

Reading the River

Lesson Plans:

The Water and Freshwater Fish

By: Lynne A.H. Poston

Sixth Grade Science

Summer 2003

Northern Kentucky University

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Lesson Plan: Determining the properties of Water for Freshwater Fish

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For: Dr. Yvonne Meichtry BIO 694 Summer 2003

Objective: To develop an understanding of the properties of water, monitoring of water and apply it to the life needs of a fish.

Divisions of Lesson

Part One-Properties of Water

Part Two-Freshwater Fish requirements

Final Project-Apply and assess properties of Water to Fish life in Water Sources.

Grade Level: 6th grade Science-

Subject: Life Science / Biology / Streams

Classtime: Total: 5 class periods (50 minutes each)

Learner Outcomes:

Students should be able to:

Accurately test the pH of sampled water from specified sites and/or other water samples.

Accurately determine the temperature of the stream at the specified sites.

Accurately test the dissolved oxygen content of the water sampled from specified sites.

Use the results from pH, temperature, hardness, and dissolved oxygen content to predict whether or not humans have impacted the stream.

Apply this knowledge to the needs of freshwater fish living requirements

Generalize this information when given a scenario that is similar

Throughout this lesson there will be suggestions for Project WET lessons.

There are suggestions of resources to use outside the classroom. Please feel free to contact me at lposton@fuse.net for assistance in obtaining these sources.*

Teacher Inquiry for Water Sampling:

Selection of water sample is important. The items need to be accurately compared. The sample of drinking water, pond, stream and lake plus the control water sample should be specific as to knowledge of location and content.

For an accurate comparison, it is preferable to choose a site that will have a non-impacted water area (control) versus an impacted water area, preferably on the same stream or tributary. Samples upstream from human impact (town, sewage treatment plant, golf course, etc.) are considered non-impacted. This site could be referred to as a control concerning water quality of this stream. Downstream samples are considered impacted. Upstream samples will be compared to downstream samples. This comparison will help determine the effect of human practices on stream life as measured by the pH, temperature, and dissolved oxygen content of the stream under investigation.

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Logistics may not allow students to participate in the collection process. Water samples can be collected by the teacher, and then divided up among multiple classes for hardness and pH determination. Temperature and dissolved oxygen content must be determined in the field to be valid.

**If you cannot find a stream that meets the above criteria, then pick two comparable water sources-- one impacted and one non-impacted.*

Schedule of Lessons:

Lesson 1		Lesson 2	Lesson 3	Lesson 4	Lesson 5
A. KWL B. What is water? C. The Problem D. Developing the hypothesis		A. What tests will we be doing? Vocabulary B. Equipment for Testing. C. What is a scientific method of testing? D. Safety /Handling.	A. What does it take to raise a healthy fish? B. Testing of all water samples C. Collection of the data. D. Starting to analyze data.	A. Finish Analyzing the Data B. Support of hypothesis C Human Impact	A. Finalize conclusion & assessment B ,Generalize data
Activities	Water Molecule	Setting up your lab manual	Testing	Enviro-scape	Assessment

*Schedule use of local Enviro-scape

Opening: Collect information about what the children know about water. (KWL)

Socratic Suggested Questions:

- What do you use water for?
- Does anyone have a pool or have swam in a pool?
- Why does the water need tested for the pool?
- What happens to your eyes if the chlorine level is high?
- What happens to your skin, hair etc... if you don't wash off?
- Who has ever swam in a lake, river, pond, or stream?
- What does the water smell like? What does the water taste like?
- What lives in the river, lake, stream or pond?
- Why would happen if fish were put into a pool to their eyes, skin, and food source?
- What is the difference between a pool, drinking water, and a river/stream/pond/lake?

The Beginning-Scientific Investigation:

What is a Scientific Investigation? *It is the testing and questioning to find out if a situation is going to be suitable.*

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Today we are going to turn into investigators for finding fish homes. We are going to test different types of environments that will help a fish to prosper.

We are now going to develop a hypothesis to determine what the outcome of this investigation will be. This is the start of our scientific method.

- *Define hypothesis in your lab book**
- *Determine what your hypothesis should be for this investigation to find a water home for fish.*

These class lessons can be improvised for inside as well as outside with proper planning

Our first mystery is: **What is water? & What is in the Water?**

Activity 1

Determining the contents of Water- H₂O two hydrogen atoms and one oxygen.

This will be determined by explaining the properties of hydrogen and oxygen. We will then discuss balancing. Then everyone will be given a ball (blue representing hydrogen and red representing oxygen) Telling them they will have to make their own water. The students will become a droplet of water. Then the class will all come together as a glass of water or puddle. (Another WET activity takes a water droplet through the water cycle for an extension-Incredible Journey) It will take two hydrogen atoms and one oxygen atom. This will enable children to understand becoming something out of two components. The students will then be asked what is water made up of in their notebooks. **This will help to select their groups for later group work.

Part One-The Water

Objective: Students will determine the tests for water to determine the quality.

Mystery 1: The Start of Investigation-The testing.

What is dissolved oxygen, pH, water hardness, temperature, and a scientific control?

- Define each term and enter it into their Science Lab Journal- (I would recommend working the children to use the KWL to determine the definition of these items. Ex: What does a fish need to survive-, food water shelter, and air; is it a plant or animal? What type of gas does it breathe in? How does it get to be dissolved oxygen? We know what Oxygen is O₂, now lets figure out what dissolved is. Then let them come to the conclusion of what dissolved oxygen is used for in water). The definitions are at the end of this lesson for your use but I suggest you use the definitions that the students come up with that are comparable

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*The control will be actual stream water with plant life, fish life and correct pH (this could possibly be an aquarium). The water will support fish life.

The students will test different types of water for: Measuring the pH, Temperature, and Dissolved Oxygen and Water Hardness content in a Stream

Follow directions completely in the testing kits*

Objective: Students will be able to identify the uses of material for testing.

The children should know why each of the following items are used:

➤ *List the following items in your science lab books:*

Materials/Technology:

metric thermometer
ruler or straight edge to help interpret pH range table
pH paper
pH test kit
dissolved oxygen test kit
journal and information sheet
Microscopes and slides if available
river/lake/stream or pond access
drinking water access
pool water access

** If the water source is a sample (not directly at the site) and the children are not gathering it directly make sure that you take the water readings directly when taking the specimens. Discuss with the students the changes of "fresh" water and water that has set awhile.*

Objective: The students will be able to understand the need to dispose of tested water properly.

Safety, Handling, Disposal of Water Samples after testing:

All water samples should be disposed of as directed on test kit instructions.
Safety near the water is essential. Review water safety techniques before entering the field. It is suggested that a stout rope and/or personal flotation devices be readily at hand
Do not risk children at any level; determine capabilities of stream prior to arrival.
(particularly if rain has happened in the past 48 hours)

Extension: The use of a water contamination unit to show how pollution infiltrates a water source. This unit shows a cross section of contaminated water and how it moves through the soil into the groundwater system. It is done with food coloring.

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Objective: *The student will develop a sense of multiple testing and the needs to re-test a hypothesis*

The water sites are collected from and each group of children is given water samples to test. Make sure that each group is duplicating the test of another groups. Each group should do at least 3 tests. The average of those three tests should be recorded for accuracy and data collection. This table will assist you in developing teams for testing each sample three times. (T=Teacher)

<i>Stream</i>	<i>Stream</i>	<i>Lake</i>	<i>Lake</i>	<i>Pool</i>	<i>Pool</i>	<i>Drinking</i>	<i>Drinking</i>	<i>Control</i>	<i>Control</i>
1	2	3	4	5	6	7	8	9	10
10	9	8	7	6	5	4	3	2	1
9	8	7	6	5	4	3	2	1	T

Objective: *The students will be able to conduct water testing on the water samples provided.*

The students will now divide into their teams of three to conduct water testing on the samples provided.

Procedure:

*Note: This may take two class periods.

1. Measure the following:
 - a. water temperature
 - b. pH (test kit and pH paper)
 - c. dissolved oxygen
 - d. water hardness
2. Record this information on your Worksheet.
3. Students compare data collected to the pH, temperature, water hardness and dissolved oxygen content indicators listed on the pH Data Table.
4. Students write a conclusion based on the interpretation of the collected data.

Analytical Skills-The data results will be recorded in their science lab reports. Discussion should include accuracy, human error, and other factors. If a figure is exceptionally diverse then the class should make a decision to re-test, throw out, or include. Every student's opinion should be accounted for during this decision-making process.

Objective: *The student will be able to identify the needs of a freshwater fish.*

Mystery #2

- What changes the affects of good quality water for freshwater fish?
- What are their requirements?

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- What types of fish have you ever fished for?
 - What type of environment does these fish need to survive?

Appendix 1 will be your resource to provide the students with the exact information. *The guidelines are in the Peterson's Freshwater Fish Booklet or Kentucky Afields fish guide and Aquarium guides. Allow at least two children to look up the requirements of those fish and the exact name. If there are any discrepancies in these documents consider analyzing which one is more credible of a source. *Requirements provided on worksheet.*

Objective: *The students will recognize that their own existence influences the water quality of our community.*

Mystery #3

Does the use of certain human practices (such as fertilizers, pesticides, irrigation runoff, town runoff, sewage disposal, waste treatment, etc.) have any noticeable affects on the quality of stream/tributary/river/lake life of freshwater fish? We will be using the statistics gathered by the pH, temperature, hardness and dissolved oxygen content of the stream under investigation?

Activity 4

*The Enviro-scape model would be very useful.

Incorporate "Sum of the Parts" from Project WET into this lesson. This could also be done prior to the entire lesson. *The part where the child develops their piece of property* could be handled before this part of the lesson. The part that incorporates the waste that we produce in our property and it makes its way to the river is to be done at this point.

- **The student will analyze their hypothesis. Was this scientific investigation a success or failure and why or why not?**

Results/Analysis:

Conclusions: From the data recorded, and information located on the pH Data Table, determine what type of organisms could exist at the particular pH, temperature, and dissolved oxygen content values. Be sure to compare the upstream site to the downstream site and the different type of samples.

Assessment

1. Give the pH values above and below the impact site and a possible reason for any difference there might be.

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2. Give the temperature values above and below the impact site and a possible reason for any difference measured.
3. Give the dissolved oxygen content values above and below the impact site and a possible reason for any difference, if one was measured.
4. What type of human activity affects the site under investigation?
5. Based on the data collected, is this activity negatively affecting the stream? Explain.

Final Assessment

Open Response Question- You have to make a choice between a piece of property with a portion of the Ohio River bordering for approximately 10 miles and another property with a pond. You will be given \$10,000 a year in a trust fund if the property will have a population of carp, catfish, bluegill and mussels. The property needs to be able to sustain this type of fish on a monthly and yearly basis. You will have to present the results on a yearly basis. Using your recent Scientific Investigation results what would you do to prove each year that the properties are capable to have carp, catfish, and bluegill. How would you prove that this water is able to sustain the freshwater fish mentioned above? Could you be sure that you would receive your \$10,000 a year trust and why or why not?

Answer: Four points should include the following: The student should include information about specific pH of the species, the range of dissolved oxygen, water temperature, and water hardness. The answer should include the guidelines of the water watch system. Each week the river should be tested for data. Although the information has not hit on energy needs of freshwater fish, food should be mentioned.

Extensions:

Students may wish to perform these tests over an extended period of time to make sure the data is a true reflection of the conditions normally found in the stream. Students may wish to perform these tests on several different streams and compare the conditions found in each over an extended amount of time. Students may compare types of organisms collected from different stream sites and the pH, temperature, and dissolved oxygen content at those particular sites. Coliform tests are very important.

Kentucky's Core Content

SC-M-2.1.1 Water, which covers the majority of the Earth's surface, circulates through the crust, oceans, and atmosphere in what is known as the water cycle. Water dissolves minerals and gases and may carry them to the oceans.

SC-M-3.1.1 Living systems at all levels of organization demonstrate the complementary nature of structure and function. Important levels of organization for structure and

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function include cells, tissues, organs, organ systems, organisms (e.g., bacteria, protists, fungi, plants, animals), and ecosystems.

- SC-M-3.2.1** All organisms must be able to obtain and use resources, grow, reproduce, and maintain stable internal conditions while living in a constantly changing external environment.
- SC-M-3.2.2** Regulation of an organism's internal environment involves sensing the internal environment and changing physiological activities to keep conditions within the range required to survive. Maintaining a stable internal environment is essential for an organism's survival.
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Program of Studies for 6th Grade Science

S-6-SI-1-Students will identify and refine questions that can be answered through scientific investigations combined with scientific information.

S-6-SI-2-Students will use appropriate equipment (e.g., binoculars), tools (e.g., beakers), techniques (e.g. ordering), technology (e.g., calculators), and mathematics in scientific investigations.

