td>
</tr>
<tr>
<td>tin cans</td>
<td>2-8</td>
<td>6.0</td>
</tr>
<tr>
<td>aluminum</td>
<td>0-1</td>
<td>0.5</td>
</tr>
<tr>
<td>other metal</td>
<td>1-4</td>
<td>3.0</td>
</tr>
<tr>
<td>dirt, ash, etc.</td>
<td>0-6</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Inorganic total 20.5
contribution of the listed categories has evolved over time, with a trend toward a
decrease in food wastes because of
increased use of kitchen food waste
grinders, an increase in plastics through the growth of their use for
packaging, and an increase in yard
wastes as burning has ceased to be
allowed by most communities
(Tchobanoglous, Theisen et al. 1993).
Excluding plastic, rubber, and leather,
the organic components listed in
Table 5-1 are, given sufficient time,
biodegradable.

Although recycling efforts divert a
significant fraction of paper away
from landfills, paper continues to be a
major component of landfilled waste.
The types of paper found in MSW are
listed in Table 5-2.

The elemental composition of
newsprint and office paper are listed
in Table 5-3.

The major elements in paper are
carbon, hydrogen, and oxygen that
together constitute 93.5% of the total
solids. The approximate molecular
ratios for newspaper and office paper
are $C_6H_9O_4$ and $C_6H_{9.5}O_{4.5}$
respectively.

**Biodegradation of cellulose,
hemicellulose, and lignin**

Cellulose and hemicellulose are the
principal biodegradable constituents
of refuse accounting for 91% of the
total methane potential. Cellulose
forms the structural fiber of many
plants. Mammals, including humans,
lack the enzymes to degrade
 cellulose. However, bacteria that can
break cellulose down into its subunits
are widely distributed in natural
systems, and ruminants, such as
cows, have these microorganisms in their digestive tract. Cellulose is a polysaccharide that is composed of glucose subunits (see Figure 5-1).

Another component of the walls of plants is hemicellulose, which sounds similar to cellulose but is unrelated other that that it is another type of polysaccharide. Hemicelluloses made up of five carbon sugars (primarily xylose) are the most abundant in nature.

Lignin is an important structural component in plant materials and constitutes roughly 30% of wood. Significant components of lignin include coniferyl alcohol and syringyl alcohol subunits (Figure 5-2).

The exact chemical structure of lignin is not known but its reactivity, breakdown products, and the results of spectroscopic studies reveal it to be a polymeric material containing aromatic rings with methoxy groups (\(-\text{OCH}_3\)) (Tchobanoglous, Theisen et al. 1993). One of the many proposed structures for lignin is shown in Figure 5-3.

Degradation of lignin requires the presence of moisture and oxygen and is carried out by filamentous fungi (Prescot, Harley et al. 1993). The biodegradability of lignocellulosic materials can be increased by an array of physical/chemical processes including pretreatment to increase surface area (size reduction), heat treatment, and treatment with acids or bases. Such treatments are useful when wood and plant materials are to be anaerobically degraded to produce methane. Research on this topic has been performed by Cornell Prof. James Gossett (Gossett and McCarty 1976; Chandler, Jewell et al. 1980; Gossett, Stuckey et al. 1982;
Three major groups of bacteria are involved in the conversion of cellulosic material to methane (Zehnder 1978): (1) the hydrolytic and fermentative bacteria that break down biological polymers such as cellulose and hemicellulose to sugars that are then fermented to carboxylic acids, alcohols, carbon dioxide and hydrogen gas, (2) the obligate hydrogen reducing acetogenic bacteria that convert carboxylic acids and alcohols to acetate and hydrogen, and (3) the methanogenic bacteria that convert primarily acetate and hydrogen plus carbon dioxide to methane. Sulfate reducing bacteria (SRB) may also play a role in the anaerobic mineralization of cellulosic material. In the presence of sulfate, the degradation process may be directed towards sulfate reduction by SRB with the production of hydrogen sulfide and carbon dioxide (Barlaz, Ham et al. 1992).

**Cellular requirements for growth**

The availability of oxygen is a prime determinant in the type of microbial metabolism that will occur. Microbial respiration of organic carbon is a combustion process, in which the carbon is oxidized (i.e., is the electron donor) in tandem with the reduction of an electron acceptor. The energy available to microorganisms is greatest when oxygen is used as the electron acceptor and therefore aerobic metabolic processes will dominate when oxygen is available. Some microorganisms require oxygen to obtain their energy and are termed “obligate aerobes.” In the absence of oxygen, other electron acceptors such as nitrate \((\text{NO}_3^-)\), sulfate \((\text{SO}_4^{2-})\) and carbon dioxide \((\text{CO}_2)\) can be used. Organisms that can only exist in an environment that contains no oxygen are termed “obligate anaerobes.” Organisms that have the ability to grow in both the presence and the absence of oxygen are said to be “facultative.”

The availability of nutrients can limit the ability of cells to grow and consequently the extent of biodegradation. Nitrogen and/or phosphorous constitute important nutrients required for cell synthesis. Inorganic bacterial nutritional requirements also include sulfur, potassium, magnesium, calcium, iron, sodium and chloride. In addition, inorganic nutrients needed in small amounts (minor or trace nutrients) include zinc, manganese, molybdenum, selenium, cobalt, copper, nickel, vanadium and tungsten. Organic nutrients (termed “growth factors”) are also sometimes needed (depending on the microorganism) and include certain amino acids, and vitamins (Metcalf & Eddy 1991).

Environmental conditions such as pH, temperature, moisture content, and salt concentration can have a great influence on the ability of bacteria to grow and survive. Most bacteria grow in the pH range from 4.0 to 9.5 (although some organisms can tolerate more extreme pH values), and typically grow best in the relatively narrow range from 6.5 to 7.5 (Metcalf & Eddy, 1991). Microorganisms have a temperature range over which they function best, and are loosely characterized as psychrophilic (ability to grow at 0°C), mesophilic (optimal growth at 25-40°C) or thermophilic (optimal growth above 45-50°C) (Brock 1970). Many common methanogens are mesophilic. Elevated temperatures also favor faster reaction rates.

While some microorganisms are very tolerant of low moisture conditions, active microbial growth and degradation of organic matter necessitates that water not be a scarce resource. Cells take water in through their semi-permeable membrane surface...
by osmosis. This uptake mechanism requires that the solute concentration inside the cell be higher than that of the outside media. Organisms that grow in dilute solutions can not tolerate high salt concentrations because their normal osmotic gradient is reversed and they can not take in water. Some cell strains, termed “halophiles” are adapted for growth at very high salt concentrations.

The above factors suggest that bacterial degradation of MSW to produce methane will occur optimally at circumneutral pH, low ionic strength, in the absence of oxygen, nitrate and sulfate, in the presence of moisture and nutrients, and under mesophilic conditions.

**Estimates of paper biodegradability**

Volatile solids (VS) content (determined by weight loss on ignition at 550°C) has been used to estimate the biodegradability of MSW components, but this measure overestimates the biodegradability of paper. Paper products have a very high volatile solids content. Newsprint, office paper, and cardboard have VS of 94%, 96.4%, and 94% respectively (Tchobanoglous, Theisen et al. 1993). Paper products also can have a high content of lignocellulosic components that are only slowly degradable. Lignin constitutes approximately 21.9%, 0.4% and 12.9% respectively of the VS in newsprint, office paper, and cardboard. Lignin content and biodegradability are strongly correlated and thus lignin content can be used to estimate biodegradability and potential methane production. Chandler et al. (1980) found a relationship between lignin content and biodegradable volatile solids using a wide variety of waste materials. The empirical relationship suggests that not only is lignin not easily biodegraded, but that lignin also reduces the biodegradability of the nonlignin components. This reduction in biodegradability may be caused by lignin polymeric material physically preventing enzymatic access to the nonlignin components. The relationship is

\[
\text{VS}_{\text{biodegradable}} = -2.8 \text{VS}_{\text{lignin}} + 0.83
\]

where \( \text{VS}_{\text{biodegradable}} \) is the biodegradable fraction of the volatile solids and \( \text{VS}_{\text{lignin}} \) is the fraction of volatile solids that are lignin. From equation 5.7 the maximum destruction of VS is limited to about 83%, a limitation due to the production of bacterial by-products. The high concentration of lignin in newsprint makes it much less biodegradable than more highly processed office paper (Table 5-4).

**Energy recovery from MSW**

Energy could be recovered from MSW by direct combustion in an incinerator or by anaerobic biodegradation and production of methane. Proximate analysis is used to measure moisture content, volatile matter, fixed carbon (combustible but not volatile), and ash. Proximate analysis can be used to predict ash
production from incineration. The energy content is measured in a bomb calorimeter. Proximate analysis results and energy content of MSW are given in Table 5-5.

Gas production from anaerobic digestion is typically 30% CO₂ and 70% CH₄. The methane is a valuable fuel and has an energy content of 862.3 kJ/mol or 50 MJ/kg. The combustion of methane produces only carbon dioxide and water.

Because paper products are a major fraction of MSW and paper energy content is significant, the majority of energy in MSW is contained in paper products. Incineration or methane production can be used to capture some of this available energy.

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

Effect of MSW particle size

The large size of pieces of MSW is suspected to decrease the ability of microbes to degrade the material. Landfill gas production has been correlated with refuse particle size (Ferguson 1993). The effect of particle size reduction was initially explained by the resultant increase in surface area available for microbial attach. Laboratory studies under saturated conditions, however, suggest that size reduction, even down to a few microns or tens of microns has little effect on the rate of degradation. According to Ferguson (1993), surface area increases only slightly with decreasing particle size for platey and fibrous particles such as paper. Thus the effect of size reduction on the methane production in landfills may be that relatively large pieces of plastic, paper, or other material shield the materials beneath them from infiltrating water. The shielded material may remain too dry for biodegradation. Pulverization breaks down the impermeable barriers and more of the waste is exposed to water (Ferguson 1993).

Potential methane production from municipal solid waste

Under anaerobic conditions microorganisms can produce both CO₂ and CH₄ (methane) without consuming any oxygen. Other significant end products include odorous gases such as ammonia (NH₃), and hydrogen sulfide (H₂S) (see Figure 5-4). Because anaerobic biodegradation produces gas it is possible to monitor the extent and rate of anaerobic biodegradation by measuring gas production (Suflita and Concannon 1995).
Gas production

Because anaerobes get relatively little energy from the organic matter their conversion of carbon to cell material (synthesis) is much lower than for aerobes. Typically 10% of the organic matter may be converted to anaerobe cell mass. Thus the majority of the biodegraded organic matter is converted to gas and the gas production can be used as a measure of biodegradation. The ideal gas law is used to determine the moles of gas produced from the pressure, volume, and temperature.

\[ n = \frac{PV}{RT} \]  

5.12

The pressure in the sealed test bottles that will be used in this laboratory is initially atmospheric. Because the number of moles is a linear function of the pressure we can write

\[ \Delta n = \frac{\Delta PV}{RT} \]  

5.13

where \( \Delta P \) is the change in pressure relative to the initial pressure in the bottle.

In these experiments the bottle volume is 120 mL and the maximum recommended pressure increase is 80 kPa (12 psi). The volume of liquid in the bottles is 20 mL and the volume contributed by solids is expected to be negligible. Thus the nominal volume of gas in the bottles will be 100 mL. Solving for the number of moles of gas (\( CH_4 \) and \( CO_2 \)) produced by anaerobic digestion

\[ \Delta n = \left( \frac{80 \times 10^3 \text{ Pa}}{8.31 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol} \cdot \text{K}} \right) \left( \frac{100 \times 10^{-6} \text{ m}^3}{308 \text{ K}} \right) = 3.13 \text{ mmole C} \]  

5.14

The molecular formula of cellulose is \( C_{6}H_{10}O_{5} \) and thus 27 g of cellulose has 1 mole of carbon. The relation obtained in equation 5.14 is used to determine the maximum amount of cellulose that can be anaerobically degraded without exceeding 80 kPa in the bottles.

\[ 3.13 \text{ mmole C} \times \frac{27 \text{ mg cellulose}}{\text{mmole C}} = 84 \text{ mg cellulose} \]  

5.15

The mass of paper containing 84 mg of biodegradable cellulose can be obtained using Table 5-4 and the results of equation 5.15. The mass of dry newspaper that will produce a pressure increase of 80 kPa is.
Similar calculations can be performed for other types of waste.

The maximum mass of glucose (CH₂O has 30 g of glucose per mole of carbon) is

$$\frac{3.13 \text{ mmole C}}{30 \text{ mg glucose/mmole C}} = 94 \text{ mg glucose}$$ 5.17

Although glucose is expected to be completely biodegradable, a small amount of glucose will be converted into refractory cell byproducts.

The above calculations are based on the assumption that all of the gas produced is volatile and is not dissolved. Carbon dioxide is soluble and thus some of the CO₂ produced will be dissolved and will not result in increased pressure.

**Acid neutralizing capacity requirements**

The high partial pressure of CO₂ resulting from anaerobic biodegradation causes a high concentration of carbonic acid \( [H_2CO_3] \) and thus would result in a reduced pH if there were insufficient Acid Neutralizing Capacity (ANC). The amount of ANC required to counteract the high partial pressure of CO₂ can be obtained from the Henry’s constant for dissolution of CO₂, and from the dissociation constant for carbonic acid.

$$K_H = \frac{[H_2CO_3^\ast]}{P_{CO_2}}$$ 5.18

where \( K_H \) has a value of \( 3.12 \times 10^{-4} \) moles/J. The first dissociation constant for carbonic acid is

$$K_1 = \frac{[H^+][HCO_3^\ast]}{[H_2CO_3^\ast]}$$ 5.19

where \( K_1 \) has a value of \( 10^{-6.3} \). The definition of ANC for a carbonate system in equilibrium with the gas phase is

$$ANC = \frac{P_{CO_2} K_H}{\alpha_0} (\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+]$$ 5.20

Where \( \alpha_0, \alpha_1, \alpha_2 \) are the fractions of total carbonate present as carbonic acid \( [H_2CO_3^\ast] \), bicarbonate \( [HCO_3^\ast] \), and carbonate \( [CO_3^{2\ast}] \) respectively and \( K_w \) is the dissociation constant for water. At circumneutral pH the hydrogen ion, hydroxide ion, and carbonate ion concentrations are negligible and equation 5.20 simplifies to

$$ANC = \frac{P_{CO_2} K_H \alpha_1}{\alpha_0}$$ 5.21
The ratio of bicarbonate to carbonic acid may be determined from equation 5.19. Solving for the ratio of bicarbonate to carbonic acid:

\[
\frac{[HCO_3^-]}{[H_2CO_3^+]} = \frac{\alpha_i}{\alpha_0} = \frac{K_1}{H^+}
\]

Equation 5.22 can be substituted into equation 5.21 to obtain

\[
ANC = \frac{P_{CO_2}KHK_1}{H^+}
\]

An estimate of the ANC required to maintain a neutral pH under a pressure of 30 kPa of CO2 can be obtained by substituting appropriate values into equation 5.23.

\[
ANC \cong 47\text{ meq/L}
\]

The basal medium that will be used in this laboratory contains 71 meq/L ANC from sodium bicarbonate. If the pressure of CO2 reaches 60 kPa (30 kPa initial pressure plus 30 kPa from the production of CO2 during an experiment) then solving equation 5.21 for pH shows that (given the 71 meq ANC in the basal medium and a CO2 pressure of 60 kPa) the pH will drop to 6.88. Thus, the basal medium is sufficiently buffered to protect against significant pH changes.

**Carbon dioxide solubility**

At pH less than \( \approx 9 \) the inorganic carbon will partition into three species, gaseous \( CO_2 \), aqueous \( H_2CO_3^+ \), and aqueous \( HCO_3^- \).

\[
n_{CO_2(gas)} = n_{CO_2(aq)} + n_{H_2CO_3^+} + n_{HCO_3^-}
\]

The number of moles of the inorganic carbon species can be determined based on the partial pressure of \( CO_2 \), the ANC of the liquid and the gas and liquid volumes. The moles of gaseous \( CO_2 \) is obtained from the ideal gas law

\[
n_{CO_2(gas)} = \frac{P_{CO_2}V_g}{RT}
\]

The number of moles of \( H_2CO_3^+ \) is obtained from the Henry’s law constant.

\[
n_{H_2CO_3^+} = P_{CO_2}K_HV_l
\]

The concentration of bicarbonate, \( HCO_3^- \), is equal to the ANC (for pH < 9).

\[
n_{HCO_3^-} = ANC \cdot V_l
\]
The total number of moles of inorganic carbon is the sum of the three species.

\[
n_{\text{CO}_2\text{_{(total)}}} = \frac{P_{\text{CO}_2} V_g}{RT} + \left(P_{\text{CO}_2} K_H + \text{ANC}\right) V_i
\]  

5.29

Therefore, the number of moles of inorganic carbon in an enclosed volume is a linear function of the partial pressure of CO\(_2\) (Figure 5-5).