S-6-SI-3-Students will use evidence (e.g., orderings, organizations), logic, and scientific knowledge to develop scientific explanations.

S-6-SI-4-Students will design and conduct different kinds of scientific investigations to answer different kinds of questions.

S-6-SI-5-Students will communicate (e.g., speak, write) designs, procedures, and results of scientific investigations.

S-6-SI-6-Students will review and analyze scientific investigations and explanations of other students.

S-6-ESS-4-Students will identify phenomena (e.g., growth of plants, winds, water cycle, ocean currents) on the Earth caused by the Sun's energy.

Life Science/Regulation and Behavior

S-6-LS-1-Students will investigate how organisms obtain and use resources, grow, reproduce, and maintain stable internal conditions. Examine the regulation of an organism's internal environment.

S-6-AC-2-Students will recognize how science is used to understand changes in populations, issues related to resources, and changes in environments.

Vocabulary*

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Scientific Investigation/Method-The basic steps of discovery are: Stating the problem, Gathering information on the problem, forming a hypothesis, performing experiments to test the hypothesis, recording and analyzing data, stating a conclusion, repeating the testing.

Hypothesis-A proposed solution to a scientific problem.

Dissolved oxygen content

The concentration of oxygen dissolved in water, expressed in mg/l or as percent saturation, where saturation is the maximum amount of oxygen that can theoretically be dissolved in water at a given altitude and temperature.

Part per million (ppm)

A measure of proportion by weight which is equivalent to one unit weight of solute (dissolved substance) per million unit weights of the solution. Since one liter of water weighs one million milligrams, one ppm is equal to one milligram per liter (mg/L). Ppm is the preferred unit of measure in water or wastewater analysis.

pH-potential Hydrogen (abr. pH)

A measure of acidity or alkalinity. A pH of 7 is neutral, less than 7 acidic and greater than 7 alkaline. Most organisms prefer a certain range of pH. Precisely, a logarithmic measure of the concentration of hydrogen ions expressed as $-\log_{10}([H^+])$.

Temperature

A physical property that indicates whether one object can transfer thermal energy to another object. In general, the intensity of heat as measured on some definite temperature scale by means of any of various types of thermometers. A measure of molecular kinetic energy.

Scientific Control-This is the part of the experiment that all of the variables are known. All factors, except for the independent variable, are held constant, and the effects of the independent variable on the dependent variable are observed. In this experiment, we know that the control supports fish life.

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Bibliography of Lesson

References/Resources:

Kentucky Department of Education Website for POS and CC, www.kde.org

Lamotte Company Test Kits: <http://www.Lamotte.com>

Matson, A. and Hopkins, J. (1994) The Nature of Science, Englewood, New Jersey

Project WET website

<http://www.projectwet.org/>

pH Worksheet Contributing Teacher: William T. Joern

<http://www.scienceteacher.org/k12resources/lessons/lesson14/wk14a.htm>

University of Pittsburg at Bradford, Science in Motion, "Investigating Source Water, Hach Analysis", 2002, <http://www.upd.pitt.edu/scienceinmotion>

Results/Analysis Worksheet

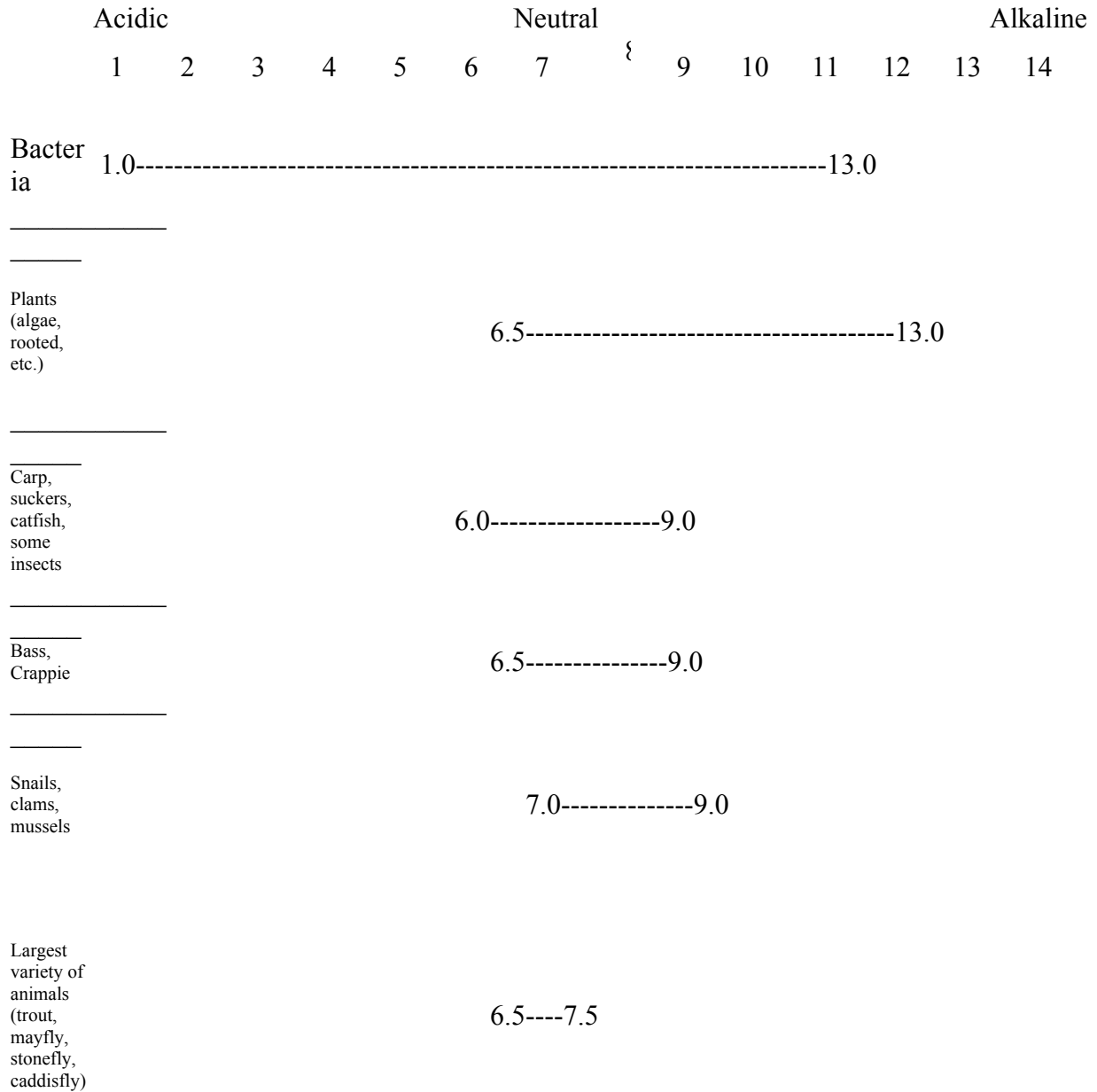
Name:	
Date:	
Site/Type	Site/Type
Temperature:	Temperature:
PH:	pH:
Dissolved Oxygen:	Dissolved Oxygen:

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pH Ranges that Support Aquatic Life



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Temperature Ranges (approximate) Required for Various Organisms	
Greater than 68 Degrees F (20 Degrees C)	Much plant life, most Bass, Bluegill, Carp, Catfish, and some Caddisfly.
55 Degrees F to 68 Degrees F (12.8 Degrees to 20 Degrees C)	Some plant life, Salmon, Trout, Stonefly, Mayfly, Caddis, Water Beetles.
Less than 55 Degrees F (12.8 Degrees C)	Trout, Caddisfly, Stonefly, Mayfly

Dissolved Oxygen Requirement for Aquatic Life in parts per million (ppm)

Below 68 Degrees F (20 Degrees C)

Cold water organisms, including Bass, Salmon, and Trout.

6 ppm-----5 ppm

Notes/Conclusions-If needed use back of page.

Above 68
Degrees F (20
Degrees C)
Warm water
organisms
including
Catfish and
Carp.

Appendix 1

Investing Source Water: HACH Analysis

Introduction:

The quality of our nation's water supply has become an ever increasing concern over the past several years due to drought, flooding, and pollution. Monitoring of water systems by state departments, with the assistance of volunteers throughout the country, is occurring on a daily basis. This monitoring can take several forms and many different parameters can be measured. One type of monitoring is **biological measurements**, which is the surveying of the different types of aquatic plant and animal life, their abundance, and their ability to survive in the sample water (see biology lab "Stream in a Bucket"). Another type of monitoring is uses **chemical measurements**.

When monitoring with chemical measurement, a variety of different parameters can be measured. These include, but are not limited to, pH, alkalinity, chloride, sulfate, ammonia, total

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dissolved solids (or turbidity), hardness, phosphorus, nitrogen, fluoride, calcium, magnesium, and iron. Physical measurements are often included in this area such as temperature, flow, water color, and the condition of stream banks and lake shores.

There are five major reasons for determining water quality: 1) characterize waters and identify changes or trends in water quality over time; 2) identify specific existing or emerging water quality problems; 3) gather information to design specific pollution prevention or remediation programs; 4) determine whether program goals -- such as compliance with pollution regulations or implementation of effective pollution control actions -- are being met; and 5) respond to emergencies, such as spills and floods.

This Lab:

In this lab, you and your classmates will be using chemical monitoring methods to investigate water quality and sources. The goal is to be able to identify the water source: garden runoff, stream or pond, or pool. The parameters being measured will be: pH, alkalinity, chloride, sulfate, ammonia, total dissolved solids (or turbidity), hardness, phosphorus, nitrogen, and temperature.

The tests being used in this lab were developed by HACH and are of the “wet chemistry” method involving observations of some type of chemical reaction. The simplest HACH kits usually involve reacting certain chemicals with water. This chemical reacts with a specific ion or substance in the water to produce a colored complex. The darker the color the more concentrated the target material is in the water sample. The concentration can be read to the part per million (ppm) level using a “color comparator.” This device involves the use of a colored standard which is matched against the sample to find the concentration of the substance of interest. These kits are available for nitrates, iron, phosphate, and sulfate, among other substances.

Since there will not be enough time for each group to perform all the tests on all the water samples, the class will be divided into 3 large groups and then further subdivided into 6 smaller groups. Each large group will be given a water sample to test while each subgroup will be given particular parameters to test for. Class data will then be compiled and discussed.

Investigating Source Water Information

pH:

The acidity or basic nature of a solution is expressed as the pH. The concentration of the hydrogen ion [H⁺] in a solution determines the pH.

Environmental Impact: A *pH range of 6.0 to 9.0* appears to provide protection for the life of freshwater fish and bottom dwelling invertebrates.

Table III below gives some special effects of pH on fish and aquatic life.

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Table III

Limiting pH Values		
Minimum	Maximum	Effects
3.8	10.0	Fish eggs could be hatched, but deformed young were often produced
4.0	10.1	Limits for the most resistant fish species
4.1	9.5	Range tolerated by trout
4.3	---	Carp died in five days
4.5	9.0	Trout eggs and larvae develop normally
4.6	9.5	Limits for perch
5.0	---	Limits for stickleback fish
5.0	9.0	Tolerable range for most fish
---	8.7	Upper limit for good fishing waters
5.4	11.4	Fish avoided waters beyond these limits
6.0	7.2	Optimum (best) range for fish eggs
1.0	---	Mosquito larvae were destroyed at this pH value
3.3	4.7	Mosquito larvae lived within this range
7.5	8.4	Best range for the growth of algae

Alkalinity:

Alkalinity refers to the capability of water to neutralize acid. It essentially protects the water body from fluctuations in pH.

Environmental Impact: Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0. Alkalinity is a measure of how much acid can be added to a liquid without causing a large change in pH. Higher alkalinity levels in surface waters will buffer acid rain and other acid wastes and prevent pH changes that are harmful to aquatic life. See Table III in the discussion on pH.

Chloride:

Chlorides are salts (ex. NaCl and MgCl₂) resulting from the combination of the gas chlorine with a metal. Chlorine in combination with a metal, such as sodium, becomes essential for life. Small amounts of chlorides are required for normal cell functions in plant and animal life.

Environmental Impact: Chlorides are not usually harmful to people. Chlorides may get into surface water from several sources including: 1) rocks containing chlorides; 2) agricultural runoff; 3) wastewater from industries; 4) oil well wastes; 5) effluent wastewater from wastewater treatment plants, and; 6) road salting. Chlorides can corrode metals and affect the taste of food products. *Chlorides can contaminate fresh water streams and lakes. Fish and aquatic communities cannot survive in high levels of chlorides.* Table VI below shows the effects of chlorides on fish:

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Table VI

Chloride Above These Levels Can Be Toxic		
mg/L (PPM)		
Short Exposure	Long Term Exposure	Species
2,540	400	Snail
6,570	430	Fathead minnow
6,740	900	Rainbow trout
8,000	800	Channel catfish
8,390	850	Carp

Sulfate:

Sulfates (SO_4^{--}) can be naturally occurring (ex. breakdown of leaves in water) or the result of municipal or industrial discharges (ex. sewage treatment). Runoff from fertilized agricultural lands also contributes sulfates to water bodies.

Environmental Impact: Sulfur is an essential plant nutrient. Aquatic organisms utilize sulfur and reduced concentrations have a detrimental effect on algal growth. The most common form of sulfur in well-oxygenated waters is sulfate. *When sulfate is less than 0.5 mg/L, algal growth will not occur.* On the other hand, *sulfate salts can be major contaminants in natural waters.*

Sulfides, especially hydrogen sulfide (H_2S), are quite soluble in water and are toxic to both humans and fish. They are produced under conditions where there is a lack of oxygen (anaerobic). Because of their foul "rotten egg" smell they are avoided by both fish and humans. Sulfides formed as a result of acid mine runoff from coal or other mineral extraction and from industrial sources may be oxidized to form sulfates, which are less toxic. Sulfates are not considered toxic to plants or animals at normal concentrations. At very high concentrations sulfates are toxic to cattle. Problems caused by sulfates are most often related to their ability to form strong acids which changes the pH. Sulfates in water to be used for certain industrial processes such as sugar production and concrete manufacturing must be reduced below 20 mg/L.

Ammonia:

Ammonia (NH_3^+) is a colorless gas with a strong pungent odor that form a weak base when it reacts with water.

Environmental Impact: About three-fourths of the ammonia produced in the United States is used in fertilizers either as the compound itself or as ammonium salts such as sulfate and nitrate. "Household ammonia" is an aqueous solution of ammonia. It is used to remove carbonate from hard water. NH_3 is the principal form of toxic ammonia. *It has been reported toxic to fresh water organisms at concentrations ranging from 0.53 to 22.8 mg/L.* Plants are more tolerant of ammonia than animals, and invertebrates are more tolerant than fish. Hatching and growth rates of fishes may be affected. In the structural development, changes in tissues of gills, liver, and kidneys may also occur. Toxic concentrations of ammonia in humans may cause loss of

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equilibrium, convulsions, coma, and death. *The un-ionized form of ammonia (NH₃) should not exceed 0.05 mg/L in order to protect aquatic organisms.*

Total Dissolved Solids:

Environmental Impact: Suspended solids can clog fish gills, either killing them or reducing their growth rate; reduce light penetration; reduces the ability of algae to produce food and oxygen; and indirectly affect other parameters such as temperature and dissolved oxygen. When the water slows down the suspended sediment settles out and drops to the bottom, a process called *siltation*. This causes the water to clear, but as the silt or sediment settles it may change the bottom. The silt may smother bottom-dwelling organisms, cover breeding areas, and smother eggs. Siltation eventually may close up channels or fill up the water body converting it into a wetland.

Hardness and water quality:

Hardness is due to the presence of multivalent metal ions which come from minerals dissolved in the water. Hardness is based on the ability of these ions to react with soap to form a precipitate or soap scum.

Table V
Classification of Water by Hardness Content

Concentration mg/L CaCO ₃	Description
0 - 75	soft
75 - 150	moderately hard
150 - 300	hard
300 and up	very hard

Environmental Impact: The most important impact of hardness on fish and other aquatic life appears to be the affect the presence of these ions has on the other more toxic metals such as lead, cadmium, chromium and zinc. Generally, the harder the water, the lower the toxicity of other metals to aquatic life. Large amounts of hardness are undesirable mostly for economic or aesthetic reasons.

Phosphorus*:

Phosphorus is one of the key elements necessary for growth of plants and animals.

Environmental Impact: Rainfall can cause varying amounts of phosphates to wash from farm soils into nearby waterways. Phosphate will stimulate the growth of plankton and aquatic plants which provide food for fish. This may cause an increase in the fish population and improve the overall water quality. However, if an excess of phosphate enters the waterway, algae and aquatic plants will grow wildly, choke up the waterway and use up large amounts of oxygen.

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Nitrogen*:

Nitrogen is found in the cells of all living things and is a major component of proteins.

Environmental Impact: Nitrogen-containing compounds act as nutrients in streams, rivers, and reservoirs. Excessive concentrations of nitrites can produce a serious condition in fish called "brown blood disease." Nitrites also can react directly with hemoglobin in the blood of humans and other warm-blooded animals to produce methemoglobin, which destroys the ability of red blood cells to transport oxygen. High nitrates in drinking water can cause digestive disturbances in people. *Nitrite/nitrogen levels below 90 mg/L and nitrate levels below 0.5 mg/L seem to have no affect on warm water fish. Nitrates/nitrites should remain below 10 mg/L in water to be used as a domestic water supply.*

***Both Phosphorus and Nitrogen can lead to a condition known as *eutrophication* or over-fertilization of receiving waters. Algal and plankton growth is accelerated which initially provides food for higher organisms but uses up large amounts of oxygen. When the excessive plant/animal life dies it uses up even more oxygen in the decaying process which in turn causes the death of aquatic life because of the lowering of dissolved oxygen levels.**

Source of information:

State of Kentucky's water quality testing project

<http://water.nr.state.ky.us/ww/ramp>

Background Information for Watershed Watch Parameters

This document provides information to put water quality measurements into perspective. Sections for each parameter include a general explanation of its importance and possible sources of problems (Summary), a listing of levels that indicate problems or exceed established standards (Limits), an overview of methods used in its measurement (Methodology), and discussion of its impact on human health and ecology (Environmental Impact).

Parameters are listed alphabetically within the following groups: Conventional Parameters, Fecal Bacteria, Nutrient Parameters, Metals and Mineral, and Pesticides and Herbicides. Choose a bookmark below to view individual text entries.

The water quality standards table summarizes limits and averages.

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For: Dr. Yvonne Meichtry BIO 694 Summer 2003

Text was compiled from the River Assessment Monitoring Project (RAMP) site of Kentucky Water Watch (Bill Davis et al.; <http://water.nr.state.ky.us/ww/ramp/>), Kentucky Water Watch's Water Resource Monitoring (WRM) site (<http://water.nr.state.ky.us/ww/waterres.htm>), Pesticide Information Profiles in the Extension Toxicology Network (EXTOXNET) web-accessible database (<http://ace.orst.edu/info/extoxnet/>), and Water-Quality Assessment of the Kentucky River Basin, Kentucky: Distribution of Metals and Other Trace Elements in Sediment and Water, 1987-90 (USGS Water-Resources Investigations Report 94-4134). Notations in brackets (RAMP, WRM, EXTOXNET, and USGS) indicate text sections or paragraphs extracted from each source.

Conventional Parameters

pH Value Buffering (Alkalinity)

Temperature Hardness

Dissolved Oxygen Chloride

Conductivity

Total Organic Carbon

Total Suspended Solids

Fecal Bacteria

Fecal Coliform Bacteria

Fecal Streptococci

Nutrient Parameters

Ammonia Phosphorus, Total

Nitrates and nitrites Sulfate

Metals and Mineral Parameters: metals in general

Aluminum Calcium Lead Selenium Thallium

Antimony Chromium Lithium Silicon Vanadium

Barium Cobalt Magnesium Sodium Zinc

Beryllium Copper Manganese Strontium

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Boron Iron Potassium Sulfur

Pesticides and Herbicides

2,4-Dichlorophenoxy(Acetic Acid)

Chlorpyrifos Triazines (Atrazine)

CONVENTIONAL PARAMETERS

pH Value

Abbreviation: ----- Units: pH units (from 0 to 7)

Summary

The acidity or basic nature of a solution is expressed as the pH. The concentration of the hydrogen ion [H⁺] in a solution determines the pH. Mathematically this is expressed as:

$$\text{pH} = -\log [\text{H}^+]$$

The pH value is the negative logarithm (base 10) of the hydrogen ion concentration. A pH of 7 is neutral. The more acidic the solution, the lower the pH; the more basic, the higher the pH. Each change in pH unit represents a tenfold change in acidity. For example, a solution at pH 3 is ten times more acidic than one at pH 4.

The pH of a water body results from the ratio of H⁺ to OH⁻ ions. In natural waters this usually is dependent on the carbonic acid equilibrium. When carbon dioxide from the air enters freshwater, small amounts of carbonic acid are formed which then dissociate into hydrogen ions and bicarbonate ions.

This increase in H⁺ ions makes the water more acidic and lowers the pH. If CO₂ is removed (as in photosynthesis) the reverse takes place and pH rises. This process is also related to the presence of carbonates, of calcium or other ions such as magnesium as discussed under alkalinity. [RAMP]

Limits

For aquatic life the pH should be between 6.0 and 9.0 pH units. [RAMP]

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Methodology

In the laboratory, pH is an electrometric measurement. The computer aided titrimer (CAT) is used to determine the pH value. This value is determined at a particular millivolt reading on the instrument. By using indicators that change color, pH values may also be determined. Phenolphthalein is an end-point indicator used in titration procedures, while litmus is commonly used in paper-coded pH measurements. In the field, a simple colorimetric method will be employed unless an electronic field pH meter is available.

[RAMP]

Environmental Impact

A pH range of 6.0 to 9.0 appears to provide protection for the life of freshwater fish and bottom dwelling invertebrates.

The table below gives some special effects of pH on fish and aquatic life.

Limiting pH Values

Minimum Maximum Effects

3.8 10.0 Fish eggs could hatch, but deformed young were often produced

4.0 10.1 Limits for the most resistant fish species

4.1 9.5 Range tolerated by trout

4.3 --- Carp died in five days

4.5 9.0 Trout eggs and larvae develop normally

4.6 9.5 Limits for perch

5.0 --- Limits for stickleback fish

5.0 9.0 Tolerable range for most fish

--- 8.7 Upper limit for good fishing waters

5.4 11.4 Fish avoided waters beyond these limits

6.0 7.2 Optimum (best) range for fish eggs

1.0 --- Mosquito larvae were destroyed at this pH value

3.3 4.7 Mosquito larvae lived within this range

7.5 8.4 Best range for the growth of algae

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One of the most significant environmental impacts of pH is the effect that it has on the solubility and thus the bioavailability of other substances. This process is important in surface waters. Runoff from agricultural, domestic, and industrial areas may contain iron, lead, chromium, ammonia, mercury or other elements. The pH of the water affects the toxicity of these substances. As the pH falls (solution becomes more acidic) many insoluble substances become more soluble and thus available for absorption. For example, 4 mg/L of iron would not present a toxic effect at a pH of 4.8. However, as little as 0.9 mg/L of iron at a pH of 5.5 can cause fish to die. [RAMP]

Temperature

Abbreviation: ----- Units: degrees Celsius or degrees Fahrenheit

Summary

In addition to having its own toxic effect, temperature affects the solubility and, in turn, the toxicity of many other parameters. Generally the solubility of solids increases with increasing temperature, while gases tend to be more soluble in cold water. Temperature is a factor in determining allowable limits for other parameters such as ammonia. An important physical relationship exists between the amount of dissolved oxygen in a body of water and its temperature. Simply put, "the warmer the water, the less dissolved oxygen, and vice versa." [RAMP]

Natural heat loadings that affect water temperatures in streams include direct sun (especially where water is not adequately shaded by surrounding vegetation) and warmer water that flows in from shallow ponds or reservoirs. Industrial wastewater or water used for cooling machinery and runoff from sun-heated roads, parking lots, and roofs can also contribute to temperature changes.

Human activities should not change water temperatures beyond natural seasonal fluctuations. To do so could disrupt aquatic ecosystems. Appropriate temperatures are dependent on the type of stream being monitored. Lowland streams, known as "warmwater" streams, are different from mountain or spring-fed streams that are normally cool. [WRM]

Limits

In a warmwater stream temperatures should never exceed 89EF. Cold water streams should never exceed 68EF. Often summer heat can cause fish kills in ponds because high temperatures reduce the available oxygen in the water. [WRM]

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Water quality standards for temperature are based on the time of the year. For aquatic life the temperature should not exceed 25EC (77EF) during the latter half of October and the average temperature during that time period should be no higher than 22.2EC (72EF).

[RAMP]

Methodology

The simplest field method is to use a thermometer; however, electronic thermal sensing devices are available with continuous read-outs. [RAMP]

Environmental Impact

The Federal Water Pollution Control Administration (1967) referred to temperature as "a catalyst, a depressant, an activator, a restrictor, a stimulator, a controller, a killer, one of the most important and most influential water quality characteristics to life in water."