The pH will change as the partial pressure of CO\(_2\) changes as shown in equation 5.23. Solving for the concentration of hydrogen ions equation 5.23 becomes

\[
\left[H^+\right] = \frac{P_{\text{CO}_2} K_H K_1}{\text{ANC}}
\]  

5.30

The relationship between pH and partial pressure of CO\(_2\) is shown in Figure 5-5.

The basal medium to be used in this experiment will be purged with a 30:70 mixture of carbon dioxide and nitrogen prior to use. As shown in Figure 5-5, the pH of the basal medium is expected to rise to approximately 7.17. The headspace will also be purged with the same gas mixture and thus there will be 5.6 mmoles of inorganic carbon in the bottles initially. After the anaerobic biodegradation has gone to completion, the carbon dioxide concentration will be measured by gas chromatography and the gas pressure by pressure sensors and thus the partial pressure of carbon dioxide will be known. Figure 5-5 or equation 5.29 can be used to determine the final mass of inorganic carbon in the bottles. The difference between the initial and final inorganic carbon concentration can be used to determine the amount of organic carbon converted to carbon dioxide.

**Methane solubility**

The Henry’s constant for methane (\(K_{H(CH_4)}\)) at 25°C is 1.48 x 10\(^{-4}\) mol/J (Mackay and Shiu 1981). Methane is significantly less soluble than carbon dioxide and does not form other soluble aqueous species. The mass of gaseous and dissolved methane is given by equations 5.32 and 5.33.
The ratio of the mass of gaseous to dissolved methane gives an indication of the significance of dissolved methane.

\[
\frac{n_{CH_4(g)}}{n_{CH_4(aq)}} = \frac{V_g}{V_lK_{H(CH_4)}RT}
\]

Substituting appropriate values into equation 5.34

\[
\frac{n_{CH_4(g)}}{n_{CH_4(aq)}} = \frac{V_g}{V_l1.48\times10^{-5} \frac{mol}{J} \left(8.31 \frac{J}{mol^\circ K}\right)(308^\circ K)}
\]

If the gas and liquid volumes are approximately equal there will be approximately 26 times as much methane in the gaseous phase as in the dissolved phase. This ratio is independent of the methane partial pressure. The total number of moles of methane can be obtained from the partial pressure of methane in the gaseous phase.

\[
n_{CH_4(total)} = P_{CH_4} \left(\frac{V_g}{RT} + K_{H(CH_4)}V_l\right)
\]

The partial pressure of methane will be determined from the pressure in the bottle and mass of methane as measured by the gas chromatograph.

**Temperature effects**

The temperature of the bottles directly affects the pressure of gas as well as influences the rate of gas production by the microbes. Cummings and Stewart found that methane production was sharply inhibited by temperatures in excess of the optimum (37°C) and was undetectable at 20°C (1995). However, Suflita and Concannon (1995) reported anaerobic digestion at “room temperature” over a period of 2 months. If desired a constant temperature water bath can be used to keep all of the digesters at a constant and optimal temperature (35°C) for anaerobic degradation.

**Experiment description**

The experimental setup is a flexible system for obtaining data on the anaerobic decomposition of various organic materials by measuring the pressure of the gas produced. A schematic of the experimental setup is shown in Figure 5-6.
Bacterial degradation of selected materials will be assayed by placing known quantities in 120 mL bottles, inoculating with an active anaerobic mixed culture, sealing the bottles with rubber septa and aluminum crimp caps, and monitoring gas pressure and composition over time. Anaerobic digester supernatant from the Ithaca Wastewater Treatment Plant will be used as a source of microbes. The bottles will be monitored for biogas production with pressure sensors connected with a needle through the septa (see Figure 5-6). Gas composition will be determined by periodic analysis of methane (CH$_4$) and carbon dioxide (CO$_2$) via gas chromatography with a thermal-conductivity detector.

Gas production measurements will be automated by using pressure sensors in a procedure comparable to that described by Suflita and Concannon (1995). With this technique, a large number of bottles can be monitored with automated data acquisition by a single computer, allowing a wide variety of chemical and environmental parameters to be explored. The automated acquisition of gas data is necessary due to the numbers of bottles and length of incubation (ca. 4 weeks) anticipated. This experiment will be set-up and left virtually unattended while other laboratory exercises continue in intervening weeks.

Each sample type should be cut into small enough pieces to easily insert into the bottle. Students may also be interested in exploring biodegradation of other organic components of municipal solid waste (banana peels, rags, plastic bags, etc.). Table 5-6 suggests one configuration of several sample types. Each sample will receive 15 mL of basal medium.

Table 5-6. Suggested sample preparation.
Each group does 2 sample types with 2 replicates. Each section does 2 water and 2 inoculum controls.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Size</th>
<th>Inoculum</th>
<th>Replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>environmental control</td>
<td>none</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>bacterial control</td>
<td>none</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>positive control (glucose)</td>
<td>90</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>filter paper</td>
<td>50</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>cardboard</td>
<td>?</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>office paper</td>
<td>?</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>newsprint</td>
<td>?</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Student selected organic</td>
<td>?</td>
<td>5 up to 4</td>
<td>up to 4 vials</td>
</tr>
</tbody>
</table>

Figure 5-6. Experimental setup (not to scale). Pressure generated by microbial gas production is monitored by pressure sensors.
control should be the microbial inoculum, plus 90 milligrams of glucose and the 
O₂-free water (to verify that the microbial population is active in the added sludge),
and one control should be plain O₂-free water to control for variations in temperature,
and air pressure. The sample sizes of the various samples should be determined so
that the bottles will not generate pressure greater than 80 kPa.

**Experimental methods**

**Safety concerns**

1) Municipal wastewater sludge will be used as a source of microbes. The sludge
may contain biological and/or chemical hazards and should be handled
accordingly.

2) Biological production of gas will generate pressure in a closed container. Testing
has shown that this system is safe up to at least 200 kPa (30 psi). At
approximately this pressure the needle is typically forced out of the septa. If the
bottle is not vented the pressure can increase until the crimp cap is forced off.
Bottles should not be capped for very long before the needles are inserted and
pressure monitoring begins. The pressure trends should be monitored and, if
excessive pressures are produced, the bottles must be vented and/or the
temperature of the bath may be reduced.

3) Sharp needles are used in the experimental setup and precautions should be taken
to avoid puncturing unintended objects (including students).

**Analysis of moisture content and volatile solids**

The fraction of volatile solids in the paper samples is the maximum that could
possibly be degraded. Note that paper products cannot be ashed accurately because
the strong flames easily carry some of the ashes away. Steps for sample moisture
content and volatile solids fraction follow:

1) Weigh an aluminum boat
2) Weigh the aluminum boat with an organic sample (boat + water + VS + ash)
3) Dry in the 105°C oven
4) Cool in a desiccator
5) Weigh (boat + VS + ash)
6) Ash in the 550°C muffle furnace
7) Cool in a desiccator
8) Weigh (boat + ash)

**Sample preparation**

The bottles will be purged initially with a mixture of 30% CO₂ and 70% N₂ to
remove any O₂ and to establish an initial carbon dioxide concentration so that the
initial pH is not excessively high. If no carbon dioxide were present in the purging
gases the carbonic acid would be stripped out of solution and the pH would rise in the basal medium.

**Acquisition of pressure data**

The biogas pressure will be measured indirectly by the pressure sensors. The specified sensors work from zero to 100 kPa (6.89476 kPa/psi). They will withstand 2.5 times rated pressure (i.e., 250 kPa) but their output may be erroneous above the upper limit of the working range. The output of the pressure sensors is zero to 0.100 volts with 0.100 volts indicating approximately 100 kPa. The outputs of the sensors are fed through a 32-channel multiplexer/signal conditioner, an A/D converter board and are monitored using LabVIEW software.

**Gas chromatograph analysis for separation of CO₂, CH₄ and N₂ (Optional)**

Permanent gases can be analyzed using a thermal conductivity detector (TCD) on a gas chromatograph. The thermal conductivity detector measures the rate at which heat is transported from the detector. If a gas with a different thermal conductivity than the carrier gas passes through the detector a peak is detected. A flame ionization detector could be used to measure methane, but would not be able to detect carbon dioxide or nitrogen since they do not burn. A micropacked column containing packing designed for analyses of permanent gases and light hydrocarbons (Supelco Carboxen 1004) is used to separate the gases.

The TCD must be calibrated with known masses of the gases of interest. Nitrogen, carbon dioxide and methane are available as compressed gases and can be sampled at atmospheric pressure by opening a valve in a compressed gas line slightly and sampling the discharge with a gas tight syringe. The ideal gas law is used to calculate the moles of gas. The current atmospheric pressure in Ithaca is available through the World Wide Web at [http://cuinfo.cornell.edu/Ithaca/Weather/](http://cuinfo.cornell.edu/Ithaca/Weather/). If the atmospheric pressure is reported in inches of mercury it can be converted to Pascals by multiplying by 3386 Pascals/Inch of Hg. The temperature of the laboratory is available from the pH meters equipped with temperature probes. If a 100 µL gas sample is used, the atmospheric pressure is 100 kPa, and the temperature is 22°C then the number of moles of gas are calculated as:

\[
n = \frac{(100,000 \text{ Pa})(100 \times 10^{-9} \text{ m}^3)}{(8.31 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}})(295 \text{K})} = 4.08 \mu\text{mol}
\]

The number of moles of gas is independent of the type of gas. The relationship between peak area and moles of gas is calculated by analyzing a known number of moles of each gas. The TCD response will be different for each gas since the thermal conductivity of each gas is different.

**Experimental method (short version)**

1) Dry 2 – 2 g samples for each sample type in the 105°C oven.
2) Take dried organic sample from the oven.
3) Keep 1 dried sample and determine the VS of the other sample.
4) Weigh appropriate amounts of the various dried samples for methane production.
5) Load bottles with organic samples (cut to smaller size as needed).
6) Add 15 mL of basal medium to each of the bottles.
7) Add 5 mL of inoculum to each of the bottles.
8) Purge the headspace of the bottles with an oxygen-free gas stream that is 30% CO₂ and 70% N₂.
9) Seal the bottles.
10) Insert the pressure sensor hypodermic needle into the bottle.
11) Sample the bottle pressures using the data acquisition software (take samples every hour and save the data as \Enviro\Courses\453\methane\pressure).

**Gas Analysis Method**

1) Calibrate the gas chromatograph using methane and carbon dioxide and using 20 µL samples
2) Take an initial headspace gas sample and analyze it using the gas chromatograph.
3) Sample gas composition after gas production has ceased using the gas chromatograph.

**Prelab questions**

1) Estimate the mass of cardboard and the mass of office paper that will produce a pressure rise of 80 kPa in the sample bottles at 35°C if the headspace volume is 100 mL. Use the predicted biodegradability based on the lignin content of the paper.

**Data analysis**

Perform the analysis on the data from your lab section.

1) Calculate total gas production in moles. For each sample use the record of pressure vs. time to determine if the reaction appears to have gone to completion.
2) For your samples, compare volatile solids (VS) and gas production by converting the mass of volatile solids to moles of carbon using an approximate molecular formula for the sample. The molecular formula for the volatile fraction of paper can be approximated by C₆H₁₀O₅. Calculate and plot the fraction of VS degraded as a function of time for each sample.
3) Compare the fuel value of the methane produced with the fuel value of the original sample for each of the samples. Use the estimates of the original fuel value (Table 5-5) and the measured methane production. The fuel value of glucose is 424.7 KJ/mole C. If you don’t have the gas composition of your samples, then assume 70% of the gas produced was methane.
Optional Analysis Requiring Gas Composition

1) Calculate the moles of CO$_2$ and CH$_4$ produced by your samples based on the gas chromatograph analysis. Include the effect of carbon dioxide solubility. Use the basal medium control to subtract the initial headspace as well as any gas production by the inoculum.

2) Calculate the final pressure based on the GC measurements and compare with the pressure transducer measurements. Remember that the pressure transducer measured gage pressure.

References


Lab Prep Notes

Setup

1) Use anaerobic digester supernatant as inoculum source. Place supernatant under fume hood. Use 5 mL per sample.

2) Setup 10 port purger with CO₂ and N₂ gas metered through rotometers. The top ball should be at 24 mm for CO₂ and at 84 mm for N₂.

3) Set the GC with 300 Kpa column pressure, 180ºC oven, 250ºC injector and detectors, and 1.2 minute run time. Use 20 µL sample. The gases should come out in the order N₂, CH₄, and CO₂ at 0.44, 0.72, and 1 minute respectively. (Only if you are doing the optional GC analysis)

4) 4 samples/group plus 2 inoculum blanks and 2 water blanks.

Class Plan

1) Sign up for samples

2) Each group chooses 2 types of samples

3) Dry samples in oven

4) Ash 1 of the 2 samples

Table 5-7. Equipment list

<table>
<thead>
<tr>
<th>Description</th>
<th>Vender</th>
<th>Catalog</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 µl syringe w/ valve</td>
<td>Supelco</td>
<td>2-2272</td>
</tr>
<tr>
<td>side port needle</td>
<td>Supelco</td>
<td>2-2289</td>
</tr>
<tr>
<td>Carboxen 1004 micropacked column</td>
<td>Supelco</td>
<td>1-2846</td>
</tr>
<tr>
<td>Hp 5890 Series II GC</td>
<td>Hewlett-Packard</td>
<td>5890A</td>
</tr>
<tr>
<td>TCD kit</td>
<td>Hewlett-Packard</td>
<td>19232E</td>
</tr>
<tr>
<td>1/8&quot; column adapter</td>
<td>Hewlett-Packard</td>
<td>option 095</td>
</tr>
<tr>
<td>pressure regulators</td>
<td>Hewlett-Packard</td>
<td>L43</td>
</tr>
<tr>
<td>RS232C board</td>
<td>Hewlett-Packard</td>
<td>option 560</td>
</tr>
<tr>
<td>Helium</td>
<td>Cornell Stores</td>
<td></td>
</tr>
<tr>
<td>Wrist action Shaker</td>
<td>Fisher Scientific</td>
<td></td>
</tr>
<tr>
<td>Vials</td>
<td>Supelco</td>
<td></td>
</tr>
<tr>
<td>Aluminum crimp tops</td>
<td>Fisher</td>
<td>03-375-23C</td>
</tr>
<tr>
<td>Butyl stopper</td>
<td>Fisher</td>
<td>03-375-22AA</td>
</tr>
<tr>
<td>Crimping tool</td>
<td>Supelco</td>
<td>3-3280</td>
</tr>
<tr>
<td>EPDM</td>
<td>Sigma</td>
<td>Z16607-3</td>
</tr>
<tr>
<td>stoppers-13x20 mm luer lock needles</td>
<td>Fisher</td>
<td>14-826-5B</td>
</tr>
<tr>
<td>21 gauge Pressure transducer, 0 to 15 psig</td>
<td>Omega</td>
<td>PX136-015GV</td>
</tr>
<tr>
<td>12 V DC Power supply</td>
<td>Omega</td>
<td>PSS-12</td>
</tr>
<tr>
<td>Incubator</td>
<td>Fisher</td>
<td>11-690-650D</td>
</tr>
<tr>
<td>Multiplexer</td>
<td>National Instruments</td>
<td></td>
</tr>
<tr>
<td>4 slot chassis</td>
<td>776570-01</td>
<td></td>
</tr>
<tr>
<td>SCXI-1000</td>
<td>776572-00</td>
<td></td>
</tr>
<tr>
<td>32 channel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCXI-1100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCXI-1200 parallel port</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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### Table 5-8. Reagents

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Vender</th>
<th>Catalog</th>
</tr>
</thead>
<tbody>
<tr>
<td>basal medium</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>glucose</td>
<td>Aldrich</td>
<td>15,896-8</td>
</tr>
<tr>
<td>paper (various types)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Whatman Filter Paper (No. 1)</td>
<td>Fisher Scientific</td>
<td>09-805-1A</td>
</tr>
</tbody>
</table>

### Table 5-9. Basal medium for anaerobic growth (DiStefano 1992).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantity (per liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Cl</td>
<td>200 mg</td>
</tr>
<tr>
<td>K₂HPO₄·3H₂O</td>
<td>100 mg</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>55 mg</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>200 mg</td>
</tr>
<tr>
<td>Resazurin</td>
<td>1 mg</td>
</tr>
<tr>
<td>FeCl₂·4H₂O</td>
<td>100 mg</td>
</tr>
<tr>
<td>Trace Metals Solution</td>
<td>10 mL</td>
</tr>
<tr>
<td>Na₂S·9H₂O</td>
<td>500 mg</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>6 g</td>
</tr>
</tbody>
</table>

The first six compounds are added to distilled-deionized water, then purged with N₂ until solution turns from blue to pink. The remaining components are added, followed by a 15-minute purge with the 70% N₂/30% CO₂ gas mixture.

### Table 5-10. Trace metals for anaerobic growth (DiStefano 1992).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantity (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl₂·4H₂O</td>
<td>100</td>
</tr>
<tr>
<td>CoCl₂·6H₂O</td>
<td>170</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>100</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>251</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>19</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>50</td>
</tr>
<tr>
<td>Na₂MoO₄·2H₂O</td>
<td>20</td>
</tr>
</tbody>
</table>

### Table 5-11. Gas chromatograph conditions

<table>
<thead>
<tr>
<th>gas</th>
<th>pressure</th>
<th>flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>carrier (He)</td>
<td>kPa</td>
<td>5 mL/min</td>
</tr>
<tr>
<td>Ref</td>
<td></td>
<td>15 mL/min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>temperatures</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>oven (isothermal)</td>
<td></td>
</tr>
<tr>
<td>Injector</td>
<td>250</td>
</tr>
<tr>
<td>TCD</td>
<td>250</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Column</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxen 1004 micropacked column</td>
<td>Supelco</td>
<td>1-2846</td>
</tr>
</tbody>
</table>

Methane Production from Municipal Solid Waste
Gas Transfer

Introduction

Exchange of gases between aqueous and gaseous phases is an essential element of many environmental processes. Wastewater treatment plants require enhanced transfer of oxygen into activated sludge tanks to maintain aerobic degradation. Water treatment plants require gas transfer to dissolve chlorine gas or ozone. Gas transfer can also be used to remove unwanted volatile chemicals such as carbon tetrachloride, tetrachloroethylene, trichloroethylene, chloroform, bromodichloromethane, and bromoform from water (Zander et al., 1989). Exchange of a dissolved compound with the atmosphere is controlled by the extent of mixing in the aqueous and gaseous phase, the surface area of the interface, the concentration of the compound in the two phases, and the equilibrium distribution of the compound. Technologies that have been developed to enhance gas transfer include: aeration diffusers, packed-tower air stripping, and membrane stripping. Each of these technologies creates a high interface surface area to enhance gas transfer.

Theory

Oxygen transfer is important in many environmental systems. Oxygen transfer is controlled by the partial pressure of oxygen in the atmosphere (0.21 atm) and the corresponding equilibrium concentration in water (approximately 10 mg/L). According to Henry’s Law, the equilibrium concentration of oxygen in water is proportional to the partial pressure of oxygen in the atmosphere.

Natural bodies of water may be either supersaturated or undersaturated with oxygen depending on the relative magnitude of the sources and sinks of oxygen. Algae can be a significant source of oxygen during active photosynthesis and can produce supersaturation. Algae also deplete oxygen levels during the night.

At high levels of supersaturation dissolved gas will form microbubbles that eventually coalesce, rise, and burst at the water surface. The bubbles provide a very efficient transfer of supersaturated dissolved gas to the gaseous phase, a process that can be observed when the partial pressure of carbon dioxide is decreased by opening a carbonated beverage. Bubble formation by supersaturated gasses also occurs in the environment when cold water in equilibrium with the atmosphere is warmed rapidly. The equilibrium dissolved oxygen concentration is a function of temperature and as the water is warmed the equilibrium concentration decreases (Figure 6-1).
Supersaturation of dissolved gases can also occur when water carrying gas bubbles from a water fall or spillway plunges into a deep pool. The pressure increases with depth in the pool and gasses carried deep into the pool dissolve in the water. When the water eventually approaches the surface the pressure decreases and the dissolved gases come out of solution and form bubbles. Bubble formation by supersaturated gases can kill fish (similar to the “bends” in humans) as the bubbles form in the bloodstream.

**Gas Transfer Coefficient**

Gas transfer rate can be modeled as the product of a driving force (the difference between the equilibrium concentration and the actual concentration) and an overall volumetric gas transfer coefficient (a function of the geometry, mixing levels of the system and the solubility of the compound). In equation form

\[
\frac{dC}{dt} = \hat{k}_{v,j} \left( C^* - C \right)
\]

where \( C \) is the dissolved gas concentration, \( C^* \) is the equilibrium dissolved gas concentration and \( \hat{k}_{v,j} \) is the overall volumetric gas transfer coefficient. Although \( \hat{k}_{v,j} \) has dimensions of \( 1/T \), it is a function of the interface surface area (\( A \)), the liquid volume (\( V \)), the oxygen diffusion coefficient in water (\( D \)), and the thickness of the laminar boundary layer (\( \delta \)) through which the gas must diffuse before the much faster turbulent mixing process can disperse the dissolved gas throughout the reactor.

\[
\hat{k}_{v,j} = f(D, \delta, A, V)
\]
The overall volumetric gas transfer coefficient is system specific and thus must be evaluated separately for each system of interest (Weber and Digiano, 1996).

A schematic of the gas transfer process is shown in Figure 6.2. Fickian diffusion controls the gas transfer in the laminar boundary layer. The oxygen concentration in the bulk of the fluid is assumed to be homogeneous due to turbulent mixing and the oxygen concentration above the liquid is assumed to be that of the atmosphere.

The gas transfer coefficient will increase with the interface area and the diffusion coefficient and will decrease with the reactor volume and the thickness of the boundary layer. The functional form of the relationship is given by

$$\hat{k}_{v,I} = \frac{AD}{V\delta}$$

Equation 6.2 can be integrated with appropriate initial conditions to obtain the concentration of oxygen as a function of time. However, care must be taken to ensure that the overall volumetric gas transfer coefficient is not a function of the dissolved oxygen concentration. This dependency can occur where air is pumped through diffusers on the bottom of activated sludge tanks. Rising air bubbles are significantly depleted of oxygen as they rise through the activated sludge tank and the extent of oxygen depletion is a function of the concentration of oxygen in the activated sludge. Integrating equation 6.2 with initial conditions of $C = C_0$ at $t = t_0$

$$\int_{C_0}^{C} \frac{dC}{C^* - C} = \int_{t_0}^{t} \hat{k}_{v,I} dt$$

$$\ln\left(\frac{C^* - C}{C^* - C_0}\right) = \hat{k}_{v,I}(t - t_0)$$

This equation can be linearized so that $\hat{k}_{v,I}$ is the slope of the line.

$$\ln\left(C^* - C\right) = \hat{k}_{v,I}t + \left[\ln\left(C^* - C_0\right) - \hat{k}_{v,I}t_0\right]$$

The simple gas transfer model given in equation 6.7 is appropriate when the gas transfer coefficient is independent of the dissolved gas concentration. This requirement can be met in systems where the gas bubbles do not change concentration significantly as they rise through the water column. This condition is met when the water column is shallow, the bubbles have large diameters, or the
difference between the concentration of dissolved gas and the equilibrium concentration is small.

**Oxygen Transfer Efficiency**

An important parameter in the design of aeration systems for the activated sludge process is the energy cost of compressing air to be pumped through diffusers. The pumping costs are a function of the pressure and the airflow rate. The pressure is a function of the hydrostatic pressure (based on the depth of submergence of the diffusers) and the head loss in the pipes and through the diffuser. The required airflow rate is a function of the BOD of the wastewater and the efficiency with which oxygen is transferred from the gas phase to the liquid phase. This oxygen transfer efficiency (OTE) is a function of the type of diffuser, the diffuser depth of submergence, as well as temperature and ionic strength of the activated sludge. Oxygen transfer is a remarkably inefficient process; only a small fraction of the oxygen carried by the rising bubbles diffuses into the activated sludge. The most efficient systems use membrane diffusers and achieve an OTE of approximately 10%.

The manufacturer typically provides oxygen transfer efficiency for a specific diffuser. In this laboratory we will measure oxygen transfer efficiency for the aeration stone that we will be using in an activated sludge tank. The molar transfer rate of oxygen through the diffuser is

\[ \dot{n} = \frac{Q_{air} P_{air} f_{O_2}}{RT} \]  

where \( f_{O_2} \) is the molar fraction of air that is oxygen (0.21), \( Q_{air} \) is the volumetric flow rate of air into the diffuser, \( P_{air} \) is the air pressure immediately upstream from the diffuser, \( R \) is the universal gas constant and \( T \) is absolute temperature.

The molar rate of dissolution into the aqueous phase is

\[ \dot{n} = \frac{V}{MW_{O_2}} \frac{dC}{dt} \]  

where \( MW_{O_2} \) is the molecular weight of oxygen, \( V \) is the reactor volume, and \( \frac{dC}{dt} \) is the change in oxygen concentration with time. The rate of change of oxygen concentration is a function of the dissolved oxygen concentration and is a maximum when the dissolved oxygen concentration is zero. Oxygen transfer efficiency could be measured for any dissolved oxygen concentration. A better method of analysis is to substitute the right side of equation 6.2 for \( \frac{dC}{dt} \).

\[ \dot{n} = \frac{V \hat{k}_{v,t} (C^* - C)}{MW_{O_2}} \]  

The oxygen transfer efficiency is the ratio of equation 6.11 to equation 6.9.
Measurement of OTE requires that the gas transfer coefficient, air flow rate, air pressure, and the air temperature be measured.

Deoxygenation

In order to measure the reaeration rate it is necessary to first remove the oxygen from the reactor. This can be accomplished by bubbling the solution with a gas that contains no oxygen. Nitrogen gas is typically used to remove oxygen from laboratory reactors. Alternately, a reductant can be used. Sulfite is a strong reductant that will reduce dissolved oxygen in the presence of a catalyst.

\[
\text{O}_2 + 2\text{SO}_3^- \xrightarrow{\text{cobalt}} 2\text{SO}_4^- 
\]

The mass of sodium sulfite required to deoxygenate a mg of oxygen is calculated from the stoichiometry of equation 6.13.

\[
\frac{\text{mole O}_2}{32000 \text{ mg O}_2} \cdot \frac{2 \text{ mole Na}_2\text{SO}_3}{\text{mole O}_2} \cdot \frac{126,000 \text{ mg Na}_2\text{SO}_3}{\text{mole Na}_2\text{SO}_3} = \frac{7.875 \text{ mg Na}_2\text{SO}_3}{\text{mg O}_2}
\]

If complete deoxygenation is desired a 10% excess of sulfite can be added. The sulfite will continue to react with oxygen as oxygen is transferred into the solution. The oxygen concentration can be measured with a dissolved oxygen probe or can be estimated if the temperature is known and equilibrium with the atmosphere assumed (Figure 6-1).

Experimental Objectives

The objectives of this lab are to:

1) Illustrate the dependence of gas transfer on gas flow rate.
2) Develop a functional relationship between gas flow rate and gas transfer.
3) Measure the oxygen transfer efficiency of a course bubble diffuser.
4) Explain the theory and use of dissolved oxygen probes. See [http://ceeserver.cee.cornell.edu/mw24/Labdocumentation/sensors.htm](http://ceeserver.cee.cornell.edu/mw24/Labdocumentation/sensors.htm) for information on how the dissolved oxygen probe works and how to calibrate it.

A small reactor that meets the conditions of a constant gas transfer coefficient will be used to characterize the dependence of the gas transfer coefficient on the gas flow rate through a simple diffuser. The gas transfer coefficient is a function of the gas flow rate because the interface surface area (i.e. the surface area of the air bubbles) increases as the gas flow rate increases.
Experimental Methods

The reactor is a 4 L container (Figure 6-3). The DO probe should be placed to minimize the risk of air bubbles lodging on the membrane on the bottom of the probe. The aeration stone is connected to a peristaltic pump (or other source of regulated air flow). A 7-kPa pressure sensor can be used to measure the air pressure.

1) Install a membrane on the oxygen probe.
2) Calibrate the DO probe (See http://ceeserver.cee.cornell.edu/mw24/Software/DOcal.htm).
3) Prepare to monitor the dissolved oxygen concentration using the Signal Monitor software. Use 5 second data intervals and log the data to \Enviro\enviro\Courses\453\gastran\netid_50 for later analysis. See http://ceeserver.cee.cornell.edu/mw24/Software/signal_monitor.htm for instructions on using Signal Monitor software.
4) Add 4 L of distilled water to the reactor.
5) Measure the static pressure due to water depth on the diffuser using a ruler and the pressure sensor.
6) Set the stirrer speed to 5.
7) Add ≈10 mg CoCl₂· 6H₂O (note this only needs to be added once because it is the catalyst). A stock solution of CoCl₂· 6H₂O (100 mg/mL – thus add 100 µL) has been prepared to facilitate measurement of small cobalt doses.
8) Set the airflow rate to 50 mL/min (or to the desired flow rate).
9) Measure the air pressure.
10) Turn the air off.
11) Add enough sodium sulfite to deoxygenate the solution. A stock solution of sodium sulfite (100 mg/mL) has been prepared to facilitate measurement of small sulfite doses. (4 L of water at 10 mg O₂/L = 40 mg O₂, therefore add 350 mg sodium sulfate or 3.5 mL of stock solution.)
12) Turn the air on and start collecting data using the Signal Monitor software.
13) Monitor the dissolved oxygen concentration until it reaches 80% of saturation value.

Repeat steps 8-13 using flow rates of 100, 200, 300, 400, and 500 mL/min.
Prelab Questions

1) Calculate the mass of sodium sulfite needed to reduce all the dissolved oxygen in 4 L of pure water in equilibrium with the atmosphere and at 30°C.

2) Sketch your expectations for dissolved oxygen concentration as a function of time for the flow rates used on a single graph. The graph can be done by hand and doesn’t need to have any numbers on the time scale.

3) Sketch your expectations for \( \hat{k}_{i,j} \) as a function of gas flow rate. Do you expect a perfectly straight line or do you expect some nonlinearities? Why? What do you expect \( \hat{k}_{i,j} \) to be when the gas flow rate is zero?

Data Analysis

1) Eliminate the data from each data set when the dissolved oxygen concentration was less than 0.5 mg/L. This will ensure that all of the sulfite has reacted.

2) Set \( t_0 \) to the time at the beginning of the remaining data. Subtract \( t_0 \) from each of the times so the remaining data now starts at zero.

3) Plot the data sets with the corrected times on a single graph.

4) Estimate \( \hat{k}_{i,j} \) using linear regression and equation 6.8 for each data set. Show a graph with the linearized data and the best fit lines.

5) Graph \( \hat{k}_{i,j} \) as a function of gas flow rate.

6) Create a graph showing OTE as a function of airflow rate and oxygen deficit \((C^* - C)\).

7) If the wastewater BOD is 325 mg/L and the wastewater flow rate is 16 L/day, what combination of airflow rate and diffusers would you use? You may assume that the entire BOD is consumed in the activated sludge tank.

8) Plot the head loss through the diffuser as a function of flow rate. Remember to account for the static pressure due to the water elevation. Based on the shape of the curve are the losses viscous (proportional to velocity) or due to turbulence (proportional to velocity squared)?

9) Comment on results and compare with your expectations and with theory.

References


**Lab Prep Notes**

**Setup**

1) Prepare the sodium sulfite immediately before class and distribute to groups in 15 mL PP bottles to minimize oxygen dissolution and reaction with the sulfite.

2) The cobalt solution can be prepared anytime and stored long term. Distribute to student stations in 15 mL PP bottles.

3) Attach two Easy-Load pump heads to the pump drives and plumb with size 18 tubing joined and connected to the hypodermic diffuser.