For this reason, heat or "thermal pollution" may be a problem, especially in shallow slow-moving streams, embayments, or pools which can get very warm in mid-summer. Most fish simply can't stand warm water and/or low levels of dissolved oxygen. Thermal pollution may also result when industries--especially electrical power companies--release the water used for cooling their machines into waterways. Water temperatures, even miles from the release points, may rise dramatically. The result may be dead fish, fish eggs that won't hatch or a total change in the fish population as warm water varieties replace the original trout or other cold water fish. As you might guess, the warm waters near power plants attract lots of "rough" fish which can tolerate the higher temperatures and lower levels of oxygen.

Reproductive events are perhaps the most thermally-restricted of all life phases. Even natural short-term temperature fluctuations appear to cause reduced reproduction of fish and invertebrates. Adults and juveniles are much better able to withstand fluctuations in temperature. Furthermore, juvenile and adult fish usually thermoregulate behaviorally by moving to water having temperatures closest to their thermal preference. This provides a thermal environment which approximates the optimal temperature for many physiological functions, including growth. As a consequence, fishes usually are attracted to heated water during the fall, winter and spring. Avoidance will occur in summer as water temperature exceeds the preferred temperature. [RAMP]

Dissolved Oxygen

Abbreviation: DO Units: milligrams per liter

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Summary

Dissolved oxygen is one of the most important parameters in aquatic systems. This gas is an absolute requirement for the metabolism of aerobic organisms and also influences inorganic chemical reactions. Therefore, knowledge of the solubility and dynamics of oxygen distribution is essential to interpreting both biological and chemical processes within water bodies. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement) and as a waste product of photosynthesis. The amount of dissolved oxygen gas is highly dependent on temperature. Atmospheric pressure also has an effect on dissolved oxygen. The amount of oxygen (or any gas) that can dissolve in pure water (saturation point) is inversely proportional to the temperature of water. The warmer the water, the less dissolved oxygen. [RAMP]

Limits

Kentucky Water Quality criteria for aquatic life require that the average dissolved oxygen remain above 5.0 mg/L and that the instantaneous minimum not fall below 4.0 mg/L. Total dissolved oxygen concentrations in water should not exceed 110 percent. Concentrations above this level can be harmful to aquatic life. [RAMP]

Methodology

When performing the dissolved oxygen test, only grab samples should be used and the analysis should be performed immediately. Therefore, this is a field test that should be performed on site.

Most of the sampling teams will use a modified Winkler method for determining dissolved oxygen. This is a multi-step chemical method which involves adding a chemical which reacts with the oxygen or "fixes" it. Other steps include addition of reagents which develop color. Then the amount of that compound is determined by addition (drop by drop) of a second chemical solution of known concentration until a color change occurs. The amount of chemical used in the last step is used to calculate the amount of dissolved oxygen.

If the instrument is available, the Yellow Springs Instruments (YSI) oxygen probe may be used to analyze dissolved oxygen. The temperature of the water and the atmospheric pressure must be known in order to calculate ppm (parts per million) of dissolved oxygen. The oxygen probe contains a solution of potassium chloride (KCl) which will absorb oxygen. As more oxygen is diffused into the solution, more current will flow through the cell. Lower oxygen pressure (less diffusion) will mean less current.

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The following table relates the solubility of oxygen to temperature in fresh water.

[RAMP]

Solubility Of Oxygen in Fresh Water (100% Saturation) Temperature

(EC)

Dissolved Oxygen

(PPM = mg/L)

Temperature

(EC)

Dissolved Oxygen

(PPM = mg/L)

0 14.6 23 8.7

1 14.2 24 8.5

2 13.9 25 8.4

3 13.5 26 8.2

4 13.2 27 8.1

5 12.8 28 7.9

6 12.5 29 7.8

7 12.2 30 7.7

8 11.9 31 7.5

9 11.6 32 7.4

10 11.3 33 7.3

11 11.1 34 7.2

12 10.8 35 7.1

13 10.6 36 7.0

14 10.4 37 6.8

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15 10.2 38 6.7

16 9.9 39 6.6

17 9.7 40 6.5

18 9.5 41 6.4

19 9.3 42 6.3

20 9.2 43 6.2

21 9.0 44 6.1

22 8.8 45 6.0

Table derived from "Standard Methods for the Examination of Water and Wastewater."

Environmental Impact

In a nutrient-rich water body the dissolved oxygen is quite high in the surface water due to increased photosynthesis by the large quantities of algae. However, dissolved oxygen tends to be depleted in deeper waters because photosynthesis is reduced due to poor light penetration and due to the fact that dead phytoplankton (algae) falls toward the bottom using up the oxygen as it decomposes. In a nutrient-poor water body there is usually less difference in dissolved oxygen from surface to bottom. This difference between surface and bottom waters is exaggerated in the summer in reservoirs, stream-pools, and embayments when thermal layering occurs which prevents mixing. The surface may become super-saturated with oxygen (>100%) and the bottom anoxic (virtually no oxygen). Shallower reservoirs and actively flowing shallow streams generally are kept mixed due to wind action in the shallow reservoirs and physical turbulence created by rocks in the stream beds.

Adequate dissolved oxygen is needed and necessary for good water quality. Oxygen is a necessary element to all forms of life. Adequate oxygen levels are necessary to provide for aerobic life forms which carry on natural stream purification processes. As dissolved oxygen levels in water drop below 5.0 mg/L, aquatic life is put under stress. The lower the concentration, the greater the stress. Oxygen levels that remain below 1-2 mg/L for a few hours can result in large fish kills. Total dissolved oxygen concentrations in water should not exceed 110 percent. Concentrations above this level can be harmful to aquatic life. Fish in waters containing excessive dissolved gases may suffer from "gas bubble disease"; however, this is a very rare occurrence. The bubbles or emboli block the flow of blood through blood vessels causing death. Aquatic invertebrates are also affected by gas bubble disease but at levels higher than those lethal to fish. [RAMP]

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Buffering Capacity (Alkalinity)

Abbreviation: ----- Units: milligrams per liter

Summary

Buffering capacity (also called alkalinity) refers to the capability of water to neutralize acid. A buffer is a solution to which an acid can be added without changing the concentration of available H^+ ions (without changing the pH) appreciably. It essentially absorbs the excess H^+ ions and protects the water body from fluctuations in pH. In most natural water bodies in Kentucky the buffering system is carbonate-bicarbonate (CO_2 HCO_3^- CO_3^{2-}). The presence of calcium carbonate or other compounds such as magnesium carbonate contribute carbonate ions to the buffering system. Alkalinity is often related to hardness because the main source of alkalinity is usually from carbonate rocks (limestone) which are mostly $CaCO_3$. If $CaCO_3$ actually accounts for most of the alkalinity, hardness in $CaCO_3$ is equal to alkalinity. Since hard water contains metal carbonates (mostly $CaCO_3$) it is high in alkalinity. Conversely, unless carbonate is associated with sodium or potassium which don't contribute to hardness, soft water usually has low alkalinity and little buffering capacity. So, generally, soft water is much more susceptible to fluctuations in pH from acid rains or acid contamination. [RAMP]

Limits

For protection of aquatic life the buffering capacity should be at least 20 mg/L. If alkalinity is naturally low, (less than 20 mg/L) there can be no greater than a 25% reduction in alkalinity. [RAMP]

Methodology

Alkalinity is an electrometric measurement which is performed by the computer aided titrimeter (CAT) and the pH electrode. A potentiometric titration is taken to an end-point reading of pH 4.5. The amount of acid required to reach a pH of 4.5 is expressed in milliliters. The calcium ions (Ca^{2+}) neutralize the acid in this reaction, and show the buffering capacity of the sample. From the amount of acid used, a calculation will indicate the amount of carbonate (CO_3) involved in the reaction. This then is expressed as mg of $CaCO_3/L$ even though actually part of the alkalinity may be contributed by $MgCO_3$, Na_2CO_3 or K_2CO_3 . [RAMP]

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Environmental Impact

Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0. Alkalinity is a measure of how much acid can be added to a liquid without causing a large change in pH. Higher alkalinity levels in surface waters will buffer acid rain and other acid wastes and prevent pH changes that are harmful to aquatic life. See Table in the discussion on pH. [RAMP]

Hardness

Abbreviation: ----- Units: milligrams per liter

Summary

Water hardness is due to the presence of multivalent metal ions which come from minerals dissolved in the water. Hardness is based on the ability of these ions to react with soap to form a precipitate or soap scum. In fresh water the primary ions are calcium and magnesium; however iron and manganese may also contribute. Carbonate hardness is equal to alkalinity but a non-carbonate fraction may include nitrates and chlorides. [RAMP]

Limits

There are no criteria for hardness. [RAMP]

Methodology

This is an electrochemical procedure. The technique for analysis uses potentiometric titration on the computer aided titrimeter (CAT) with a copper ion-specific electrode. A reference substance, EDTA, is used as a titrant. Hardness is expressed in mg/L of CaCO₃ (even though all the hardness may not be due to CaCO₃). [RAMP]

Classification of Water by Hardness Content

CaCO₃ (mg/L) Description

0 - 75	soft
75 - 150	moderately hard
150 - 300	hard
300 and up	very hard

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The most important impact of hardness on fish and other aquatic life appears to be the effect the presence of these ions has on the other more toxic metals such as lead, cadmium, chromium and zinc. Generally, the harder the water, the lower the toxicity of other metals to aquatic life. In hard water some of the metal ions form insoluble precipitates and drop out of solution and are not available to be taken in by the organism. Large amounts of hardness are undesirable mostly for economic or aesthetic reasons. If a stream or river is a drinking water source, hardness can present problems in the water treatment process. Hardness must also be removed before certain industries can use the water. For this reason, the hardness test is one of the most frequent analyses done by facilities that use water. [RAMP]

Chloride

Abbreviation: Cl⁻ Units: milligrams per liter

Summary

Chlorides are salts resulting from the combination of the gas chlorine with a metal. Some common chlorides include sodium chloride (NaCl) and magnesium chloride (MgCl₂). Chlorine alone as Cl₂ is highly toxic and it is often used as a disinfectant. In combination with a metal such as sodium it becomes essential for life. Small amounts of chlorides are required for normal cell functions in plant and animal life. [RAMP]

Limits

Public Drinking Water Standards require chloride levels not to exceed 250 mg/L. Criteria for protection of aquatic life require levels of less than 600 mg/L for chronic (long-term) exposure and 1200 mg/L for short-term exposure. [RAMP]

Chloride Above These Levels Can Be Toxic [given in mg/L = PPM]

Short-term Exposure Long-term Exposure Species

2,540 400 Snail

6,570 430 Fathead minnow

6,740 900 Rainbow trout

8,000 800 Channel catfish

8,390 850 Carp

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Methodology

Although analysis can be performed by potentiometric titration using the computer-aided titrimer (CAT) with an ion-specific chloride electrode, Ion Chromatography (IC) is the preferred method of identification. Essentially, an analytical column is used to separate out various anions. The time required for the anion to pass through the column indicates its concentration. To determine the identification of the anion, the IC uses a conductivity meter. Since each anion has a different conductivity, its identity can easily be determined. [RAMP]

Environmental Impact

Chlorides are not usually harmful to people; however, the sodium part of table salt has been linked to heart and kidney disease. Sodium chloride may impart a salty taste at 250 mg/L; however, calcium or magnesium chloride are not usually detected by taste until levels of 1000 mg/L are reached.

Chlorides may get into surface water from several sources including:

- 1) rocks containing chlorides
- 2) agricultural runoff
- 3) wastewater from industries
- 4) oil well wastes
- 5) effluent wastewater from wastewater treatment plants
- 6) road salting.

Chlorides can corrode metals and affect the taste of food products. Therefore, water that is used in industry or processed for any use has a recommended maximum chloride level. Chlorides can contaminate freshwater streams and lakes. Fish and aquatic communities cannot survive in high levels of chlorides. The table below shows the effects of chlorides on fish. [RAMP]

Fluoride

Abbreviation: F Units: milligrams per liter

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Summary

Fluorides are compounds containing the element fluorine. Some of the most common of these compounds include the following: sodium fluoride (NaF), sodium silicofluoride (Na_2SiF_6), and calcium fluoride (CaF_2). Fluorine is the most reactive nonmetallic element. It will form compounds with all elements except helium, neon and argon. It will also form salts by combining with metals. [RAMP]

Limits

The Kentucky Water Quality Standards maximum for fluoride in streams is a concentration of 1 mg/L or 1 part per million. Higher levels may be harmful to aquatic life. Fluoride concentration in water to be used for domestic water supply should not exceed 1.0 mg/L. [RAMP]

Methodology

Fluoride analysis is an electrometric measurement. An ion-specific fluoride electrode is used on the computer-aided titrimer (CAT) to measure fluoride. [RAMP]

Environmental Impact

Fluoride ions may be present either naturally or artificially in drinking water and are absorbed to some degree in the bone structure of the body and tooth enamel. Fluoride at extremely high levels can cause mottling (discoloration) of the teeth. Some fluoride compounds may also cause corrosion of piping and other water treatment equipment. Natural fluorides occur in rocks in some areas. Another source of fluorides in streams and reservoirs is releases from sewage treatment plants, since most public water supplies add fluoride to drinking water to reduce dental decay. [RAMP]

Conductivity

Abbreviation: ----- Units: micromho per centimeter or milligrams per liter

Summary

Conductivity is a measurement of the ability of an aqueous solution to carry an electrical current. An ion is an atom of an element that has gained or lost an electron which will create a negative or positive state. For example, sodium chloride (table salt) consists of sodium ions (Na^+) and chloride ions (Cl^-) held together in a crystal. In water it breaks apart into an aqueous solution of sodium and chloride ions. This solution will conduct an electrical current.