4) Verify that DO probes, membranes, and potassium chloride solutions are available at each station. Students will install the membranes.

5) Verify that the top row of ports has a maximum voltage of 0.5 volts.

6) Provide clamps to mount DO probes on magnetic stirrers.

<table>
<thead>
<tr>
<th>Table 6-1. Reagent list</th>
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<tr>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
</tr>
<tr>
<td>CoCl$_2$·6H$_2$O</td>
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<th>Table 6-2. Stock solutions list</th>
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<tr>
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<td>CoCl$_2$·6H$_2$O</td>
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<tr>
<th>Table 6-3. Equipment list</th>
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<tr>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>magnetic stirrer 100-1095 µL pipette</td>
</tr>
<tr>
<td>10-109.5 µL pipette</td>
</tr>
<tr>
<td>15 mL PP bottles</td>
</tr>
<tr>
<td>variable flow digital drive</td>
</tr>
<tr>
<td>Easy-Load pump head</td>
</tr>
<tr>
<td>PharMed tubing # 18</td>
</tr>
<tr>
<td>4 prong hypodermic tubing diffuser</td>
</tr>
<tr>
<td>1/4” plug</td>
</tr>
<tr>
<td>1/4” union</td>
</tr>
<tr>
<td>stainless steel hypodermic tubing</td>
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Soil Washing to Remove Mixed Wastes

Objective

The goal of this laboratory exercise is to acquaint students with some of the chemical reactions that result in the binding of inorganic and organic pollutants in subsurface materials. Extractants used by engineers to release contaminants at hazardous waste sites (where mixtures of both types of contaminants are present) may or may not prove effective, depending upon their mechanism of action. In this laboratory exercise, students will test the efficacy of a variety of proposed extractants in the removal of a mixture of an inorganic metal cation, and an organic compound from a contaminated porous medium.

Introduction

Many Superfund site soils are contaminated with a mixture of contaminants including toxic metals and organic compounds. A pressing environmental problem is to devise clean-up strategies that can effectively remove mixed wastes. Many kinds of contaminants bind to soils and aquifer media (collectively referred to here as porous media). Binding reactions limit the effectiveness of “pump and treat remediation” in which a contaminated porous medium is flushed with water to remove contaminants. In such cases, it can prove useful to engineer the properties of the aqueous phase to improve the mobility of the pollutants of interest.

In the case of toxic metals, release of medium-bound or “adsorbed” metals can be enhanced by introduction to the pore solution of a dissolved compound that will bind to the metal in the aqueous phase and form a dissolved “complex”. Such compounds are referred to as “ligands”, and ligands that bind metals very strongly are called “chelating agents”. Metal solubility and adsorption can also be strongly influenced by the oxidation state of the metal, and use of oxidants or reductants to alter the redox conditions in a porous medium can modify metal mobility both directly and indirectly. Direct effects would be observed if oxidized and reduced metal species have different adsorption characteristics (ex. \( \text{Cr}_2\text{O}_7^{2-} \) vs. \( \text{Cr}^{3+} \)). Indirect effects would be observed if a metal were bound to a solid phase that would be dissolved under different redox conditions (ex. \( \text{Fe(OH)}_3 \) may dissolve under reducing conditions). Addition of acids or bases could also alter metal mobility. Adsorption of metals is very sensitive to pH shifts, with a decrease in pH favoring the release of cationic metal species (ex. \( \text{Cd}^{2+} \), \( \text{Pb}^{2+} \)) and an increase in pH favoring release of anionic species (ex. \( \text{Cr}_2\text{O}_7^{2-} \), \( \text{SeO}_3^{2-} \)).

Organic cations and anions will have a pH dependent adsorption behavior similar to that described above for metal ions. However, many organic pollutants of interest are nonionic and their binding to the matrix of the porous medium is not greatly influenced by pH. “Hydrophobic interactions” of nonionic organic compounds with organic matter in porous media appear to be a major driving force for their binding. The addition of surfactants to the pore solution can help to release sorbed nonionic organic pollutants. Under suitable conditions many organic pollutants can be degraded by addition of oxidants or by indigenous or added bacteria [i.e.; given that...
the bacteria have the necessary genetic capabilities, nutrients (N, P, etc.) and a suitable electron acceptor]. Metals, however, are elements and cannot be degraded.

Porous media is not inert. The mineral and organic constituents of the porous matrix can react with added ligands, acids, bases, oxidants, reductants, and surfactants. A consequence, in some cases, is that a desired addition may be rendered impractical.

Given the variability and possible dissimilarity of conditions that influence the mobility of metal vs. organic pollutants, it is a challenging task to identify a remediation strategy that will successfully treat a given medium that is contaminated with mixed wastes. In this laboratory exercise, students will evaluate the utility of several alternative extractants for remediation of a soil that is contaminated with both a metal cation and an organic compound.

**Theory**

**Binding Reactions**

The binding reactions of pollutants to the porous matrix may be classified, at least in part, by where and how the binding reaction takes place. The term “adsorption” is used for reactions that take place at the interface between the solid and the solution. All other factors being equal, solids with a greater specific surface area (ex. units: m²/gram) will adsorb greater amounts of a dissolved solute. In adsorption reactions, the surface is referred to as an “adsorbent” and the solute as an “adsorbate”. Some adsorption reactions are driven by electrostatic attraction between the surface and the solute. “Ion exchange” is the term used for this type of reaction. All other factors being equal, surfaces with a greater number of charged sites per unit surface area will be able to bind greater quantities of dissolved ions. The concentration of surface exchange sites is commonly quantified as an “ion exchange capacity”. Surfaces with a high density of negatively charged sites (cation exchangers) will selectively bind positively charged ions while those with a high density of positively charged sites will be selective for anions.

“Absorption” is a process in which a solute penetrates within the solid matrix. “Partitioning” is a term that is synonymous with absorption. As an example, we would carry out a partitioning process if we were to add a pollutant to a separatory funnel containing water and an organic liquid such as octanol and then observe the resulting distribution of the contaminant between the aqueous and octanol liquid phases. The distributed contaminant would exist as a dissolved solute in each phase. As is noted below, the phase distribution behavior of nonionic organic pollutants in soils and aquifer media displays many characteristics of absorption reactions. The absorption of nonionic organics appears to be primarily into the organic matter content of the porous medium. This reaction is driven by the water loving nature of the solute, or lack thereof (i.e., pollutant “hydrophobicity”). All other factors being equal, porous media with higher organic carbon contents would have greater uptake of nonionic organic pollutants.

The term “sorption” is somewhat loosely used when the exact mechanistic nature of the pollutant’s distribution between the solution and the porous medium is not
understood, or when both adsorption and absorption reactions may contribute to the contaminant’s phase distribution.

Contaminant sorption reactions result from an reaction between a material that is dissolved in an aqueous solution with a solid phase. The physical/chemical properties of the contaminant, the solution and the sorbent all influence the resulting contaminant phase distribution. These influences are discussed below.

**Sorbent Surface Charge**

As noted above, if the sorbate is an ion, then electrostatic attraction to the surface can play an important role in contaminant adsorption. Virtually all soil surfaces are charged.

**Oxide Minerals**

Surface charge can result from the ionization of surface functional groups in response to the hydrogen ion concentration of the aqueous phase. Oxide minerals are often modeled as diprotic acids (Westall and Hohl, 1980). Accordingly the surface may donate two hydrogen ions as indicated by the following reactions:

\[
\text{SOH}_2^+ \xrightarrow{K_1} \text{SOH} + H^+ 
\]

\[
\text{SOH} \xrightarrow{K_2} \text{SO}^- + H^+ 
\]

where \( \text{SO} \) represents the oxide surface that may exchange two hydrogen ions, and \( K_1 \) and \( K_2 \) are equilibrium constants for the first and second acid dissociation reactions.

Note, each dissociation constant can be thought of as an expression of the relationship between the concentration of protonated and deprotonated surface sites and the solution hydrogen ion concentration. Accordingly:

\[
K_1 = \frac{[\text{SOH}][H^+]}{[\text{SOH}_2^+]} 
\]

\[
K_2 = \frac{[\text{SO}^-][H^+]}{[\text{SOH}]} 
\]

\( K_1 \) therefore represents the solution hydrogen ion concentration at which the concentration of positively charged, diprotic, surface sites \( [\text{SOH}_2^+] \) is equal to that of surface sites containing a single proton \( [\text{SOH}] \). Similarly, when \( [H^+] \) equals \( K_2 \) then \( [\text{SO}^-] = [\text{SOH}] \).

Although other models of the acid base behavior of oxide surface are conceivable, the above model is helpful in that it predicts that the surfaces can have both positively and negatively charged sites. With this model, \( H^+ \) release from the surface will occur
in response to a decrease in the solution H⁺ concentration (i.e., an increase in pH, where pH is defined as \(-\log[H^+]\)). Accordingly, we would expect increasingly higher solution pH conditions to favor formation of negatively charged surfaces, and this is observed. Different surfaces would have different acidity constants (K₁ and K₂) and would be expected to have different surface charges at the same solution pH. Each surface, at one unique pH, would have an equal concentration of \(\text{SOH}_2^+\) and \(\text{SO}^-\) sites and would have no net charge. This is also observed and is referred to as the pH point of zero charge (PZC). \(\text{SiO}_2\), a common oxide in porous media (the main component of sand), has a low PZC (≈ pH 2 to 3) while iron and aluminum oxides (that commonly occur as surface coatings) have considerably higher PZCs (≈ pH 7 to 8) (Parks and DeBruyn, 1962).

**Soil Organic Matter**

Another pH-dependent origin of surface charge is the ionization of the acidic functional groups in soil organic matter. The carboxyl groups of humic-type organic matter typically have acidity constants \(\leq 10^{-5}\) (pK ≤ 5) and are therefore highly ionized at circumneutral pH.

**Isomorphic Substitution**

A final source of charge in soil is isomorphic substitution in the crystalline lattice of some clay minerals. Substitution of \(\text{Al}^{3+}\) for \(\text{Si}^{4+}\) and \(\text{Mg}^{2+}\) for \(\text{Al}^{3+}\) will result in a net negative charge for the clay mineral phase.

The combined effects of isomorphic substitution, ionization of organic functional groups and the low PZC of silicon oxide minerals make it likely that many porous media will have a net negative charge. Consequently, stronger binding of cationic contaminants is generally anticipated.

**Sorbent Ion Exchange Reactions**

Ion exchange reactions involve the exchange of ions of the same charge at an oppositely charge site on the solid surface. Exchange reactions are often characterized by “selectivity coefficients” that may be thought of as equilibrium constants for the exchange reaction. For example, in the exchange of two monovalent cations, the exchange reaction may be depicted as:

\[
\text{SO}^- - x^+ + y^+ \xrightarrow{K'_x} \text{SO}^- - y^+ + x^+ \tag{7.5}
\]

where:

\[
K'_x = \frac{[\text{SO}^- - y^+]}{[\text{SO}^- - x^+]} \cdot \frac{[x^+]}{[y^+]} \tag{7.6}
\]

The magnitude of the selectivity coefficient, \(K'_x\), reflects the extent to which ion \(x^+\) vs. \(y^+\) will accumulated at the surface. Ions with high selectivity coefficients can displace more weakly held ions from an exchange site.
In a negatively charged soil, anionic compounds (ex. ionized organic acids, NO$_3^-$, Cr$_2$O$_7^{2-}$, etc.) will be repelled from the surface and therefore may be highly mobile. Cationic species (ex. quaternary ammonium organic compounds, divalent transition metals, etc.) will be attracted to the surface and have restricted mobility. In principle, exchangeable pollutant cations may be mobilized by introduction of high concentrations of an innocuous cation. The practicality of such an approach would be dictated by the extent to which other exchangeable cations (that are not of environmental concern) are also exchanged. Since cations such as Na$^+$, K$^+$, Ca$^{2+}$ Mg$^{2+}$ are abundant in porous media, the amount of a cation added for exchange of a trace pollutant would have to be in great excess of the pollutant cation. As a result, release of contaminant cations by an ion exchange mechanism does not appear to be economically feasible.

**Sorbent Hydrophobic Interactions**

The mechanisms responsible for the adsorption of charged species differ considerably from those for nonionic compounds. Adsorption of charged ions may, in some cases, involve more than the simple electrostatic attraction of ions to a surface of opposite charge. Transition metal cations, for example, will often adsorb to oxide surfaces even under solution conditions that confer a positive charge on the surface (see additional discussion below under the topic of solution characteristics).

The sorption of nonionic organic pollutants behaves as if it is a partitioning process into the organic matter that is present as part of the soil matrix. Some of the general characteristics that lead to this conclusion are the observance of linear sorption isotherms at high solution concentrations (that can approach the solubility limit of solute compounds). [Note, an “isotherm” is simply the relationship between the quantity of pollutant that is bound (per unit mass or unit surface area of the sorbent) and the concentration of contaminant in solution.] In contrast, adsorption reactions are limited by the availability of surface sites and adsorption isotherms are typically non-linear at high solute concentrations. Partition reactions are also relatively free from competition (i.e., the presence of a second solute does not affect the sorptive uptake of the first) while competition for surface sites is an expected characteristic in an adsorption process. The extent of sorption of a given nonionic organic onto a variety of sorbents is highly correlated with their organic content as expressed by the weight fraction of organic carbon, $f_{oc}$ (Karickhoff, 1984). For the same sorbent, the sorption of different nonionic solutes is highly correlated with their octanol-water partition coefficients ($K_{ow}$) (Karickhoff, 1984). Collectively, these observations lead to the conclusion that the sorption of nonionic organic pollutants is primarily driven by hydrophobic interactions between the solute and the organic matter in the sorbent.

**Solution pH**

Solution conditions can have dramatic effects on the adsorption of cationic contaminants. For example the adsorption of cationic transition metals to oxide surfaces typically increases markedly over a narrow range of 1 to 2 pH units referred to as the “adsorption edge”. The pH dependence of metal ion adsorption can be explicitly accounted for by writing the adsorption reaction as:
\[
\text{SOH}_x + Me^{+z} \xrightarrow{k_d} \text{SOME}^{-x} + xH^+
\]

where \(K_d\) is the pH-dependent metal distribution coefficient, and according to Honeyman and Santschi (1988)

\[
K_d = \frac{\left[ \text{SOME}^{-x} \right]}{\left[ \text{SOH}_x \right] \cdot [Me^{+z}]} \cdot [H^+]^x
\]

A plot of \(\log \left( \frac{\left[ \text{SOME}^{-x} \right]}{\left[ \text{SOH}_x \right] \cdot [Me^{+z}]} \right)\) versus pH, is referred to as a “Kurbatov plot” (after Kurbatov et. al., 1951), and may be used to reveal the magnitude of the exponent, \(x\) for \([H^+]\) in the distribution coefficient. The ratio \(\frac{\left[ \text{SOME}^{-x} \right]}{\left[ \text{SOH}_x \right]}\) is the quantity of adsorbed metal per unit surface. Since the above reaction and its equilibrium constant, \(K_d\), are an over simplification of the actual adsorption mechanism, measured values of \(x\) are rarely integers. Nevertheless, \(x\) values ranging from 1 to 2 are common for adsorption of metal cations on oxide surfaces and demonstrate the strong dependence of the adsorption processes on pH. For example, if \(x = 2\), an increase of 1 pH unit would result in a 100 fold increase in the amount of bound metal per unit surface (at the same solution concentration of metal ion). In general, adsorbed metal cations will be released as a consequence of a decrease in solution pH. Since the surfaces in the porous medium also have acid/base properties, and because many porous media contain acid-reactive components (such as carbonate minerals) a very large acid dose may be required to effectively alter the pH of the pore water. For this reason, acid extraction of adsorbed metals may not always be feasible.

**Metal-Ligand Complexes**

Another influence of solution conditions on metal adsorption is through the reactions of metals with ligands to form complexes. In some cases, metal-ligand complexes adsorb weakly or not at all (ex. Cl\(^-\) complexes of Cd and Hg), in other cases metal-ligand complexes may adsorb with a binding strength greater than that of the free metal (ex. organic complexes of Cu) (Benjamin and Leckie, 1982). Judicious selection of a ligand for introduction into a porous medium may, therefore, be used to accomplish the release of adsorbed cations. Added ligands may, in some cases, undergo exchange reactions with the porous media or react to form complexes with cations that are not of environmental concern. For this reason the dose of a ligand needed to effectively release adsorbed metals will vary with the composition of the porous media and ligand addition may not prove feasible in some cases.

**Oxidants and Reductants**

Changing solution composition by the introduction of oxidizing or reducing agents may accomplish the release of adsorbed metals. Iron oxides are strong metal binding
agents and may be solubilized by reduction from ferric (Fe III) to ferrous (Fe II) iron. Many transition metals (e.g. Cd, Co, Cu, Ni, Pb, Zn) will remain as divalent cations during such a shift in redox status, and may therefore simply re-absorb to another surface. In some cases, alteration of the media redox conditions may directly influence metal mobility. For example reducing conditions would favor the presence of a cationic form of chrome (Cr$^{3+}$) over the more mobile anionic form (Cr$_2$O$_7^{2-}$). Addition of oxidants may therefore help to mobilize chrome, however the organic matter in soils and ferrous minerals will also react with added oxidants.

In a manner similar to the role of iron oxides, the organic matter in porous media can be responsible for the binding of metal cations. The reaction of an added oxidant with humic-type organic matter may therefore accomplish solubilization of some metals (Lion et al., 1982). Strong oxidants will also act to break down organic contaminants.

**Hydroxyl Radicals**

One application that has been used for remediation of organic contaminated soils is the introduction of Fenton’s reagent. Fenton’s reagent is a mixture of hydrogen peroxide and ferrous iron (Fe$^{2+}$). These chemicals react to produce hydroxyl radicals$^3$ (OH•) according to the following reaction:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}\cdot$$

The hydroxyl radicals produced by Fenton’s reagent are highly reactive and can effectively degrade recalcitrant aromatic compounds by ring substitution followed by ring cleavage (Sedlak and Andren, 1991).

**Surfactants**

Additions of surfactants may aid in the release of sorbed nonionic organic pollutants. In the case of sorption reactions that are driven by hydrophobic interactions, surfactant additions can have two beneficial effects: 1) a decrease in the aqueous activity coefficient for the dissolved nonionic organic compound and 2) formation of micelles in the aqueous phase.

The effect of the aqueous activity coefficient can be illustrated by examination of the sorption isotherm for the organic pollutant. If the isotherm is linear, then we may write:

$$\Gamma = K^S_L \gamma C_L$$

where $\Gamma$ is the mass of solute sorbed per mass of solid, $K^S_L$ is the sorptive distribution coefficient, $C_L$ is the aqueous concentration of the sorbate, and $\gamma$ is the activity coefficient of the dissolved sorbate.

Surfactants may act to decrease the activity coefficient, $\gamma$, for a nonionic molecule increasing the concentration in the aqueous phase in equilibrium with a given adsorbed amount, $\Gamma$. Surfactants increase the solubility of nonionic molecules

---

$^3$ Radicals contain an odd number of electrons.
because the hydrophobic-nonionic molecules adsorb to the long hydrocarbon group while the ionic sulfonic group provides high solubility (Figure 7-1).

However, since surfactants are surface-active, they may also sorb to the porous medium, increase its organic content, and consequently increase the sorption of a nonionic organic contaminant. High concentrations of water-soluble cosolvents such as methanol and acetone can also act to decrease the activity coefficient, \( \gamma \), and act to solubilize sorbed nonionic organic compounds (Schwarzenbach et al., 1993).

Surfactant molecules can aggregate into micelles in which their polar functional groups are oriented towards the aqueous solvent and their non-polar tails are oriented inward toward each other. The space within the micelles therefore provides a hydrophobic refuge for nonionic contaminants (Edwards et al., 1991). Surfactants will form micelles at aqueous concentrations greater than their “critical micelle concentration” (CMC). Since, as noted above, surfactants will sorb at the surface of the porous media, a high dose of surfactant may be required in order to maintain an aqueous concentration greater than the CMC.

**Bacterial Polymers**

Many of the solution modifications discussed above involve the addition of synthetic agents to contaminated soil to accomplish the release of sorbed contaminants. Natural constituents that occur in soils and aquifers may also enhance contaminant transport (McCarthy and Zachara, 1989). Bacterial polymers naturally occur in soil solution and have well-documented metal binding properties. The presence of bacterial polymers may therefore act as a natural process by which metal mobility is enhanced (Chen et al., 1995). The extracellular polymers produced by bacteria are hetero-polysaccharides and have high molecular weight. Interestingly, these large molecules have also been show to be effective at binding nonionic organic pollutants and at enhancing their transport in aquifer materials (Dohse and Lion, 1994). In principle, bacterial polymers with suitable binding properties could be produced in engineered reactor systems and be applied to contaminated waste sites to enhance the mobility of metal and nonionic organic contaminant mixtures. The efficacy of this type of remediation process has yet to be determined.

**Apparatus**

Students will apply a range of extractant types (or mixtures of different types) to remove contaminants (Zn and methylene blue) from a porous medium. Laboratory extractions will mimic an engineered soil washing system in which the contaminated soil is actively mixed with the extractant and then separated. A rotator will be used to provide agitation of samples of the medium with extractants, and a centrifuge will be used to provide phase separation. A UV/visible spectrophotometer with a diode array detector will be used to measure the concentration of the extracted organic pollutant.
Extracted metal concentrations will be measured with an atomic absorption (AA) spectrophotometer.

**Experimental Procedures**

Each group will develop their own hypothesis and experimental protocol. Different concentrations of extractants, different organic contaminants, and different washing techniques could be the investigation subjects. Alternate organic contaminants should be cleared with the instructor prior to the lab period. Each group should limit the investigation to approximately 10 samples and should include appropriate controls and replicates.

The following protocol assumes that a common sand is employed to represent the porous medium. It is desirable, but not essential, to characterize each medium to be used (prior to the laboratory exercise) with respect to its carbon content [the “Walkley Black” method is one common procedure (Allison, 1965)], cation exchange capacity, and specific surface area [by sorption of ethylene glycol monoethyl ether (EGME) (Cihacek and Bremmer, 1979)].

**I. Creation of a Contaminated Porous Medium**

A stock solution containing the soil contaminants will be provided [50 mg/L Zn and 100 mg/L methylene blue]. For each extractant used in part II below, 2 samples of contaminated sand and one sample of clean sand will be used. The following procedure is based on the assumption that each student group will evaluate 3 extractants or 3 concentrations of an extractant.

1) Weigh out 9 aliquots of sand, 2.5±0.05 g each, and pour into 10 mL plastic centrifuge tube.
2) Record the mass of the centrifuge tube with the sand (see Table 7-1).
3) Add 5 mL of the contaminant stock solution to 6 of the samples.
4) Add 5 mL distilled water to 3 of the samples (clean controls).
5) Place all of the samples on a rotator to mix the sand and the contaminant/clean solutions. Agitate for 15 minutes.
6) Centrifuge the suspensions at 3000 x g for 5 minutes.
7) Pour the supernatant from the 6 contaminated sand samples into a 125 mL bottle.
8) Pour the supernatant from the 3 clean sand samples into a separate 125 mL bottle.
9) Weigh the centrifuge tubes with the sand and pore water. Calculate the volume of pore water by subtracting the centrifuge tube and sand masses.

**II. Determination of the Amount of Contaminant Sorbed by the Sand**

*Methylene blue - UV/Vis Spectroscopy*

Nitrate absorbs ultraviolet light and is present in the contaminated samples from the addition of Zn(NO₃)₂·6H₂O. We could account for this either by preparing a nitrate standard and using it as a component in spectral analysis or by eliminating the ultraviolet part of the spectrum from the analysis. We will eliminate the nitrate interference by using a wavelength of 660 nm when measuring methylene blue. See
1) Measure the absorbance of 1, 5, and 10 mg/L methylene blue solutions as “Standards.” Save the file as \Enviro\enviro\Courses\453\soilwash\netid_MBstd.

2) Measure the absorbance of the combined supernatant from the 3 clean sand samples, the combined supernatant from the 6 contaminated sand samples, and the contaminating solution (diluted by a factor of 10) as “Samples.” Save the file as \Enviro\enviro\Courses\453\soilwash\netid_contamsuper.

3) Record the concentration of methylene blue in the clean supernatant and contaminated supernatant (see Table 7-2). You can drag the blue cursor on the "standard graph" to the wavelength of choice and read the exact absorbance (and wavelength) in the digital display to the left of the graph and concentration in the digital display at the bottom of the Spectrophotometer window. If the clean supernatant has significant absorbance at 660 nm then alternate analytical techniques may need to be used.

4) The difference between the methylene blue concentration in the contaminant solution and the concentration in the supernatant may be used to determine the sorbed contaminant concentration as:

\[
\Gamma = \frac{(C_{\text{initial}} - C_{\text{final}}) \text{(solution volume)}}{\text{mass of sand}}
\]

where \(C_{\text{initial}}\) is the contaminant solution concentration and \(C_{\text{final}}\) is the concentration of the supernatant. Solution volume is the volume of contaminant added initially.

**Zinc - Atomic Absorption Spectroscopy**

1) Calibrate the AA using the zinc standards (1, 2, and 6 mg/L).

2) Dilute all of the following samples by a factor of 10 to ensure sufficient sample volume for the analysis and to ensure that the results are in the calibrated range.

3) Measure and record the zinc concentration of the combined supernatant from the 3 clean sand samples.

4) Measure and record the zinc concentration of the combined supernatant from the 6 contaminated sand samples (see Table 7-3).

5) Measure and record the zinc concentration in the contaminating solution (the zinc concentration should be close to 50 mg/L).

6) The difference between the zinc concentration in the contaminant stock and the concentration in the supernatant may be used to determine the sorbed contaminant concentration using equation 7.12.

**III. Soil Washing Solutions**

Students may wish to experiment with extractant mixtures. Some combinations of extractant solutions may react violently! All proposed mixtures of extractants should
be cleared with the course instructor prior to their use. The following combinations should be avoided: mixtures of oxidants with reductants, mixtures of acids with bases, and mixtures of oxidants with organic extractants including: surfactants, chelating agents or cosolvents. The following extractant solutions will be available for testing. At least one group should measure the extractant capabilities of distilled water because it is by far the cheapest!

1) Distilled water.
2) Acid: \(\approx 1\) M solution of HCl prepared by diluting 27.4 mL of the concentrated acid to 1 L with distilled water.
3) Cosolvent: 1:1 (v/v) mixture of acetone and distilled water.

4) Non-ionic surfactant: 10% (v/v) solution of Triton X-100 prepared by diluting 100 mL to 1 L with distilled water. Note: Triton X-100 is a non-ionic surfactant with a CMC of \(2\times10^{-5}\) M (Edwards et al., 1991). The chemical formula for Triton X-100 is:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \text{-C-CH}_2 \text{-C-} \\
\text{CH}_3 \text{-C-CH}_2 \text{-C-} \\
\text{CH}_3 \\
\end{array}
\]

where: \(x = 9\) to 10, giving the surfactant a molecular weight of \(\approx 607\) g/mole.

5) Anionic surfactant: 100 mM solution of dodecyl sulfate, sodium salt \((\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}\) with MW of 288.4 so 28.84 g/L). This extractant works very well at full strength; lower concentrations could be investigated.

6) Chelating agent: \(\approx 0.1\) M solution of ethylenediamine-tetraacetate (EDTA) prepared by dissolving 37.22 g of the disodium salt in distilled water and diluting to 1 L.

7) Base: \(\approx 1\) M NaOH solution prepared by dissolving 40 g of NaOH distilled water and diluting to 1 L.

8) Oxidant: 1:1 (v/v) mixture of 30% \(\text{H}_2\text{O}_2\) and distilled water.

9) Reductant: \(\approx 1\) M solution of \(\text{Na}_2\text{S}_2\text{O}_3\cdot5\text{H}_2\text{O}\) prepared by dissolving 248 g in distilled water and diluting to 1 L.

**IV. Soil Washing Protocol**

The ability of each extractant to remove the zinc and methylene blue from the contaminated soil will be measured by exposing the contaminated soil to the extractant and then measuring the concentration of the zinc and methylene blue in the extractant.

1) Add 5 mL of each extractant to be tested to 2 contaminated sand samples and 1 clean sand sample.
2) Place the sand extractant mixtures on a rotator to mix for 15 minutes.
3) Centrifuge the suspensions at 3000 x g for 5 minutes.
4) Decant the supernatant from each centrifuge tube into labeled 15 mL bottles. A small air line can be used to help force the supernatant from the centrifuge tubes.
V. Analysis of Extracted Metal and Organic Pollutants

**Methylene blue - UV/Vis Spectroscopy**

Note that it is unnecessary to measure the methylene blue concentration in samples that do not appear to have any blue. Samples that are visually free of methylene blue can be recorded as 0 mg/L methylene blue.

1) Measure the absorbance of each of the clean sand extracts as “Samples.” All of the clean extracts can be analyzed together if desired. Save as \Enviro\Courses\453\soilwash\netid_cleanext.

2) Measure concentration of methylene blue in each of the clean extracts based on the absorbance at 660 nm (see Table 7-2).

3) Measure the absorbance of each of the extracts of the contaminated sand as “unknowns.” There will be 2 replicates for each extract. All of the contaminated extracts can be analyzed as a group so that their results are saved in a single file. Save as \Enviro\Courses\453\soilwash\netid_contamext.

4) Measure concentration of methylene blue in each of the contaminated extracts based on the absorbance at 660 nm (see Table 7-2). Note that it may be necessary to choose a different analytical wavelength or to dilute the sample if the absorbance exceeds $\approx 2.5$ at 660 nm.

5) Calculate the mass extracted per mass of sand as:

$$\Delta \Gamma = \frac{(C_{\text{extracted}})(\text{solution volume})}{\text{mass of sand}}$$  \hspace{1cm} 7.13

where solution volume is the sum of residual pore water volume after decanting the contaminant plus the extractant volume.

**Zinc - Atomic Absorption Spectroscopy**

1) Dilute all samples by a factor of 10 prior to analysis.

2) Measure and record the absorbance of the supernatant from the 3 clean sand samples (see Table 7-3).

3) Measure and record the absorbance of the supernatant from the 6 contaminated sand samples. Dilute the supernatant with distilled water if the absorbance is not less than the absorbance of the 6-mg/L standard.

4) Calculate the concentration of zinc in each of the sand extracts.

5) Calculate the mass of Zn removed per mass of sand using equation 7.13.

The results for any extractant must justify the cost of its use. The results obtained by extraction of contaminated soil using distilled water serve as a basis for comparison to which results obtained with extractants should be compared. Results from all extractants or extractant combinations evaluated should be compared to provide an inter-comparison of their relative effects of the removal of metal and organic pollutants.
Prelab Questions

1) The point of zero charge for SiO₂ is approximately at pH = 2.5. Is the charge of SiO₂ positive or negative at a pH of 7?

2) Do cations or anions generally bind most strongly to soil?

3) Develop a hypothesis concerning soil washing, and write an experiment protocol to test your hypothesis that you can do in a lab period. Include detail of concentrations of extractants and contaminants for each vial. You may want to work with your lab partner(s) because this will be your experiment! Design your experiment to use no more than 9 vials.

Data Analysis

1) Report the contaminated sand concentration (grams of contaminant/gram of sand) for zinc and methylene blue.

2) Calculate the fractional removal of zinc and methylene blue for each extractant or extractant concentration. The fractional removal based on the amount of contaminant initially sorbed is \( f = \frac{\Delta \Gamma}{\Gamma} \) where \( \Gamma \) is defined in equation 7.12 and \( \Delta \Gamma \) is defined in equation 7.13. Present this using an appropriate graph.

3) Discuss which extractant performed best at removal of the zinc. Which was best at removing the test organic? Which extractant worked best at removing both contaminants? Discuss these results in terms of the chemical change that the extractant was designed to accomplish. (Note that these questions may need to be modified based on the samples you analyzed.)

4) Discuss any difficulties in evaluating extractant effectiveness and propose improved analytical techniques.

5) Discuss your results and their implications for the hypothesis that you developed.

6) Analyze your results including the reproducibility of replicate analyses in terms of possible sources of error.

7) Suggest options for additional research.

References


Table 7-1. Data table.

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<thead>
<tr>
<th>bottle #</th>
<th>contaminated or clean</th>
<th>mass sand (g)</th>
<th>mass bottle + sand (g)</th>
<th>mass bottle + sand + pore water (g)</th>
</tr>
</thead>
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<tr>
<td>clean</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cont.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cont.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>clean</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cont.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cont.</td>
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<td></td>
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Table 7-2. Methylene blue data table.