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There are several factors that determine the degree to which water will carry an electrical current. These include:

- 1) the concentration or number of ions
- 2) mobility of the ion
- 3) oxidation state (valence)
- 4) temperature of the water.

Resistance, which is an electrical measurement expressed in ohms, is the opposite of conductivity. Conductivity is then expressed in reciprocal ohms (mho). A more convenient unit of measurement in the chemical analysis of water is the μmho [one millionth of a mho]. The specific conductance or conductivity measurement is related to ionic strength and does not tell us what specific ions are present. [RAMP]

Limits

Water quality criteria have been established only for the main stem of the Ohio River. The limit is $800 \mu\text{mho/cm}$. [RAMP]

Methodology

The specific conductance of a sample is measured by a self-contained conductivity electrode. [RAMP]

Environmental Impact

Conductivity is a measurement used to determine a number of applications related to water quality. These are as follows. 1) Determining mineralization: this is commonly called total dissolved solids. Total dissolved solids information is used to determine the overall ionic effect in a water source. Certain physiological effects on plants and animals are often affected by the number of available ions in the water. 2) Noting variation or changes in natural water and waste waters quickly. 3) Estimating the sample size necessary for other chemical analyses. 4) Determining amounts of chemical reagents or treatment chemicals to be added to a water sample.

Elevated dissolved solids can cause "mineral tastes" in drinking water. Corrosion or encrustation of metallic surfaces by waters high in dissolved solids causes problems with industrial equipment and boilers as well as domestic plumbing, hot water heaters, toilet flushing mechanisms, faucets, and washing machines and dishwashers.

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Indirect effects of excess dissolved solids are primarily the elimination of desirable food plants and habitat-forming plant species. Agricultural uses of water for livestock watering are limited by excessive dissolved solids and high dissolved solids can be a problem in water used for irrigation. [RAMP]

Total Organic Carbon

Abbreviation: TOC Units: milligrams per liter

Summary

Organic contaminants (natural organic substances, insecticides, herbicides, and other agricultural chemicals) enter waterways in rainfall runoff. Domestic and industrial wastewaters also contribute organic contaminants in various amounts. As a result of accidental spills or leaks, industrial organic wastes may enter streams. Some of the contaminants may not be completely removed by treatment processes; therefore, they could become a problem for drinking water sources. It is important to know the organic content in a waterway. [RAMP]

Limits

No criteria are provided. [RAMP]

Methodology

Total organic carbon (TOC) provides a speedy and convenient way of determining the degree of organic contamination. A carbon analyzer using an infrared detection system is used to measure total organic carbon. Organic carbon is oxidized to carbon dioxide. The CO₂ produced is carried by a "carrier gas" into an infrared analyzer that measures the absorption wavelength of CO₂. The instrument utilizes a microprocessor that will calculate the concentration of carbon based on the absorption of light in the CO₂. The amount of carbon will be expressed in mg/L. Two other test methods that offer organic contamination information are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). However, TOC provides a more direct expression of the organic chemical content of water than BOD or COD. [RAMP]

Environmental Impact

By using TOC measurements, the number of carbon-containing compounds in a source can be determined. This is important because knowing the amount of carbon in a freshwater stream is an indicator of the organic character of the stream. The larger the carbon or organic content, the more oxygen is consumed. A high organic content means an increase in the growth of microorganisms which contribute to the depletion of oxygen supplies. The source of this organic material could be a wastewater treatment plant

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releasing treated sewage into the stream. Both the plant effluent and the stream must be monitored for organic levels. Industrial waste effluent may contain carbon-containing compounds with various toxicity levels. Both of these situations can create unfavorable conditions for aquatic life, such as the depletion of oxygen and the presence of toxic substances.

Total Suspended Solids

Abbreviation: TSS Units: milligrams per liter

Summary

One of the biggest sources of water pollution in Kentucky is suspended solids. When these suspended particles settle to the bottom of a water body, they become sediments. The terms "sediment" and "silt" are often used to refer to suspended solids. Suspended solids consist of an inorganic fraction (silts, clays, etc.) and an organic fraction (algae, zooplankton, bacteria, and detritus) that are carried along by water as it runs off the land. The inorganic portion is usually considerably higher than the organic. Both contribute to turbidity, or cloudiness of the water. Waters with high sediment loads are very obvious because of their "muddy" appearance. This is especially evident in rivers, where the force of moving water keeps the sediment particles suspended.

The geology and vegetation of a watershed affect the amount of suspended solids. If the watershed has steep slopes and is rocky with little plant life, top soil will wash into the waterway with every rain. On the other hand, if the watershed has lots of firmly rooted vegetation, it will act as a sponge to trap water and soil and thereby eliminate most erosion. Most suspended solids come from accelerated erosion from agricultural land, logging operations (especially where clear-cutting is practiced), surface mining, and construction sites. Another source of suspended solids is the resuspension of sediments which accompanies dredging that is undertaken to keep navigation channels open in larger rivers. [RAMP]

Limits

There are no quantitative criteria for TSS; however, Kentucky Water Quality Standards for aquatic life state that suspended solids "shall not be changed to the extent that the indigenous aquatic community is adversely affected" and "the addition of settleable solids that may adversely alter the stream bottom is prohibited." The National Academy of Sciences has recommended that the concentration of TSS should not reduce light penetration by more than 10%. In a study in which TSS were increased to 80 mg/L, the macroinvertebrate population was decreased by 60%. [RAMP]

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Methodology

Several methods may be employed to determine suspended solids or the turbidity which it causes. The method employed in this study determines total suspended solids (TSS). A well mixed sample is filtered through a preweighed glass filter. The filter is then dried in a drying oven and reweighed. The weight gain represents the total suspended solids. It is expressed in mg/L. Turbidity is measured using a turbidity meter and expressed in turbidity units. In deep waters, a Secchi disk may be used to determine light penetration or transparency. A Secchi disk is a weighted disk painted with alternating quarters of black and white. Recording the depth at which the disk disappears from view provides an estimation of the water's transparency. [RAMP]

Environmental Impact

Suspended solids can clog fish gills, either killing them or reducing their growth rate. They also reduce light penetration. This reduces the ability of algae to produce food and oxygen. When the water slows down, as when it enters a reservoir, the suspended sediment settles out and drops to the bottom, a process called siltation. This causes the water to clear, but as the silt or sediment settles it may change the bottom. The silt may smother bottom-dwelling organisms, cover breeding areas, and smother eggs.

Indirectly, the suspended solids affect other parameters such as temperature and dissolved oxygen. Because of the greater heat absorbency of the particulate matter, the surface water becomes warmer and this tends to stabilize the stratification (layering) in stream pools, embayments, and reservoirs. This, in turn, interferes with mixing, decreasing the dispersion of oxygen and nutrients to deeper layers.

Suspended solids interfere with effective drinking water treatment. High sediment loads interfere with coagulation, filtration, and disinfection. More chlorine is required to effectively disinfect turbid water. They also cause problems for industrial users. Suspended sediments also interfere with recreational use and aesthetic enjoyment of water. Poor visibility can be dangerous for swimming and diving. Siltation, or sediment deposition, eventually may close up channels or fill up the water body converting it into a wetland. A positive effect of the presence of suspended solids in water is that toxic chemicals such as pesticides and metals tend to adsorb to them or become complexed with them which makes the toxics less available to be absorbed by living organisms. (RAMP)

FECAL BACTERIA

Fecal Coliform Bacteria

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For: Dr. Yvonne Meichtry BIO 694 Summer 2003

Abbreviation: ----- Units: colonies per 100 milliliters

Summary

Malfunctioning sewer or septic tank systems can release human pathogens into rivers and streams. It is expensive and difficult to test for the many different types of pathogens, but the existence of a leaking or overflowing sanitary system can be signaled by the presence in the water of indicator organisms: bacteria that are common in human feces. Indicator organisms such as fecal coliform bacteria usually do not themselves cause disease, but they are used to detect the possibility of pathogens in water.

Coliform bacteria are a collection of relatively harmless microorganisms that live in large numbers in the intestines of man and warm- and cold-blooded animals. They aid in the digestion of food. A specific subgroup of this collection is the fecal coliform bacteria, the most common member being *Escherichia coli*. These organisms may be separated from the total coliform group by their ability to grow at elevated temperatures and are associated only with the fecal material of warm-blooded animals. [RAMP]

Limits

The criterion for swimming is fewer than 200 colonies/100 mL; for fishing and boating, fewer than 1000 colonies/100 mL; and for domestic water supply fewer than 2000 colonies/100 mL. [RAMP]

Methodology

Membrane filtration is the method of choice for the analysis of fecal coliforms in water. Samples to be tested are passed through a membrane filter of particular pore size (generally 0.45 μm). The microorganisms present in the water remain on the filter surface. When the filter is placed in a sterile petri dish and saturated with an appropriate medium, growth of the desired organisms is encouraged, while that of other organisms is suppressed. Each cell develops into a discrete colony which can be counted directly and the results calculated as microbial density. Sample volumes of 1 ml and 10 ml will be used for the ambient water testing, with the goal of achieving a final desirable colony density range of 20-60 colonies/filter. Excessively contaminated sources may require dilution to achieve a "countable" membrane. [RAMP]

Environmental Impact

The presence of fecal coliform bacteria in aquatic environments indicates that the water has been contaminated with the fecal material of man or other animals. At the time this occurred, the source water may have been contaminated by pathogens or disease producing bacteria or viruses which can also exist in fecal material. Some waterborne pathogenic diseases include typhoid fever, viral and bacterial gastroenteritis, and hepatitis

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A. The presence of fecal contamination is an indicator that a potential health risk exists for individuals exposed to this water. Fecal coliform bacteria may occur in ambient water as a result of the overflow of domestic sewage or nonpoint sources of human and animal waste. [RAMP]

Fecal Streptococci

Abbreviation: fecal strep Units: colonies per 100 milliliters

Summary

Like fecal coliform bacteria, fecal streptococci are indicator organisms whose presence in water shows that it has been contaminated by feces. In the mid-1970s the idea was advanced that the source of contamination could be determined by the relative abundance of the two types of fecal bacteria (coliform and streptococci). High ratios of fecal coliform to fecal strep (greater than four) were attributed to human fecal contamination, intermediate ratios (between one and four) were attributed to domesticated animal manure, and lower ratios (less than 0.1) were attributed to wild animal wastes. Evaluation of this method has revealed a number of important limitations that put the value of the ratios in question. The two classes of bacteria react differently to environmental conditions in the water, so the ratios will often diverge quickly from the ratios observed in animal wastes. Samples need to be taken within 24 hours of contamination, and even then ratios can be strongly affected by environmental factors, requiring careful analysis. For example, if the pH of the water is outside the range of 4 to 9, fecal coliform bacteria will die faster than fecal streptococci and skew the ratio.

Limits

None. See above for application of the ratio of fecal coliform to fecal strep.

Methodology

Analysis of fecal streptococci is similar to that of fecal coliform bacteria, as described above.

Environmental Impact

The presence of fecal coliform bacteria in aquatic environments indicates that the water has been contaminated with the fecal material of man or other animals. At the time this occurred, the source water may have been contaminated by pathogens or disease producing bacteria or viruses which can also exist in fecal material. Some waterborne pathogenic diseases include typhoid fever, viral and bacterial gastroenteritis, and hepatitis A. The presence of fecal contamination is an indicator that a potential health risk exists for individuals exposed to this water. Fecal coliform bacteria may occur in ambient water

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as a result of the overflow of domestic sewage or nonpoint sources of human and animal waste. [RAMP]

Under certain conditions, the relative amounts of fecal streptococci and fecal coliform bacteria may provide an indication of the type of contamination that is taking place. The ratio may therefore provide a starting point for identifying and addressing the sources of the contamination (for instance, straight pipes, failed septic systems, agricultural runoff, or livestock defecating in the creek). Like human wastes, animal wastes may contain viruses or bacteria that can make people sick.