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<tr>
<th>concentration</th>
<th>clean sand supernatant</th>
<th>contaminated sand supernatant</th>
<th>extractant 1 clean sand</th>
<th>extractant 1 cont. sand rep 1</th>
<th>extractant 1 cont. sand rep 2</th>
<th>extractant 2 clean sand</th>
<th>extractant 2 cont. sand rep 1</th>
<th>extractant 2 cont. sand rep 2</th>
<th>extractant 3 clean sand</th>
<th>extractant 3 cont. sand rep 1</th>
<th>extractant 3 cont. sand rep 2</th>
</tr>
</thead>
</table>

Table 7-3. Zinc concentration measurements data table.

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<th>concentration</th>
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<td>clean sand supernatant</td>
<td></td>
</tr>
<tr>
<td>contaminated sand supernatant</td>
<td></td>
</tr>
<tr>
<td>extractant 1 clean sand</td>
<td></td>
</tr>
<tr>
<td>extractant 1 cont. sand rep 1</td>
<td></td>
</tr>
<tr>
<td>extractant 1 cont. sand rep 2</td>
<td></td>
</tr>
<tr>
<td>extractant 2 clean sand</td>
<td></td>
</tr>
<tr>
<td>extractant 2 cont. sand rep 1</td>
<td></td>
</tr>
<tr>
<td>extractant 2 cont. sand rep 2</td>
<td></td>
</tr>
<tr>
<td>extractant 3 clean sand</td>
<td></td>
</tr>
<tr>
<td>extractant 3 cont. sand rep 1</td>
<td></td>
</tr>
<tr>
<td>extractant 3 cont. sand rep 2</td>
<td></td>
</tr>
</tbody>
</table>
**Lab Prep Notes**

Table 7-4. Reagent list.

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<thead>
<tr>
<th>Description</th>
<th>Supplier</th>
<th>Catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(NO₃)₂·6H₂O</td>
<td>Fisher Scientific</td>
<td>M291-25</td>
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<tr>
<td>Methylene Blue HCl</td>
<td>Fisher Scientific</td>
<td>S318-500</td>
</tr>
<tr>
<td>NaOH</td>
<td>Fisher Scientific</td>
<td>H325-500</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Fisher Scientific</td>
<td>S445-500</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>Fisher Scientific</td>
<td>N840-7</td>
</tr>
<tr>
<td>nitrilotriacetic acid</td>
<td>Aldrich</td>
<td>N840-7</td>
</tr>
<tr>
<td>Triton X-100 acetone</td>
<td>Aldrich</td>
<td>A929-1</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Aldrich</td>
<td>31,007-7</td>
</tr>
<tr>
<td>alginate acid, sodium salt</td>
<td>Aldrich</td>
<td>18,094-7</td>
</tr>
<tr>
<td>Fe(NO₃)₃·9H₂O</td>
<td>Aldrich</td>
<td>21,682-8</td>
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<tr>
<td>Humic acid</td>
<td>Aldrich</td>
<td>H1,675-2</td>
</tr>
<tr>
<td>Nitric Acid 6 N</td>
<td>Fisher Scientific</td>
<td>LC17-70-2</td>
</tr>
<tr>
<td>Dodecyl sulfate, sodium salt (C₁₂H₂₅SO₄Na)</td>
<td>Aldrich</td>
<td>85,192-2</td>
</tr>
<tr>
<td>Zinc reference solution</td>
<td>Fisher Scientific</td>
<td>SZ13-100</td>
</tr>
</tbody>
</table>

Table 7-5. Stock Solutions (100 mL each).

<table>
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<th>Description</th>
<th>MW (g/M)</th>
<th>conc. (g/L)</th>
<th>100 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₆H₁₈N₃SCl</td>
<td>319.87</td>
<td>10</td>
<td>1 g</td>
</tr>
<tr>
<td>Zn(NO₃)₂·6H₂O</td>
<td>297.4</td>
<td>227.4048</td>
<td>22.74 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5 g as Zn</td>
</tr>
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</table>

Table 7-6. Contaminating Solution (1 L)

<table>
<thead>
<tr>
<th>Description</th>
<th>MW (g/M)</th>
<th>conc. (mg/L)</th>
<th>1 L</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₆H₁₈N₃SCl</td>
<td>319.87</td>
<td>100</td>
<td>10 mL stock</td>
</tr>
<tr>
<td>Zn(NO₃)₂·6H₂O</td>
<td>297.48</td>
<td>50 (as Zn)</td>
<td>10 mL stock</td>
</tr>
</tbody>
</table>
Table 7-7. Equipment list

<table>
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<th>Description</th>
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<th>Catalog number</th>
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<tbody>
<tr>
<td>refrigerated centrifuge MP4R</td>
<td>Fisher Scientific</td>
<td>05-006-4</td>
</tr>
<tr>
<td>4-place rotor 4B</td>
<td>Fisher Scientific</td>
<td>05-006-9</td>
</tr>
<tr>
<td>rototorque rotator</td>
<td>Cole Parmer</td>
<td>H-07637-00</td>
</tr>
<tr>
<td>Diode array spectrophotometer</td>
<td>Hewlett-Packard</td>
<td>8452A</td>
</tr>
<tr>
<td>10 mL centrifuge vials</td>
<td>Fisher Scientific</td>
<td>05-529-1A</td>
</tr>
<tr>
<td>repipet II Dispensor PP bottles 15 mL</td>
<td>Fisher Scientific</td>
<td>13-687-62B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>02-923-8G</td>
</tr>
</tbody>
</table>

Zinc Disposal Guidelines

The amount of zinc that can be disposed to the sanitary sewer is limited. The wastewater treatment plant has a limit on the concentration of zinc that can be in the sludge. The Zinc stock solution should not be disposed to the sanitary sewer. Zinc that is sorbed to the sand can be dried and sent to the landfill in the trash.

Setup

1) Use repipet dispensors for contaminating solution, distilled water and possibly for additives.

2) Prepare calibration standards for the AA and for the UV-Vis spectrophotometers.

3) Each group needs 9 centrifuge vials, 20 15-mL bottles, and 2 125-mL bottles.

4) Connect a very fine tube to an air line at each island to be used to help empty the supernatant from the centrifuge vials.

5) Devise technique to filter samples prior to AA analysis!

Class Plan

1) Demonstrate use of AA when samples contain particulate matter. (Keep sipper tube off of the bottom of the vial!)

2) EDTA works well for Zn at 0.1 M

3) Dodecyl sulfate works well for MB at 0.01 M
**Volatile Organic Carbon Contaminated Site Assessment**

**Introduction**

Roughly 75 percent of the major cities in the U.S. depend, at least in part, on groundwater for their water supply. Various estimates of the nationwide extent of groundwater contamination are stated to range from one to over two percent of the nation's usable groundwater (Council on Environmental Quality, 1981). Volatile organic compounds (VOCs) are the most frequently detected organic pollutants of groundwater in the United States. In fact, the VOCs are so ubiquitous that their analysis has been considered by the U.S. Environmental Protection Agency as a screening procedure to establish the need for more extensive characterization of groundwater samples from hazardous waste disposal sites. In the upstate region of New York (excluding Long Island), of approximately 570 groundwater contamination incidents reported by 1985, 98% involved either the volatile components of gasoline and petroleum or solvents and degreasers (NY State DEC, 1985).

Volatile organics may be transported in the subsurface as dissolved components in groundwater. However, by virtue of their volatility, VOCs will also exist in the gas phase of unsaturated porous media. As a result, volatile contaminants can be transported by advection and diffusion in the vapor phase. VOC transport processes are illustrated in Figure 8-1.

---

**Experiment Description**

Students will use soil gas sampling to prospect for a VOC that has leaked from a subsurface source into an unsaturated soil system. A rectangular “soil box” contaminated with a combination of liquid acetone, octane and toluene will be used. A soil with high organic

---

**Figure 8-1.** Subsurface VOC transport processes. The vadose zone is the region of the soil profile in which some pores contain gas and are therefore, unsaturated.
content (potting soil) or low organic content (sand) may be used as the box filling material (porous medium). The VOCs will be identified and measured using a gas chromatograph (GC).

**Experimental Procedures**

**Calibration (Peak Times)**

Each compound will have a unique retention time in the gas chromatograph. The time for each of the 3 VOC peaks can be obtained by injection of 100 µl head space samples from crimp cap sealed vials containing a small volume liquid acetone, octane, and toluene. Use the syringe technique described below. Analyze each compound 4 times (12 samples) using a gas chromatograph (see [http://ceeserver.cee.cornell.edu/mw24/Software/gas_chromatograph.htm](http://ceeserver.cee.cornell.edu/mw24/Software/gas_chromatograph.htm) for information on using the gas chromatograph). These analyses will also serve to “calibrate” the GC by generating the peak area that corresponds to the saturated vapor concentration. Gas chromatogram peak areas may be assumed to be directly proportional to the mass of vapor injected.

**Syringe technique for sampling vial headspace**

The purpose of this syringe technique is to minimize the effects of sorption to the Teflon and glass surfaces in the syringe and to eliminate carryover of sample in the needle. Using separate needles to collect samples and to inject into the GC eliminates needle carryover of sample.

1) Remove GC needle.
2) Purge syringe 5 times with room air to remove any residual VOCs.
3) Put on sample needle.
4) Insert into sample bottle (with syringe at zero volume)
5) Fill syringe fully with gas, wait 4 seconds, and purge syringe contents back into the source bottle (repeat 3 times).
6) Fill syringe and adjust to 100 µL.
7) Close syringe valve and remove syringe from sample vial and remove sample needle.
8) Put on GC needle.
9) Instruct GC to measure sample.
10) Insert needle in injection port, open syringe valve, inject sample, hit start button (or Enter) all as quickly as possible.
11) Remove syringe from the GC injection port.

**Soil Moisture Content**

The dry weight of moist soil may be readily determined by placing ≈ 5 g moist soil into a tarred aluminum weighing pan. Weigh the pan and its contents to obtain the soil’s wet weight, and place the pan into a 105°C oven for ≥ 1 hour. Remove the soil
from the oven and place in a desiccator and allow it 5 minutes to cool. Weigh the cooled soil to obtain the dry weight. The moisture content is

\[
\text{Moisture Content} = \frac{\text{wet weight} - \text{dry weight}}{\text{wet weight}}
\]

**Soil Density**

To determine the approximate density of the soil, \( \rho_{\text{soil}} \), place a weighed quantity of dry soil (\( \approx 30 \) g) into a 100 mL graduated cylinder containing 60 mL water. Record the volume occupied by the water plus the soil.

\[
\rho_{\text{soil}} = \frac{M_{\text{soil}}}{V_{\text{total}} - V_{H_2O}}
\]

where \( \rho_{\text{soil}} = \rho_b/\theta \), \( \rho_b \) = bulk density of the soil and \( \theta \) = fraction of void volume.

**Soil Gas Sampling**

See Table 8-1 for physical properties of the VOCs. See Tables 8-2, 8-3, and 8-4 (in the Lab Prep Notes) for necessary reagents, equipment and GC method. Prior to the laboratory the instructor will create a “spill” of a VOC by injecting 10 mL of liquid of two or more NAPLs into the “soil box” to be sampled by students. During the lab students will analyze approximately 50 soil gas samples from the “soil box” using the syringe technique outlined below. Results from the soil box analyses may be mapped using units of concentration (g/m³).

**Syringe technique for soil gas sampling**

1) Remove GC needle.
2) Purge syringe 10 times with room air to remove any residual VOCs.
3) Put on sample needle.
4) Insert into soil bed (with syringe at zero volume).
5) Fill syringe and adjust to 100 µl.
6) Close syringe valve, remove syringe from soil bed and remove sample needle.
7) Put on GC needle.
8) Instruct GC to measure sample (using software).
9) Insert needle in injection port, open syringe valve, inject sample, hit the enter key (or OK) all as quickly as possible.

10) Remove syringe from the GC injection port.

**Analysis of Soil Gas Sampling**

Students will use their analysis of VOC standards to obtain the corresponding GC retention times and use this information to identify the unknown VOCs in the contaminated soil box. The vapor pressure and ideal gas law are used to estimate the mass of each compound present in the samples used to calibrate the GC.

\[
n = \frac{PV}{RT}
\]

where \( n \) is the number of moles of the compound, \( P \) is the vapor pressure of the compound [kPa], \( V \) is the syringe volume [L], \( R \) is the Gas Constant (8.31 \( [L\cdot kPa]/[mol\cdot K]\)), and \( T \) is the temperature of the gas in the syringe [K]. The relationship between peak area (as measured by the GC) and mass of the compound is determined from the calibration.

Soil gas concentrations should be reported and plotted as contour lines on a map of the soil box (see Figure 8-2 for an illustration).

**Procedure (short version)**

1) Instructor will demonstrate syringe technique (be careful not to pull plunger out of barrel) and Gas Chromatograph technique.

2) Place \( \approx 5 \) g of accurately weighed soil in oven to determine moisture content. (Weigh both the empty dish and the soil + dish.)

3) “Calibrate” GC by analyzing 4 samples for each VOC.

4) Take soil gas samples.

5) Convert the soil gas peak areas to concentrations (g/m³). This data will be shared between groups.

6) Finish soil moisture content measurement (cool dry soil in desiccator and then weigh).

7) Measure soil density using dry soil.

8) Pour waste potting soil into designated waste container.

9) Clean plasticware.


**Prelab Questions**

1) How are the identities of the chromatogram peaks determined when using a gas chromatograph?

2) Explain why different needles are used for sampling from source vials and injecting the sample into the GC. Consider the temperature of the injection port (see Table 8-4) and the fact that these compounds absorb to most surfaces.

**Data Analysis**

1) Calculate the mass of each VOC in 100 µL of headspace.

2) Calculate the concentration of saturated vapor for each compound in g/m³.

3) Plot isoconcentration lines of the identified VOCs (expressed as gas concentration in g/m³) on maps of the contaminated site (see Figure 8-2 for example). Prepare a map for each compound showing isoconcentration lines. (The Excel 3-D surface plot with contour lines can be used. Note that the grid needs to have uniform distance between samples for the Excel 3-D surface plot to work correctly.)

4) Compare the saturated vapor concentration with the peak concentration observed in the “sand box.”

5) Calculate the soil moisture content and density.

**References**


### Lab Prep Notes

#### Setup

1) Prepare 1 soil box under fume hood.

2) Moisten the sand but not so much that there is standing water.

3) Pipette 10 mL of liquid acetone, octane, and toluene in sand box and record injection locations. This should be done in the morning before the lab exercise.

4) Dry approximately 100 g of potting soil for each group that will be used for density determinations.

5) Replace injection port septa on both GC’s.

6) Verify that GC’s are working properly by injecting gas samples from each VOC source bottle. If the baseline is above 30 (as read on the computer display) then heat the oven to 200°C to clean the column.

7) Verify that sufficient gas is in the gas cylinders (hydrogen, air, nitrogen).

8) Prepare VOC source vials that contain liquid acetone, octane, and toluene (they can be shared by two groups of students).

#### Class Plan

1) Setup uniform spreadsheets for data entry

2) Make sure spreadsheet is completely filled out by end of lab

---

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<th>Description</th>
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<td>Fisher Scientific</td>
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<table>
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<td>Rs232c board</td>
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<th>flow</th>
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</thead>
<tbody>
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<td>15 mL/min</td>
</tr>
<tr>
<td>Air</td>
<td>230 kPa</td>
<td>300 mL/min</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>130 kPa</td>
<td>45 mL/min</td>
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</table>

<table>
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<tbody>
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</tr>
<tr>
<td>Injector</td>
<td>250</td>
</tr>
<tr>
<td>FID</td>
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<table>
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<td>Supelco</td>
<td>2-5301</td>
</tr>
<tr>
<td>30 meters</td>
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</table>

Run length of 66 seconds with octane, acetone, and toluene at 0.57, 0.63, 0.96 minutes respectively. Maximum sample volume is about 100 µL. Larger samples can lead to a significant broadening of the peak.