NUTRIENT PARAMETERS

Ammonia Nitrogen

Abbreviation: NH_4^+ , NH_3 Units: milligrams per liter

Summary

Ammonia (NH_3) is a colorless gas with a strong pungent odor. It is easily liquefied and solidified and is very soluble in water. One volume of water will dissolve 1,300 volumes of NH_3 . Ammonia will react with water to form a weak base. [RAMP] This ammonia ion, called ammonium, is abbreviated NH_4^+ .

Limits

The un-ionized form of ammonia (NH_3) should not exceed 0.05 mg/L in order to protect aquatic organisms. This is calculated from total ammonia using temperature and pH in a formula. [RAMP]

Methodology

An ammonia ion-specific electrode can be used with the computer-aided titrimeter (CAT). However, the Ion Chromatography is a more accurate and efficient method for anion identification. Ammonia concentration is usually reported as total (NH_3 and NH_4^+) ammonia nitrogen. [RAMP]

Ammonia measurements indicate the total mass of ammonia per unit of water. Ammonia nitrogen measurements indicate the mass of nitrogen contained in ammonia, rather than the total mass (which includes the mass of the hydrogen in the molecule). This allows easy comparison with measurements of nitrogen in other forms, such as nitrates.

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Environmental Impact

About three-fourths of the ammonia produced in the United States is used in fertilizers either as the compound itself or as ammonium salts such as sulfate and nitrate. Large quantities of ammonia are used in the production of nitric acid, urea and nitrogen compounds. It is used in the production of ice and in refrigerating plants. "Household ammonia" is an aqueous solution of ammonia. It is used to remove carbonate from hard water. Since ammonia is a decomposition product from urea and protein, it is found in domestic wastewater. Aquatic life and fish also contribute to ammonia levels in a stream.

NH₃ is the principal form of toxic ammonia. It has been reported to be toxic to fresh water organisms at concentrations ranging from 0.53 to 22.8 mg/L. Toxic levels are both pH and temperature dependent. Toxicity increases as pH decreases and as temperature decreases. Plants are more tolerant of ammonia than animals, and invertebrates are more tolerant than fish. Hatching and growth rates of fishes may be affected. In the structural development, changes in tissues of gills, liver, and kidneys may also occur. Toxic concentrations of ammonia in humans may cause loss of equilibrium, convulsions, coma, and death. (RAMP)

Nitrate and Nitrite Nitrogen

Abbreviation: NO₃⁻, NO₂⁻ Units: milligrams per liter

Summary

Nitrogen is one of the most abundant elements. About 80 percent of the air we breathe is nitrogen. It is found in the cells of all living things and is a major component of proteins. Inorganic nitrogen may exist in the free state as a gas N₂, or as nitrate NO₃, nitrite NO₂ or ammonia NH₃. Organic nitrogen is found in proteins, and is continually recycled by plants and animals. [RAMP]

Limits

Nitrates/nitrites should remain below 10 mg/L in water to be used as a domestic water supply. [RAMP]

Methodology

This test used to be done using a colorimetric test. However, Ion Chromatography is now used for nitrate and nitrite analysis. [RAMP]

Nitrate concentrations are indicated both in terms of total mass (which includes the mass of the oxygen in the molecule) and in terms of the mass of nitrogen contained in nitrates.

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This allows easy comparison with measurements of nitrogen in other forms, such as ammonia.

Environmental Impact

Nitrogen-containing compounds act as nutrients in streams, rivers, and reservoirs. The major routes of entry of nitrogen into bodies of water are municipal and industrial wastewater, septic tanks, feed lot discharges, animal wastes (including birds and fish), runoff from fertilized agricultural field and lawns and discharges from car exhausts. Bacteria in water quickly convert nitrites to nitrates and this process uses up oxygen. Excessive concentrations of nitrites can produce a serious condition in fish called "brown blood disease." Nitrites also can react directly with hemoglobin in the blood of humans and other warm-blooded animals to produce methemoglobin. Methemoglobin destroys the ability of red blood cells to transport oxygen. This condition is especially serious in babies under three months of age. It causes a condition known as methemoglobinemia or "blue baby" disease. Water with nitrate levels exceeding 1.0 mg/L should not be used for feeding babies. High nitrates in drinking water can cause digestive disturbances in people. Nitrite/nitrogen levels below 90 mg/L and nitrate levels below 0.5 mg/L seem to have no effect on warm water fish.

The major impact of nitrates/nitrites on fresh water bodies is that of enrichment or fertilization called eutrophication. Nitrates stimulate the growth of algae and other plankton which provide food for higher organisms (invertebrates and fish); however an excess of nitrogen can cause over-production of plankton and as they die and decompose they use up the oxygen which causes other oxygen-dependent organism to die. [RAMP]

Phosphorus, Total

Abbreviation: P, PO₄²⁻ Units: milligrams per liter

Summary

Phosphorus is one of the key elements necessary for growth of plants and animals. Phosphates PO₄²⁻ are formed from this element. Phosphates exist in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate. Each compound contains phosphorous in a different chemical formula. Ortho forms are produced by natural processes and are found in sewage. Poly forms are used for treating boiler waters and in detergents. In water, they change into the ortho form. Organic phosphates are important in nature. Their occurrence may result from the breakdown of organic pesticides which contain phosphates. They may exist in solution, as particles, loose fragments or in the bodies of aquatic organisms. [RAMP]

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Limits

There are no criteria for phosphorus content of water bodies. However, the following criteria for total phosphorus have been proposed:

1. no more than 0.1 mg/L for streams which do not empty into reservoirs,
2. no more than 0.05 mg/L for streams discharging into reservoirs, and
3. no more than 0.025 mg/L for reservoirs. [RAMP]

Methodology

The analysis of phosphorus uses a spectrophotometer. Phosphorus is oxidized to the phosphate ion (PO_4^{2-}). Reagent dye is added and the absorbance read. [RAMP]

Environmental Impact

Rainfall can cause varying amounts of phosphates to wash from farm soils into nearby waterways. Phosphate will stimulate the growth of plankton and aquatic plants which provide food for fish. This may cause an increase in the fish population and improve the overall water quality. However, if an excess of phosphate enters the waterway, algae and aquatic plants will grow wildly, choke up the waterway and use up large amounts of oxygen. This condition is known as eutrophication or over-fertilization of receiving waters. This rapid growth of aquatic vegetation eventually dies and as it decays it uses up oxygen. This process in turn causes the death of aquatic life because of the lowering of dissolved oxygen levels. Phosphates are not toxic to people or animals unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphate. [RAMP]

Sulfate

Abbreviation: SO_4^{2-} Units: milligrams per liter

Summary

Sulfate is second to bicarbonate as the major anion in hard water reservoirs. Sulfates (SO_4^{2-}) can be naturally occurring or the result of municipal or industrial discharges. When naturally occurring, they are often the result of the breakdown of leaves that fall into a stream, of water passing through rock or soil containing gypsum and other common minerals, or of atmospheric deposition. Point sources include sewage treatment plants and industrial discharges such as tanneries, pulp mills, and textile mills. Runoff from fertilized agricultural lands also contributes sulfates to water bodies. [RAMP]

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Limits

Recommended limits for water used as a Domestic Water Supply are below 250 mg/L. [RAMP]

Methodology

Sulfate can be analyzed by colorimetric method or ion chromatography. [RAMP]

Environmental Impact

Sulfur is an essential plant nutrient. Aquatic organisms utilize sulfur and reduced concentrations have a detrimental effect on algal growth. The most common form of sulfur in well-oxygenated waters is sulfate. When sulfate is less than 0.5 mg/L, algal growth will not occur. On the other hand, sulfate salts can be major contaminants in natural waters.

A sulfur cycle exists which includes atmospheric sulfur dioxide (SO₂), sulfate ions (SO₄²⁻) and sulfides (S²⁻). Sulfides, especially hydrogen sulfide (H₂S), are quite soluble in water and are toxic to both humans and fish. They are produced under conditions where there is a lack of oxygen (anaerobic). Because of their foul "rotten egg" smell they are avoided by both fish and humans. Sulfides formed as a result of acid mine runoff from coal or other mineral extraction and from industrial sources may be oxidized to form sulfates, which are less toxic.

Sulfates are not considered toxic to plants or animals at normal concentrations. In humans, concentrations of 500 - 750 mg/L cause a temporary laxative effect. However, doses of several thousand mg/L did not cause any long-term ill effects. At very high concentrations sulfates are toxic to cattle. Problems caused by sulfates are most often related to their ability to form strong acids which changes the pH. Sulfate ions also are involved in complexing and precipitation reactions which affect solubility of metals and other substances.

Sulfates in water to be used for certain industrial processes such as sugar production and concrete manufacturing must be reduced below 20 mg/L.

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METALS AND MINERAL PARAMETERS

Metals

Abbreviations: see individual metals Units: milligrams per liter or micrograms (μg) per liter

Summary

The metals scan includes calcium, magnesium, and iron, which play major roles in water chemistry. Other metals include aluminum, barium, cadmium, chromium, lead, manganese, sodium, and zinc, which tend to be present in smaller amounts.

The toxicity of metals is dependent on their solubility and this in turn, depends heavily on pH and on the presence of different types of anions and other cations. [RAMP] More detailed information on the individual metals covered in the metal scan are presented on the following pages.

Limits

High pH in a stream can cause precipitation of metal salts which makes them temporarily unavailable. Because of this relationship of toxicity to hardness, Warm Water Aquatic Habitat Criteria for metals are calculated by a rather complex mathematical formula employing the natural log of the hardness.

As hardness increases, the allowable concentration increases. The metal criteria in this manual were calculated based on a hardness of 100 mg/L. If the hardness values in the test results vary much from 100 mg/L, the criteria can be recalculated. Even though metal concentrations may be very low (below a toxic level), aquatic organisms can bioaccumulate (or concentrate) certain metals (for example, mercury, lead, and cadmium). If more is absorbed than excreted, the levels can then build up over time to a toxic level.

When looking at the metals individually, the intended use of the water is very important. Industry requires varying amounts of metals and or hardness for many of its manufacturing techniques, while agriculture has its own requirements. [RAMP]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

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Environmental Impact

Metal ions are dissolved in groundwater and surface water when the water comes in contact with rock or soil containing the metals, usually in the form of metal salts. Activity that disturbs soil or rock can lead to entry of metals into groundwater or surface water. Metals can also enter with discharges from sewage treatment plants, industrial plants, and other sources. The metals most often found in the highest concentrations in natural waters are calcium and magnesium. These are usually associated with the carbonate anion (CO_3^{2-}) and come from the dissolution of limestone rock. As mentioned under the discussion of hardness, the higher the concentration of these metal ions, the harder the water; however, in some waters other metals can contribute to hardness. Calcium and magnesium are non-toxic and normally absorbed by living organisms more readily than the other metals, so if water is hard, the toxicity of a given concentration of a toxic metal is reduced. Conversely, in soft, acidic water the same concentrations of metals may be more toxic. (RAMP)

Aluminum Abbreviation: Al

Summary

Aluminum is one of the most abundant elements in the earth's crust and occurs in many rocks and ores, but never as a pure metal. The presence of aluminum ions in streams may result from industrial wastes but is more likely to come from the wash water of drinking water treatment plants. Many aluminum salts are readily soluble; however, there are some that are very insoluble. Those that are insoluble will not exist long in surface water, but will precipitate and settle. Waters containing high concentrations of aluminum can become toxic to aquatic life if the pH is lowered (as in acid rain). [RAMP]

Limits

Although Kentucky has not established a water-quality criterion for aluminum, the USEPA has established acute and chronic aquatic-life criteria for acid-soluble aluminum of 750 $\mu\text{g/L}$ and 87 $\mu\text{g/L}$, respectively (U.S. Environmental Protection Agency, 1988). The USEPA has established a secondary maximum contaminant level (SMCL) for aluminum in finished drinking water of 50 to 200 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1991). [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

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Environmental Impact

See summary section.

Antimony Abbreviation: Sb

Summary

Antimony is a USEPA priority pollutant that can be toxic to plants and animals. The concentrations of antimony in natural waters are very low; however, relatively few determinations of antimony have been reported (Hem, 1989). In addition to the natural occurrence of antimony in bedrock and streambed sediments in the Knobs Region of the Kentucky River Basin, antimony salts are used in the fireworks, rubber, textile, ceramic, glass, and paint industries (National Academy of Sciences-National Academy of Engineering, 1972). [USGS]

Limits

The proposed maximum contaminant level (MCL) in finished drinking water for antimony ranges from 5 to 10 $\mu\text{g/L}$, and the Kentucky domestic water supply source criterion (KDWSSC) for antimony is 146 $\mu\text{g/L}$. Kentucky acute and chronic aquatic life criteria for antimony are 9,000 $\mu\text{g/L}$ and 1,600 $\mu\text{g/L}$, respectively. [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Barium Abbreviation: Ba

Summary

Barium is a yellowish-white alkaline earth metal. Barium combines with water to produce barium hydroxide and is found in nature as barites, BaSO_4 , witherite (BaCO_3) and other ores. Barium and its salts are often used in metallurgical industries for special alloys, in paints, and concrete. Because of the insolubility of most of its compounds, it is not considered to be an ecological threat. [RAMP]

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Limits

The allowable level for water to be used as a domestic water supply is 1.0 mg/L. [RAMP]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Beryllium Abbreviation: Be

Summary

Beryllium is an uncommon alkaline-earth element that is recognized as a USEPA priority pollutant and potential carcinogen. [USGS]

Limits

The USEPA has proposed a MCL of 1 $\mu\text{g/L}$ for beryllium, and Kentucky has adopted the USEPA lowest-observed effect levels (LOEL) for protection of aquatic life, which are 130 $\mu\text{g/L}$ and 5.3 $\mu\text{g/L}$ for acute and chronic toxicity, respectively. In addition, Kentucky water-quality criteria establish a beryllium criterion of 0.117 $\mu\text{g/L}$ for the protection of human health from the consumption of fish tissue. The criterion is based upon an acceptable risk level of no more than one additional cancer case in a population of 1 million people. [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Boron Abbreviation: B

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Summary

Boron is an essential trace element for the growth of plants; however, boron is toxic to a number of sensitive plants at concentrations exceeding 1,000 µg/L. Although water from thermal springs contains large concentrations of boron, most surface water contains only a few hundred micrograms per liter (Hem, 1989). [USGS]

Limits

An upper limit of 5,000 µg/L was recommended by the National Academy of Sciences-National Academy of Engineering (1972) for livestock waters. [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Calcium Abbreviation: Ca

Summary

Calcium salts and calcium ions are among the most commonly occurring in nature. They may result from the leaching of soil and other natural sources or may come from man-made sources such as sewage and some industrial wastes. Calcium is usually one of the most important contributors to hardness. Even though the human body requires approximately 0.7 to 2.0 grams of calcium per day as a food element, excessive amounts can lead to the formation of kidney or gallbladder stones. High concentrations of calcium can also be detrimental to some industrial processes. Thus, both domestic and industrial water users have to consider calcium concentrations. Calcium also serves an important role in the health of bodies of water. In natural water it is known to reduce the toxicity of many chemical compounds on fish and other aquatic life. [RAMP]

Limits

No criteria exist for this metal. [RAMP]

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Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Chromium Abbreviation: Cr

Summary

Chromium is ubiquitous in the environment, occurring naturally in the air, water, rocks and soil. It is used in stainless steel, electroplating of chrome, dyes, leather tanning and wood preservatives. It occurs in several forms, or oxidation states. The two most common are chromium VI and chromium III. The form depends on pH. Natural sources of water contain very low concentrations of chromium. It is a micronutrient (or essential trace element). High doses of chromium VI have been associated with birth defects and cancer; however, chromium III is not associated with these effects. Plants and animals do not bioaccumulate chromium; therefore, the potential impact of high chromium levels in the environment is acute toxicity to plants and animals. In animals and humans this toxicity may be expressed as skin lesions or rashes and kidney and liver damage. [RAMP]

Limits

The criteria for total chromium in a domestic water supply is 0.05 mg/L. The aquatic life criteria are less than 0.011 mg/L for chromium VI and less than 0.207 mg/L for chromium III. (The second value is based on a formula involving hardness). [RAMP]

Hexavalent chromium is listed as a USEPA priority pollutant, and the MCL has been established at 100 µg/L (U.S. Environmental Protection Agency, 1991). The toxicity of chromium to aquatic life varies with the valance state and form of chromium, oxidation-reduction and pH relations and synergistic or antagonistic effects of other constituents. The Kentucky acute and chronic aquatic-life criteria for hexavalent chromium are 16 µg/L and 11 µg/L, whereas the criteria for trivalent chromium are 1,700 µg/L and 210 µg/L, based on a total hardness concentration of 100 mg/L as CaCO₃. [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

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Environmental Impact

See summary section.

Cobalt Abbreviation: Co

Summary

Cobalt is a transition metal that is a micronutrient for the growth of plants and animals. Concentrations of cobalt in natural water are generally less than a few micrograms per liter (Hem, 1989). [USGS]

Limits

Not available.

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

Transport estimates for cobalt reveal elevated yields from coal mining areas drained by the North Fork Kentucky River at Jackson. Mean annual loads of cobalt were largest in the Kentucky River main stem; however, load estimates were of the same magnitude in the North Fork. The primary source of cobalt in the Kentucky River appears to be land disturbance in the North Fork Kentucky River Subbasin. Concentrations of cobalt are larger in samples of fire clay, mudstone, and black shale than in other geologic materials in the Kentucky River Basin. [USGS]

Copper Abbreviation: Cu

Summary

Copper is a USEPA priority pollutant that is a micronutrient for the growth of plants and animals, but even small concentrations of copper in surface water can be toxic to aquatic life. Copper sulfate is frequently used to control nuisance growths of algae in water-supply reservoirs. [USGS]

Limits

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The toxicity of copper is a function of the total hardness of the water, because copper ions are complexed by anions that contribute to water hardness. Assuming a hardness of 100 mg/L, the Kentucky acute and chronic aquatic-life criteria for copper are 18 µg/L and 12 µg/L, respectively. Although detectable concentrations of copper in water are not known to have an adverse effect on humans, the SMCL for copper has been established at 1,000 µg/L, which corresponds with the taste-threshold concentration for this element (National Academy of Sciences-National Academy of Engineering, 1972). [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

The primary source of copper in the basin seems to be the weathering of shales and the transport of soils derived from shale bedrock in the Knobs and Eastern Coal Field Regions. However, elevated concentrations of copper in streambed sediments also were found downstream from point-source discharges in the Inner Bluegrass Region. [USGS]

Iron Abbreviation: Fe

Summary

Iron is the fourth most abundant element, by weight, in the earth's crust. Natural waters contain variable amounts of iron depending on the geological area and other chemical components of the waterway. Iron in groundwater is normally present in the ferrous or bivalent form [Fe²⁺] which is soluble. It is easily oxidized to ferric iron [Fe³⁺] or insoluble iron upon exposure to air. This precipitate is orange-colored and often turns streams orange. [RAMP]

Limits

The current aquatic life standard is less than 1.0 mg/L based on toxic effects. (It is one of the few for which the criterion is not calculated based on hardness.) [RAMP]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

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Environmental Impact

Iron is a trace element required by both plants and animals. It is a vital part of the oxygen transport mechanism in the blood (hemoglobin) of all vertebrate and some invertebrate animals. Ferrous Fe^{2+} and ferric Fe^{3+} ions are the primary forms of concern in the aquatic environment. Other forms may be in either organic or inorganic wastewater streams. The ferrous form Fe^{2+} can persist in water void of dissolved oxygen and usually originates from groundwater or mines that are pumped or drained. Iron in domestic water supply systems stains laundry and porcelain. It appears to be more of a nuisance than a potential health hazard. Taste thresholds of iron in water are 0.1 mg/L for ferrous iron and 0.2 mg/L ferric iron, giving a bitter or an astringent taste. Water to be used in industrial processes should contain less than 0.2 mg/L iron. Black or brown swamp waters may contain iron concentrations of several mg/L in the presence or absence of dissolved oxygen, but this iron form has little effect on aquatic life. [RAMP]

Lead Abbreviation: Pb

Summary

The primary natural source of lead is in the mineral galena (lead sulfide). It also occurs as carbonate, as sulfate and in several other forms. The solubility of these minerals and also of lead oxides and other inorganic salts is low. Major modern day uses of lead are for batteries, pigments, and other metal products. In the past lead was used as an additive in gasoline and became dispersed throughout the environment in the air, soils, and waters as a result of automobile exhaust emissions. For years this was the primary source of lead in the environment. However, since the replacement of leaded gasoline with unleaded gasoline in the mid-1980's, lead from that source has virtually disappeared. Mining, smelting and other industrial emissions and combustion sources and solid waste incinerators are now the primary sources of lead. Another source of lead is paint chips and dust from buildings built before 1978 and from bridges and other metal structures. [RAMP]

Limits

The level considered protective for aquatic life at a hardness of 100 is less than 0.003 mg/L. Use as a domestic water source requires less than 0.05 mg/L. Drinking water must contain less than 0.015 mg/L. [RAMP]

The MCL (U.S. Environmental Protection Agency, 1991) and Kentucky's domestic water supply criterion for lead have recently been lowered from 50 to 5 $\mu\text{g/L}$. The toxicity of lead to aquatic organisms is a function of water hardness. Based upon a total hardness concentration of 100 mg/L, the Kentucky acute and chronic aquatic life criteria are 82 $\mu\text{g/L}$ and 3 $\mu\text{g/L}$, respectively. [USGS]

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Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

Lead is not an essential element. In humans it can affect the kidneys, the blood and most importantly the nervous system and brain. Even low levels in the blood have been associated with high blood pressure and reproductive effects. It is stored in the bones.

Lead reaches water bodies either through urban runoff or discharges such as sewage treatment plants and industrial plants. It also may be transferred from the air to surface water through precipitation (rain or snow). Toxic to both plant and animal life, lead's toxicity depends on its solubility and this, in turn, depends on pH and is affected by hardness. [RAMP]

Lithium Abbreviation: Li

Summary

Lithium is an alkali metal that generally is present in surface waters at concentrations of less than 2 µg/L (Hem, 1989). According to Bradford (1963), lithium can be toxic to plants at concentrations of 60 to 100 µg/L. Concentrations of dissolved lithium in streams of the Kentucky River Basin are commonly less than the analytical detection limit. However, streambed- sediment concentrations of lithium are elevated in oil-producing areas of the Kentucky River Basin, and dissolved lithium concentrations in streams affected by oil well brine discharges have been known to range from 140 to 650 µg/L (Evaldi and Kipp, 1991). [USGS]

Limits

Not available.

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

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Environmental Impact

Natural sources of lithium in the basin are probably limited to the weathering of sedimentary rocks, notably shales, mudstones, and siltstones. Mean annual loads of dissolved lithium in the Kentucky River increased from Lock 10 downstream to Lock 2, possibly indicating effects of oil well brine discharges in the Knobs Region. [USGS]

Magnesium Abbreviation: Mg

Summary

Magnesium is widely distributed in ores and minerals. It is also very chemically active; therefore it is not found in the elemental state in nature. With the exception of magnesium hydroxide, which has a high pH value, its salts are very soluble. Magnesium ions are of particular importance in water pollution. They may contribute to water hardness. Concentrations of magnesium and calcium in water may also be a factor in the distribution of certain crustaceans, fish and other organisms in streams. [RAMP]

Limits

No criteria exist for this metal. [RAMP]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Manganese Abbreviation: Mn

Summary

Manganese is a transition element which is gray, white or silver in color. It is soft and ductile if pure but usually occurs in compounds. In natural waters it rarely exceeds 1 mg/L. At 0.1 mg/L, taste and staining problems may occur. Manganese forms a number of salt compounds. These compounds can include KMnO_4 (potassium permanganate) and K_2MnO_3 (potassium manganate). Frequently manganese salts will occur in association with iron salts. The primary uses of manganese are in metal alloys, dry cell batteries, and micronutrient fertilizer additives. [RAMP]

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Limits

Water to be used as a domestic water source should contain less than 0.05 mg/L manganese. [RAMP]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

Manganese is a vital micronutrient for both plants and animals. When it is not present in sufficient quantities, plants exhibit a yellowing of leaves (chlorosis) or failure of the leaves to develop properly. Inadequate quantities of manganese in domestic animal food result in reduced reproduction and deformed or poorly maturing young. In humans, very large doses of ingested manganese can cause some diseases and liver damage, but these are not known to occur in the United States. Permanganates have been reported to kill fish in 8 to 18 hours at concentrations of 2.2 to 4.1 mg/L, but they are not persistent. Manganese is not known to be a problem in water consumed by livestock. No specific criterion for manganese has been proposed for agricultural waters. Consumer complaints arise when high levels of manganese are found in drinking water or domestic water because of the brownish staining of laundry and objectionable tastes in beverages which may occur. [RAMP]

Nickel Abbreviation: Ni

Summary

Nickel is a USEPA priority pollutant that can adversely affect humans and aquatic organisms. Nickel is an important industrial metal that is used extensively in stainless steel. Substantial amounts of nickel can be contributed to the environment by waste disposal (Hem, 1989) and atmospheric emissions. Nickel ions are toxic particularly to plant life, and can exhibit synergism when present with other metallic ions (National Academy of Sciences-National Academy of Engineering, 1972). [USGS]

Limits

For water with total hardness of 100 mg/L, the Kentucky acute and chronic warmwater aquatic habitat criteria are 1,418 µg/L and 158 mg/L, respectively. The Kentucky domestic water-supply source criterion for nickel has been set at 13.4 µg/L, and the Kentucky criterion for protection of human health from the consumption of fish tissue is 100 µg/L. [USGS]

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Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Potassium Abbreviation: K

Summary

Potassium is an alkali metal that is abundant in minerals of the earth's crust.