**Syringe clean up**

Disassemble and heat syringes to 45°C overnight to remove residual VOCs. Place syringe barrels upside down on top of openings above fan in oven to facilitate mass transfer.
Volatile Organic Carbon Sorption to Soil

Introduction

Volatile organic carbon compounds (VOCs) can exist as vapors, non-aqueous phase liquids, dissolved in water, or sorbed to surfaces. Sorption is the term used to refer to the binding reactions between organic pollutants and the subsurface medium. Sorption slows the rate of transport of both dissolved and volatile organic pollutants. Laboratory experiments will be performed to evaluate the sorption of acetone, hexane, and octane vapors to a soil and to estimate the extent to which VOC transport is slowed by binding to the soil media.

Theory

Gas-Liquid Partitioning

The equilibrium between gas and solution is described by the following reaction:

\[ C_{\text{Liquid}} \leftrightarrow C_{\text{Gas}} \]  \hspace{1cm} (9.1)

The equilibrium constant \( H_L^G \) for the reaction is given by:

\[ H_L^G = \frac{C_G}{C_L} \]  \hspace{1cm} (9.2)

where \( C_G \) is the concentration in the gas phase (Example units: g/m\(^3\)) and \( C_L \) is the concentration in the aqueous phase (g/m\(^3\)).

Alternately, the liquid-vapor equilibrium is sometimes expressed as:

\[ H = \frac{P_G}{C_L} \]  \hspace{1cm} (9.3)

where \( P_G \) is the partial pressure of the gas (atm), and

\[ H_L^G = \frac{H}{RT} \]  \hspace{1cm} (9.4)

where \( R \) is the universal gas constant \( \left( 8.21 \times 10^{-5} \text{ m}^3 \cdot \text{atm} / \text{mol} \cdot \text{K} \right) \) and \( T \) is the absolute temperature (°K).

Both \( H \) and \( H_L^G \) are referred to as “Henry's law constants” and may be viewed conceptually as distribution coefficients for gases between the aqueous solution phase and the vapor phase. All other factors being equal, VOCs with higher Henry's law constants will have a greater fraction of their total mass in the gas phase of an unsaturated porous medium.
**Liquid-Solid Partitioning**

The sorption of organic pollutants that are dissolved in water onto soils and aquifer materials also may be described in many cases by a distribution coefficient ($K_{L}^{S}$):

$$K_{L}^{S} = \frac{\Gamma}{C_{L}}$$  \hspace{1cm} (9.5)

where $\Gamma$ is the mass of solute sorbed per mass of solid.

Equation (9.5) predicts that the amount of pollutant bound to the soil ($\Gamma$) will increase linearly with the concentration in the aqueous phase ($C_{L}$). Any relationship between the amount bound to the soil and the concentration in solution applies at a constant temperature and is referred to as an “isotherm.” Equation (9.5) is an example of a “linear isotherm.” The success of the linear isotherm in describing sorption of nonionic organic pollutants in saturated soils has been remarkable. Linear isotherms have been found to describe sorption of a wide array of nonionic compounds onto sediments and soils (Karickhoff *et al.* 1979, Chiou *et al.* 1979).

Many investigations have demonstrated that the distribution coefficient ($K_{L}^{S}$) for sorption of a single organic contaminant onto a variety of soil materials can be related to the organic content of the sorbent. This observation permits the definition of an organic normalized partitioning coefficient ($K_{oc}$):

$$K_{oc} = \frac{K_{L}^{S}}{f_{oc}}$$  \hspace{1cm} (9.6)

where $f_{oc}$ is the weight fraction of organic carbon in the soil.

$K_{oc}$ values for a range of different organic compounds have been shown to be related to their octanol-water partitioning coefficients ($K_{ow}$) and also to their aqueous solubilities (Karickhoff, 1984). An important implication of these results is that sorptive distribution coefficients of organic pollutants in water saturated aquifers ($K_{L}^{S}$) may be predicted given knowledge of the organic content of the soil ($f_{oc}$) and the octanol-water partitioning coefficient ($K_{ow}$) of the contaminant or a related parameter such as its aqueous solubility.

**Gas-Solid Partitioning**

Sorption of gases is frequently described using the classic equation developed by Brunauer, Emmett and Teller (1938), i.e., the BET equation:

$$\frac{\Gamma}{\Gamma_{M}} = \frac{B}{\left(\frac{P_{0} - P}{P_{0}}\right)^{1/2} + \frac{B}{P_{0}} + B}$$  \hspace{1cm} (9.7)

where $\Gamma$ is the amount of sorbed gas per unit of surface (with units such as moles/m$^2$ or µg/g if the surface area is not known), $\Gamma_{M}$ is the amount of sorbed gas corresponding to monolayer surface coverage, $P$ is the partial pressure of the sorbed
gas, $P_o$ is its saturated vapor pressure, and $B$ is a parameter related to solute binding intensity; more specifically:

$$B = e^{\frac{\epsilon - \epsilon_v}{kT}}$$

where $\epsilon$ is the energy of the adsorbate vapor-adsorbent surface interaction (cal/mole), $\epsilon_v$ is the vaporization energy of the organic (cal/mole), $k$ is the Boltzmann constant, and $T$ is the absolute temperature (°K).

To the extent that it is valid in soil, the BET equation predicts vapor sorption isotherms to be nonlinear. Nonlinear isotherms have been observed for sorption of organic vapors onto dry soils at high vapor concentrations by several investigators (Chiou, 1990; Rhue, et al., 1988; and Ong and Lion, 1991c). Under conditions of low vapor pressure, $P \ll P_o$, the BET equation reduces to:

$$\frac{\Gamma}{\Gamma_m} = \frac{B}{\left(\frac{P}{P_0}\right) + B}$$

which is the “Langmuir adsorption equation” that applies to monolayer limited adsorption.

The BET equation further reduces to a linear isotherm when $B \ll (P_o/P)$.

$$\frac{\Gamma}{\Gamma_m} = B\left(\frac{P}{P_0}\right)$$

Figure 9-1 illustrates linear, Langmuir and BET isotherms that share a common set of $B$ and $\Gamma_m$ values. Linear sorption isotherms for vapors are a reasonable expectation at low vapor concentrations (Ong and Lion, 1991a).

At higher vapor concentrations, surface site limitations and the phenomenon of vapor condensation at the surface (for which the BET model attempts to account) will result in nonlinear VOC sorption isotherms. Results obtained at Cornell (Ong
et al., 1991; Ong and Lion, 1991c) have confirmed that condensation of organic vapors will occur at high vapor pressures in moist porous media. Condensed water and organic vapors compete for the available pore space. Since soils are generally wet prior to the introduction of organic contaminants, vapor condensation is expected to be limited to the pore volume not occupied by water. The extent to which organic vapor condensation is significant will, therefore, be a function of the soil moisture content, and the relative vapor concentration (P/P₀).

Since the unsaturated zone in an aquifer will typically contain condensed water, description of the sorption of organic vapors in the unsaturated zone must, at a minimum, consider a binary mixture of the organic and water vapor. The organic vapor of concern may accumulate in the unsaturated zone through at least three processes: (a) by direct sorption from the vapor phase, including vapor sorption to dry mineral surfaces (if present), vapor sorption at the gas-water interface, and vapor condensation, (b) by solubilization in condensed pore water as governed by Henry's Law (equation 9.2 or 9.3), and (c) by sorption from condensed pore-water solution onto the soil (as governed by equation 9.5). Since, at very low vapor pressures, a linear isotherm is expected to govern vapor sorption, we may write a linear isotherm in terms of the gas concentration:

\[ \Gamma = K_G^S C_G \]  

9.12

where the magnitude of \( K_G^S \) depends on the sorbent’s moisture content.

The relative contributions to \( \Gamma \) of processes such as vapor dissolution into soil moisture and sorption at the liquid-air interface can be assessed through the use of a mass balance. The total mass of vapor sorbed onto the soil, under equilibrium conditions, can be viewed as being distributed between:

- (Mass sorbed at the solid-liquid interface)
- (Mass dissolved in the liquid phase)
- (Mass sorbed at liquid-air interface + condensation)

\[ \Gamma = \frac{M_s}{X} + C_L V_L + \omega \]  

9.13

where \( M_s \) is the mass of the sorbent (soil or other porous media) and \( \omega \) is a lumped parameter that includes the effects of water surface sorption and condensation.

From equation 9.5 for liquid-phase sorption: \( X = K_L^S M_s C_L \) where \( \Gamma = X/M_s \) and \( M_s \) is the mass of the sorbent. Also, from Henry's Law: \( C_G = H_L^G C_L \). Substituting these two relationships and equation 9.12 into equation 9.13 gives:

\[ K_G^S = \frac{K_L^S}{H_L^G} + \frac{V_L}{M_s H_L^G} + \frac{\omega}{C_G M_s} \]  

9.14

If the density of water on the soil surface is expressed as \( \rho_{H,O} = M_{H,O}/V_L \), the term \( V_L/M_s \) becomes \( \frac{M_{H,O}}{M_s \rho_{H,O}} \). Assuming water surface sorption and condensation are negligible (\( \omega \approx 0 \)), then for high moisture content equation 9.14 will plot as a
straight line, with the ordinate intercept equal to the contribution of aqueous phase sorption to vapor-phase partitioning ($K^S_L / H^G_L$).

$$K^G_S = \frac{K^S_L}{H^G_L} + \frac{\text{Moisture Content } \%}{100H^G_L} \quad 9.15$$

Equation 9.15 indicates that the linear vapor distribution coefficient, $K^S_G$, can be predicted from the saturated distribution coefficient and the Henry’s law constant for a given VOC. Experiments by Ong and Lion (1991a) have shown that such predictions are reasonable as long as the moisture content of the soil is high enough to ensure that the VOC that is dissolved in sorbent-bound water behaves as if the liquid were comparable to the water in a bulk aqueous phase. In general, a moisture content equivalent to an average surface coverage of $\approx 5$ layers of water molecules is adequate for this assumption to be obeyed (Ong and Lion, 1991a). Many soil ambient moisture contents are in excess of this limiting value.

**Pollutant Transport in Porous Media**

The advective dispersion equation is used to describe pollutant movement in porous media. For one-dimensional (ex., horizontal) transport of a conservative ($K^S_L = 0$) pollutant:

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + E \frac{\partial^2 C}{\partial x^2} \quad 9.16$$

where $t$ is time, $x$ is distance, $U$ is the groundwater pore velocity and $E$ is the macroscopic dispersion coefficient (Freeze and Cherry, 1979).

Since volatile organic pollutants react with the surfaces of the porous media through which the contaminant flows, equation 9.16 must be modified to account for the sorption reaction by addition of the term: $-\frac{\rho_b}{\theta} \frac{\partial \Gamma}{\partial t}$ where $\rho_b$ is the bulk density of the porous medium (g/cm$^3$), and $\theta$ is the volumetric moisture content (volume of liquid per unit bulk volume of the porous medium). $\theta$ is equal to the porosity, $\phi$, in a saturated porous medium.

From the chain rule, $\frac{\rho_b}{\theta} \frac{\partial \Gamma}{\partial t} = \frac{\rho_b}{\theta} \frac{\partial \Gamma}{\partial t} \frac{\partial C}{\partial t}$ and for a linear isotherm, $\frac{\partial \Gamma}{\partial C} = K^S_L$. Therefore, the advection-dispersion equation for a compound that experiences sorptive binding to the soil matrix becomes:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} + E \frac{\partial^2 C}{\partial x^2} - \frac{\rho_b}{\theta} K^S_L \frac{\partial C}{\partial t} \quad 9.17$$

$$\frac{\partial C}{\partial t} + \rho_b K^S_L \frac{\partial C}{\partial x} = -u \frac{\partial C}{\partial x} + E \frac{\partial^2 C}{\partial x^2} \quad 9.18$$

The retardation factor, $R$, for a pollutant in soil is defined as:
\[ R = \left(1 + \frac{\rho_b K_L^s}{\theta}\right) \]  

Therefore the advective dispersion equation modified for sorptive binding becomes:

\[
\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} + \frac{E}{R} \frac{\partial^2 C}{\partial x^2} \quad 9.20
\]

From equation 9.20 it is apparent that the velocity and dispersion of a sorbed compound will be reduced by the magnitude of retardation factor, \( R \). So,

\[
R = \frac{\text{pore water velocity}}{\text{contaminant velocity}} \geq 1 \quad 9.21
\]

Note that \( R \) may be determined directly from knowledge of the medium properties (\( \rho_b \) and \( \theta \)) and from the distribution coefficient for sorption (\( K_L^s \) for water saturated media or \( K_G^s \) for a vapor).

Interestingly, equation 9.20 may also be applied to describe vapor movement in a gas chromatograph (GC). GC columns are selected to ensure that the components of a vapor mixture will be separated (by virtue of their different retardation factors) by the time they arrive at the GC detector (situated at the end of the column).

In the absence of pressure gradients, transport of vapors will occur primarily through the process of diffusion and equation 9.20 reduces to:

\[
\frac{\partial C}{\partial t} = \frac{E_s}{E_{bulk}} \frac{\partial^2 C}{\partial x^2} \quad 9.22
\]

where \( E_s \) is the effective diffusion coefficient of the VOC in the porous media.

Vapor diffusion coefficients in unsaturated porous media are different from those in a bulk gas phase because the vapor must follow a tortuous path to move through the open pores. The relationship proposed by Millington and Quirk (1961) is commonly used to correct vapor diffusion coefficients for the conditions in the soil media.

\[
E_s = a^{10/3} \frac{E_{bulk}}{\phi^2} \quad 9.23
\]

where \( E_{bulk} \) is the vapor diffusion coefficient in air, \( a \) is the volumetric air content of the porous medium (volume of gas per unit bulk volume of medium), and \( \phi \) is the porosity (\( a + \theta = \phi \)).

**Analysis of the Unsaturated Distribution Coefficient (\( K_G^s \))**

A mass balance calculation will be used to determine the unsaturated vapor distribution coefficient (\( K_G^s \)). After equilibration the VOC mass will be distributed between the vapor phase and the solid phase (sorbed VOC).
\[ M_{VOC} = C_G V_G + \Gamma M_s \]  
\[ \text{where } \Gamma M_s \text{ is the mass of sorbed VOC and equals } K_G^S M_s C_G \text{ (from equation 9.12).} \]

In control bottles there is no sorbent so the VOC mass must reside entirely in the vapor phase:

\[ M_{VOC_{uc}} = C_{uc} V_{uc} \]

\[ \text{where the subscript uc indicates that volumes and concentrations are those measured in the unsaturated control bottles.} \]

Setting equations 9.24 and 9.25 equal to one another (the mass of VOC was the same for all vials) and rearranging gives:

\[ M_{VOC_{uc}} = C_G V_G + K_G^S M_s C_G \]

Solving for \( K_G^S \)

\[ K_G^S = \frac{M_{VOC_{uc}} - C_G V_G}{M_s C_G} \]

Using the measured soil moisture contents and values of \( K_G^S \), students may check the validity of equation 9.15.

**Unsaturated Mass Fraction Distribution**

The total mass of the VOC is distributed between the gas and sorbed phases (equation 9.24)

\[ 1 = f_G + f_S \]

\[ \text{where } f_G \text{ is the fraction of the VOC mass in the gas phase and } f_S \text{ is the fraction of the VOC mass sorbed to the soil. The relationship between the fraction of VOC in each phase is obtained from the definition of the unsaturated distribution coefficient (equation 9.12)} \]

\[ \frac{f_S}{f_G} = \frac{K_G^S M_s}{V_G} \]

Thus we have two equations in two unknowns. Solving we obtain

\[ f_G = \frac{1}{1 + \frac{K_G^S M_s}{V_G}} \]

\[ f_S = \frac{1}{1 + \frac{V_G}{K_G^S M_s}} \]

where
\[ V_{G} = V_{vial} - \frac{M_{s}}{\rho_{soil}} \quad 9.32 \]

Determination of \( K_{G}^{s} \) requires a measurement of the fraction sorbed given measurements of the total mass added and the mass in the gas phase. This analysis becomes inaccurate as the magnitude of \( f_{s} \) decreases and approaches the coefficient of variation of \( M_{ VOC_{ic}} \).

**Analysis of the Saturated Distribution Coefficient ( \( K_{L}^{s} \))**

A mass balance calculation will be used to determine the saturated vapor distribution coefficient ( \( K_{L}^{s} \)). The calculation assumes that students can reproduce the introduction of the mass of VOC (\( M_{VOC} \)) into each sample bottle. After equilibration the VOC mass can be distributed between the vapor phase the aqueous phase and the solid phase (sorbed VOC).

\[ M_{VOC} = C_{G} V_{G} + C_{L} V_{L} + \Gamma M_{s} \quad 9.33 \]

where \( \Gamma M_{s} \) is the mass of sorbed VOC and equals \( K_{L}^{s} C_{L} M_{s} \) (from equation \( 9.5 \)).

In saturated control bottles there is no sorbent so the VOC mass must just be distributed between the vapor phase and the aqueous phase:

\[ M_{VOC_{sc}} = C_{G_{sc}} V_{G_{sc}} + C_{L_{sc}} V_{L_{sc}} \quad 9.34 \]

where the subscript \( sc \) indicates that volumes and concentrations are those measured in the control bottles. Henry’s law (equation \( 9.2 \)) can be used to eliminate \( C_{L_{w}} \).

\[ M_{VOC_{sc}} = C_{G_{sc}} \left( V_{G_{sc}} + \frac{V_{L_{sc}}}{H_{L}^{G}} \right) \quad 9.35 \]

Equation \( 9.35 \) can be used to obtain an estimate of Henry’s law constant by assuming that the mass of VOC added is the same for the vials with and without water. Solving for \( H_{L}^{G} \) and substituting \( M_{VOC_{ic}} \) for \( M_{VOC_{sc}} \) we obtain:

\[ H_{L}^{G} = \frac{V_{L_{sc}} C_{G_{sc}}}{M_{VOC_{ic}} - V_{G_{sc}} C_{G_{sc}}} \quad 9.36 \]

Equation \( 9.33 \) can now be used to obtain an estimate of \( K_{L}^{s} \). The mass of VOC added to the bottles was the same for all vials. Thus (\( M_{VOC} \)) in equation \( 9.33 \) is equal to \( M_{VOC_{sc}} \). In addition, \( C_{L} \) and \( C_{G} \) are interrelated through Henry’s law (equation \( 9.2 \)). Substituting into equation \( 9.33 \) gives:

\[ M_{VOC_{ic}} = C_{G} V_{G} + \frac{C_{G}}{H_{L}^{G}} V_{L} \cdot M_{s} K_{L}^{s} \frac{C_{G}}{H_{L}^{G}} \quad 9.37 \]

Solving for \( K_{L}^{s} \)
Measured VOC headspace concentrations are substituted into equation 9.38. Values for Henry’s law constants are given in Table 8-1. \( M_{voc_{sc}} \) is obtained from equation 9.35. In vials containing soil, \( V_{G} \) is determined by subtracting both \( V_{L} \) (50 mL) and the volume of the sorbent from the total vial volume. The volume of the sorbent may be calculated from the sorbent weight and density as:

\[
V_{soil} = \frac{M_{s}}{\rho_{soil}}
\]

It is instructive to calculate the phase distribution of each VOC in bottles that contain no soil. The fraction (f) of VOC mass in the gas phase is given by

\[
f = \frac{C_{G}V_{G}}{C_{G}V_{G} + C_{L}V_{L}} = \frac{V_{G}}{V_{G} + \frac{V_{L}}{H_{L}^{G}}}
\]

Assuming the total volume of the bottle is 120 mL and 50 mL of liquid are added, then

\[
f = \frac{70}{70 + 50/\sqrt{H_{L}^{G}}}
\]

f values for octane, acetone, and toluene are therefore 0.994, 0.009, and 0.278 respectively indicating that only toluene has a significant mass fraction in both the gas and aqueous phases. In the absence of strong sorption by soil, octane will reside primarily in the gas phase and acetone will reside primarily in the aqueous phase. Determinations of \( K_{L}^{s} \) for these two compounds may therefore not be feasible using the headspace technique.

**Saturated Mass Fraction Distribution**

The total mass of the VOC is distributed between the gas, sorbed, and liquid phases (equation 9.33)

\[
1 = f_{G} + f_{S} + f_{L}
\]

where \( f_{L} \) is the fraction of the VOC mass in the liquid phase. The relationship between the fractions of VOC in the solid and liquid phases is obtained from the definition of the saturated distribution coefficient (equation 9.5).

\[
f_{S} = \frac{K_{L}^{s}M_{S}}{V_{L}} \quad f_{L}
\]

The relationship between the fractions of VOC in the gas and liquid phases is obtained from the definition of the Henry’s law constant (equation 9.2).
Thus we have three equations in three unknowns. Solving we obtain

\[ f_L = \frac{V_L}{V_L + K_L^S M_S + H_L^G V_G} \]  

\[ f_S = \frac{K_L^S M_S}{V_L + K_L^S M_S + H_L^G V_G} \]  

\[ f_G = \frac{H_L^G V_G}{V_L + K_L^S M_S + H_L^G V_G} \]  

where

\[ V_G = V_{vial} - V_L - \frac{M_S}{\rho_S} \]

Determination of \( K_L^S \) requires a measurement of the fraction sorbed given measurements of the total mass added, the mass in the gas phase, and knowledge of the Henry’s law constant. This analysis becomes inaccurate when \( f_S \) decreases and approaches the coefficient of variation of \( M_{VOC_{SOC}} \).

**Experimental procedures**

VOC distribution coefficients will be determined using crimp top vials sealed with Teflon backed septa and aluminum crimp caps. VOCs will be analyzed by students using a gas chromatograph (GC).

A data table is available in spreadsheet form as “isotherm calculator.”

**Analysis of the Unsaturated Distribution Coefficient (\( K_L^S \))**

The distribution coefficient for three VOCs (acetone, octane, and toluene) with the unsaturated soil medium (\( K_L^S \)) will be determined using the headspace method of Peterson et al. (1988). Students will prepare 120 mL vials (actually 121.5 ± 0.5 mL) in triplicate containing 0 and 20 g of moist soil (6 vials total). The weight of replicates need not be precisely matched, but the weight of soil should be measured accurately. Seal the vials using Teflon-backed septa (the shiny Teflon side faces the vial contents) and aluminum crimp cap.

The 3 VOCs are added to the vials by introduction of 1 mL of the saturated vapor taken from the headspace of “source vials” (crimp capped vials containing liquid octane, toluene, and acetone). Use a dedicated syringe for each VOC and leave dedicated needles in the source bottles.

The vials should be placed on a wrist action shaker to continue agitation for \( \geq 30 \) minutes to permit the VOC time to sorb to the soil medium. After equilibration, vials are removed from the wrist action shaker and the head space sampled using a 500 µL
gas tight syringe. Use the syringe technique as described previously for sampling vial headspace.

**Analysis of the Saturated Distribution Coefficient (\(K^S\))**

The saturated distribution coefficient (\(K^S\)) for three VOCs (acetone, octane, and toluene) with the soil medium will be determined using the headspace method of Garbarini and Lion (1985) as modified by Peterson et al. (1988). These vapors are selected to demonstrate the effect of VOC Henry's law constant on VOC phase distribution (see Table 8-1).

Students will prepare 120 mL vials (actually 121.5 ± 0.5 mL) in triplicate containing 0 and 20 g of potting soil (6 vials total). The weight of replicates need not be precisely matched, but the weight of soil should be measured accurately. Soil density should be separately measured as described below. If moist soil is used students should also determine the dry weight unless the instructor provides this information (see below). Into each vial students will add 50 mL of tap water.

Seal the vials using a Teflon-backed septa (the shiny Teflon side faces the vial contents) and aluminum crimp cap. Octane and toluene are then added to the vials by introduction of 1 mL of the saturated vapor taken from the headspace of “source vials” (crimp capped vials containing liquid octane and toluene). Use different needles for collecting and delivering the VOC to reduce the transfer of VOC on the needles. The needle used to collect the VOC from the source bottle can be left in the source bottle and simply attached to the syringe when needed. Acetone is added by introduction of 200 µl of the liquid compound using a gas tight syringe.

The vials should be placed on a wrist action shaker to continue agitation for ≥ 30 minutes to permit the VOC time to sorb to the soil medium. After equilibration, vials are removed from the wrist action shaker and the head space sampled using a 500 µL gas tight syringe. To sample the vial headspace, use a 100 µL sample and the syringe technique described previously.

**Procedure (short version)**

1. Weigh soil and add to isotherm vials (6 vials with 20 g).
2. Add 50 mL tap water to 6 vials (3 each with 0 and 20 g soil).
3. Seal 12 vials.
4. Add octane, toluene, and acetone to all vials (1 mL gas from source vials for all VOC’s except 200 µL liquid acetone for vials with tap water).
5. Place vials on shaker for 30 minutes.
6. “Calibrate” GC by analyzing 4 100-µL samples for each VOC.
7. Take vials off of shaker.
8. Measure VOC concentrations for each vial and record peak areas in spreadsheet.
9. Reanalyze the VOC concentrations for any vials for which anomalous data was obtained.
10. Remove vial caps.
11) Pour waste potting soil into designated container.
12) Wash vials.

**Prelab Questions**

1) Why does the determination of $K_G^S$ become inaccurate as the magnitude of $f_S$ decreases and approaches the coefficient of variation of $M_{VOC_{ce}}$?
2) What conditions are necessary to obtain linear isotherms for gas/solid partitioning of organic vapors?
3) When can equation 9.15 be used to predict the relationship between liquid/solid partitioning and gas/solid partitioning based on soil moisture content and Henry’s law constant?

**Data Analysis**

**A Note on Units**

Express mass of VOC in grams (as measured by the GC). Express concentrations in g/mL. Remember to account for the fact that the syringe volume for GC analysis is 100 µL Express all volumes in mL.

1) Estimate the mass of each VOC added to the unsaturated sample vials based on $M_{VOC_{ce}}$ (from equation 9.25). Report mean and coefficient of variation (standard deviation/mean) for each VOC.

2) Calculate the unsaturated vapor distribution coefficient ($K_G^S$) using equation 9.27. Report a single mean and coefficient of variation for each VOC.

3) Calculate the mass fraction associated with the soil and gas phases under unsaturated conditions for each of the VOCs. Use equations 9.30, 9.31, and 9.32. Assume $M_s = 20$ g and bottle volume is 121.5 mL. Use the average $K_G^S$ calculated in 2 above. Compare the coefficient of variation of $M_{VOC_{ce}}$ to the mass fractions to evaluate which $K_G^S$ determinations are potentially accurate. Create a stacked bar graph of the mass fractions for each VOC.

4) Estimate the Henry’s law constant ($H_L^G$) for octane and toluene using equation 9.36 (different masses of acetone were used for the saturated and unsaturated vials and thus equation 9.36 can not be used for acetone). Report mean and coefficient of variation. Compare your results to the Henry’s law constants reported in table 8-1 on page 93.

5) Estimate the mass of each VOC added to the saturated sample vials based on $M_{VOC_{ce}}$ (from equation 9.35) using tabulated Henry’s constants (see table 8-1 on page 93). Report mean and coefficient of variation for each VOC.

6) Calculate the saturated vapor distribution coefficient ($K_L^S$) using equation 9.38. Report a single mean and coefficient of variation for each VOC. Use tabulated Henry’s constants reported in table 8-1 on page 93.
7) Calculate the mass fraction associated with the soil, gas, and water phases under saturated conditions using equations \([9.45]-[9.48]\). Assume \(M_s = 20\) g, \(V_L = 50\) mL, and bottle volume is 121.5 mL. Use the average calculated \(K_L^s\) and the Henry’s law constants reported in the table 8-1 on page 93. Compare the coefficient of variation of \(M_{voc}\) to the mass fractions to evaluate which \(K_L^s\) determinations are potentially accurate. Create a stacked bar graph of the mass fractions for each VOC.

8) Calculate \(K_G^s\) for toluene using equation \([9.15]\) and compare with the measured value of \(K_G^s\).

9) Assuming a typical soil porosity (\(\theta\)) of 0.33 and bulk density (\(\rho_b\)) of 1.7 g/cm\(^3\), equation \([9.19]\) may be used to calculate the retardation of dissolved VOCs and VOC vapors. Assuming a pore water velocity of 1 m/day, how long will it take for the dissolved toluene to be transported a distance of 100 m? Include a range of the estimate based on 1 standard deviation.

10) If toluene is removed by withdrawing vapor at a velocity of 100 m/day, how long will it take toluene vapor to travel 100 m? [Note in this case \(K_G^s\) replaces \(K_L^s\) and \(a\) replaces \(\theta\) in equation \([9.19]\). Assume the soil voids are filled with gas so \(a = \theta = 0.33\).] Include a range of the estimate based on 1 standard deviation.

11) Discuss how the results of this experiment would guide you in remediating a site contaminated with toluene, acetone, and, octane.

**References**


**Additional References Relevant to Data Reduction**


## Symbol List

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{LG}^G$</td>
<td>Henry’s Constant</td>
</tr>
<tr>
<td>$K_{LS}^G$</td>
<td>Liquid/solid partitioning coefficient</td>
</tr>
<tr>
<td>$K_{G}^S$</td>
<td>Gas/solid partitioning coefficient</td>
</tr>
<tr>
<td>B</td>
<td>Solute binding intensity</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>E</td>
<td>Dispersion coefficient</td>
</tr>
<tr>
<td>f</td>
<td>Mass fraction</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$K_{oc}$</td>
<td>Liquid/organic carbon partitioning coefficient</td>
</tr>
<tr>
<td>$K_{ow}$</td>
<td>Octanol-water partitioning coefficients</td>
</tr>
<tr>
<td>M</td>
<td>Mass</td>
</tr>
<tr>
<td>P</td>
<td>Partial pressure</td>
</tr>
<tr>
<td>$P_0$</td>
<td>Saturated vapor pressure</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>R</td>
<td>Retardation factor</td>
</tr>
<tr>
<td>T</td>
<td>Absolute Temperature (°K)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>U</td>
<td>Groundwater pore velocity</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>X</td>
<td>Mass sorbed at the solid-liquid interface</td>
</tr>
<tr>
<td>x</td>
<td>Distance</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Mass of solute sorbed per mass of solid</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Vapor-adsorbent surface interaction</td>
</tr>
<tr>
<td>$\varepsilon_v$</td>
<td>Vaporization energy of the organic</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Porosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Volumetric moisture content</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of water</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Mass sorbed at liquid-air interface + condensation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>Bulk</td>
</tr>
<tr>
<td>G</td>
<td>Gas phase</td>
</tr>
<tr>
<td>L</td>
<td>Aqueous phase</td>
</tr>
<tr>
<td>M</td>
<td>Monolayer</td>
</tr>
<tr>
<td>oc</td>
<td>Organic carbon</td>
</tr>
<tr>
<td>S</td>
<td>Soil phase or sorbent</td>
</tr>
<tr>
<td>sc</td>
<td>Saturated control</td>
</tr>
<tr>
<td>uc</td>
<td>Unsaturated control</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic carbon</td>
</tr>
</tbody>
</table>
Lab Prep Notes

For equipment list and gas chromatograph method see page 96.

**Setup**

1) Replace injection port septa on all GC’s.

2) Verify that GC’s are working properly by injecting gas samples from each VOC source bottle. If the baseline is above 30 (as read on the computer display) then heat the oven to 200°C to clean the column.

3) Verify that sufficient gas is in the gas cylinders (hydrogen, air, nitrogen).

4) Verify that sufficient vials/aluminum crimp tops and Teflon seals are available.

5) Prepare VOC source vials that contain liquid acetone, octane, and toluene (they can be shared by two groups of students).

6) Fill repipet dispensers with tap water and place on each lab bench.

<table>
<thead>
<tr>
<th>Table 9-2. Each group of students requires the following syringes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane (gas)</td>
</tr>
<tr>
<td>Toluene (gas)</td>
</tr>
<tr>
<td>Acetone (gas)</td>
</tr>
<tr>
<td>Acetone (liquid)</td>
</tr>
<tr>
<td>Source vial (gas)</td>
</tr>
<tr>
<td>Isotherm (gas)</td>
</tr>
</tbody>
</table>

**Syringe clean up**

Disassemble and heat syringes to 45°C overnight to remove residual VOCs. Place syringe barrels upside down on top of openings above fan in oven to facilitate mass transfer.

<table>
<thead>
<tr>
<th>Table 9-1. Reagents list</th>
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</thead>
<tbody>
<tr>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>Octane</td>
</tr>
<tr>
<td>Acetone</td>
</tr>
<tr>
<td>Toluene</td>
</tr>
<tr>
<td>Potting soil</td>
</tr>
</tbody>
</table>