Limits

Not available.

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Selenium Abbreviation: Se

Summary

Selenium is a nonmetallic trace element that is listed as a primary pollutant by the USEPA. Selenium is an essential micronutrient for plants and animals but can be toxic in excessive amounts. Selenium is a relatively rare element, and concentrations of selenium in natural waters seldom exceed 1 µg/L (Hem, 1989). Sources of selenium in the Kentucky River Basin include sedimentary rocks and fly ash from coal-fired power plants that operate in Kentucky. [USGS]

Limits

Kentucky acute and chronic warmwater aquatic habitat criteria for total recoverable concentrations of selenium are 20 µg/L and 4 µg/L, respectively. The Kentucky domestic

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water supply source criterion for selenium has been set at 10 µg/L; however the MCL is 50 µg/L (U.S. Environmental Protection Agency, 1991). [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Silicon Abbreviation: Si

Summary

Silicon is a nonmetallic element that is more abundant in the earth's crust than any other element except oxygen. It is an essential nutrient for certain types of algae (diatoms).

Limits

Not available.

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Silver Abbreviation: Ag

Summary

Silver is a USEPA priority pollutant that is extensively used for photography and various industrial and commercial purposes. Although average concentrations of silver in natural waters are small (0.3 µg/L), elevated silver concentrations can be acutely or chronically toxic to aquatic organisms, and sublethal amounts can bioaccumulate in fish and invertebrate organisms (Hem, 1989). [USGS]

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Limits

The Kentucky warmwater aquatic habitat acute-toxicity criterion is 4 µg/L, given a total water hardness of 100 mg/L. Although Kentucky water-quality standards do not specify a chronic aquatic-life criterion, the USEPA chronic criterion for silver is 0.12 µg/L. The MCL and Kentucky domestic water supply source criteria for silver are 50 µg/L. [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Sodium Abbreviation: Na

Summary

Sodium is a very reactive metal, and therefore does not occur in its free form in nature. The aquatic toxicity encountered with sodium depends largely on the anion involved; chromate is extremely toxic and sulfate is the least toxic. High sodium levels in drinking water can have adverse effects on humans with high blood pressure or pregnant women suffering from toxemia. [RAMP]

Limits

No criteria exist for this metal. [RAMP]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Strontium Abbreviation: Sr

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Summary

Strontium is an alkaline-earth metal that is fairly common in igneous and sedimentary rocks. Concentrations of strontium are generally larger in ground water than in surface water (Hem, 1989). [USGS]

Limits

Not available.

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Thallium Abbreviation: Tl

Summary

Thallium is a USEPA priority pollutant that can be toxic to humans and aquatic life. Thallium salts are used as poison for rats and other rodents, as well as in dyes, pigments in fireworks, and optical glass (National Academy of Sciences-National Academy of Engineering, 1972). [USGS]

Limits

The Kentucky domestic water supply source criterion for thallium is 13 $\mu\text{g/L}$. Kentucky acute and chronic LOEL aquatic-life criteria for thallium are 1,400 $\mu\text{g/L}$ and 40 $\mu\text{g/L}$, respectively. The Kentucky water-quality criterion for protection of human health from the consumption of fish tissue for thallium is 48 $\mu\text{g/L}$. [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

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Environmental Impact

See summary section.

Vanadium Abbreviation: V

Summary

Vanadium is a transition metal that is involved in biochemical processes in plants and animals; however, vanadium can bioaccumulate in the food chain, resulting in chronic toxicity to organisms that feed upon prey that have accumulated excessive amounts of vanadium (National Academy of Sciences- National Academy of Engineering, 1972). Vanadium was concentrated by certain marine organisms during the formation of coal and oil-producing strata millions of years ago (Hem, 1989). [USGS]

Limits

Analytical detection limit [is] 6 µg/L. Smoot and others (1991) reported a maximum dissolved vanadium concentration of 67 µg/L. [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

See summary section.

Zinc Abbreviation: Zn

Summary

Zinc is found naturally in many rock-forming minerals. Because of its use in the vulcanization of rubber, it is generally found at higher levels near highways. It also may be present in industrial discharges. It is used to galvanize steel, and is found in batteries, plastics, wood preservatives, antiseptics and in rat and mouse poison (zinc phosphide).

Zinc is an essential element in the diet. It is not considered very toxic to humans or other organisms. [RAMP]

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Limits

Criteria for aquatic life has been set at less than 0.106 mg/L based on hardness of 100 mg/L. [RAMP]

Given a total hardness concentration of 100 mg/L, the Kentucky acute and chronic warmwater aquatic habitat criteria for zinc are 117 µg/L and 106 µg/L, respectively. The SMCL for zinc is 5,000 µg/L. [USGS]

Methodology

Atomic Absorption Spectrometry analysis has been used in the past to identify these metals. However, in addition to atomic absorption, the laboratory now uses Inductively Coupled Plasma Emission Spectroscopy (ICP). [RAMP]

Environmental Impact

Adverse synergistic effects can occur when zinc is present with cadmium, copper, or other heavy metals, and zinc is known to biomagnify through the aquatic food chain (National Academy of Sciences-National Academy of Engineering, 1972). The toxicity of zinc depends on the total hardness of the water because zinc ions are complexed by anions that contribute to total water hardness. [USGS]

PESTICIDES AND HERBICIDES

Atrazine (triazines)

Abbreviation: ----- Units: milligrams per kilogram (of body weight) or milligrams per liter or parts per million

Summary

Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, Christmas trees, and other crops, and in conifer reforestation plantings. It is also used as a nonselective herbicide on non-cropped industrial lands and on fallow lands. Over 64 million acres of cropland were treated with atrazine in the U.S. in 1990. [EXTOXNET]

Regulatory Status: Atrazine has been classified as a Restricted Use Pesticide (RUP) due to its potential for groundwater contamination [2]. RUPs may be purchased and used only by certified applicators.

Acute toxicity: Atrazine is slightly to moderately toxic to humans and other animals. It can be absorbed orally, dermally, and by inhalation. Symptoms of poisoning include

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abdominal pain, diarrhea and vomiting, eye irritation, irritation of mucous membranes, and skin reactions.

Methodology

KRWW grab samples were analyzed by the contract laboratory.

Environmental Impact

Ecological Effects: Atrazine is slightly toxic to fish and other aquatic life. Atrazine has a low level of bioaccumulation in fish. In whitefish, atrazine accumulates in the brain, gall bladder, liver, and gut

Breakdown in soil and groundwater: Atrazine is highly persistent in soil. Atrazine is moderately to highly mobile in soils with low clay or organic matter content. Because it does not adsorb strongly to soil particles and has a lengthy half-life (60 to >100 days), it has a high potential for groundwater contamination despite its moderate solubility in water [20]. Atrazine is the second most common pesticide found in private wells and in community wells [16]. Trace amounts have been found in drinking water samples and in groundwater samples in a number of states [23,21]. A 5-year survey of drinking water wells detected atrazine in an estimated 1.7% of community water systems and 0.7% of rural domestic wells nationwide. Levels detected in rural domestic wells sometimes exceeded the MCL [23]. The recently completed National Survey of Pesticides in Drinking Water found atrazine in nearly 1% of all of the wells tested [EXTOXNET].

Breakdown in water: Atrazine is moderately soluble in water. Chemical hydrolysis, followed by biodegradation, may be the most important route of disappearance from aquatic environments. Hydrolysis is rapid under acidic or basic conditions, but is slower at neutral pHs. Atrazine is not expected to strongly adsorb to sediments. Bioconcentration and volatilization of atrazine are not environmentally important [21]. Atrazine has been detected in each of 146 water samples collected at 8 locations from the Mississippi, Ohio and Missouri Rivers and their tributaries. For several weeks, 27% of these samples contained atrazine concentrations above the EPA's maximum contaminant level (MCL).

For more information, see complete profile for atrazine at EXTOXNET site.

Chlorpyrifos

Abbreviation: ----- Units: milligrams per kilogram (of body weight) or milligrams per liter or parts per million

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Summary

Chlorpyrifos is a broad-spectrum organophosphate insecticide. While originally used primarily to kill mosquitoes, it is no longer registered for this use. Chlorpyrifos is effective in controlling cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, and lice. It is used as an insecticide on grain, cotton, field, fruit, nut and vegetable crops, and well as on lawns and ornamental plants. It is also registered for direct use on sheep and turkeys, for horse site treatment, dog kennels, domestic dwellings, farm buildings, storage bins, and commercial establishments. Chlorpyrifos acts on pests primarily as a contact poison, with some action as a stomach poison.

Chlorpyrifos is moderately toxic to humans [43]. Poisoning from chlorpyrifos may affect the central nervous system, the cardiovascular system, and the respiratory system. It is also a skin and eye irritant [2]. While some organophosphates are readily absorbed through the skin, studies in humans suggest that skin absorption of chlorpyrifos is limited [2]. [EXTOXNET]

Methodology

KRWW grab samples were analyzed by the contract laboratory.

Environmental Impact

Effects on aquatic organisms: Chlorpyrifos is very highly toxic to freshwater fish, aquatic invertebrates and estuarine and marine organisms [43]. Cholinesterase inhibition was observed in acute toxicity tests of fish exposed to very low concentrations of this insecticide. Application of concentrations as low as 0.01 pounds of active ingredient per acre may cause fish and aquatic invertebrate deaths [43]. Chlorpyrifos toxicity to fish may be related to water temperature. The 96-hour LC₅₀ for chlorpyrifos is 0.009 mg/L in mature rainbow trout, 0.098 mg/L in lake trout, 0.806 mg/L in goldfish, 0.01 mg/L in bluegill, and 0.331 mg/L in fathead minnow [50]. When fathead minnows were exposed to Dursban for a 200-day period during which they reproduced, the first generation of offspring had decreased survival and growth, as well as a significant number of deformities. This occurred at approximately 0.002 mg/L exposure for a 30-day period [8]. Chlorpyrifos accumulates in the tissues of aquatic organisms. Studies involving continuous exposure of fish during the embryonic through fry stages have shown bioconcentration values of 58 to 5100 [51]. Due to its high acute toxicity and its persistence in sediments, chlorpyrifos may represent a hazard to sea bottom dwellers [52]. Smaller organisms appear to be more sensitive than larger ones [50]. [EXTOXNET]

Effects on other organisms: Aquatic and general agricultural uses of chlorpyrifos pose a serious hazard to wildlife and honeybees [13,48]. Chlorpyrifos is moderately to very highly toxic to birds [43]. [EXTOXNET]

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Breakdown in soil and groundwater: Chlorpyrifos is moderately persistent in soils. The half-life of chlorpyrifos in soil is usually between 60 and 120 days, but can range from 2 weeks to over 1 year, depending on the soil type, climate, and other conditions [12,19]. The soil half-life of chlorpyrifos was from 11 to 141 days in seven soils ranging in texture from loamy sand to clay and with soil pHs from 5.4 to 7.4. Chlorpyrifos was less persistent in the soils with a higher pH [51]. Soil half-life was not affected by soil texture or organic matter content. In anaerobic soils, the half-life was 15 days in loam and 58 days in clay soil [43]. Adsorbed chlorpyrifos is subject to degradation by UV light, chemical hydrolysis and by soil microbes. When applied to moist soils, the volatility half-life of chlorpyrifos was 45 to 163 hours, with 62 to 89% of the applied chlorpyrifos remaining on the soil after 36 hours [51]. In another study, 2.6 and 9.3% of the chlorpyrifos applied to sand or silt loam soil remained after 30 days [51]. Chlorpyrifos adsorbs strongly to soil particles and it is not readily soluble in water [19,51]. It is therefore immobile in soils and unlikely to leach or to contaminate groundwater [51]. TCP, the principal metabolite of chlorpyrifos, adsorbs weakly to soil particles and appears to be moderately mobile and persistent in soils [43].

Breakdown in water: The concentration and persistence of chlorpyrifos in water will vary depending on the type of formulation. For example, a large increase in chlorpyrifos concentrations occurs when emulsifiable concentrations and wettable powders are released into water. As the pesticide adheres to sediments and suspended organic matter, concentrations rapidly decline. The increase in the concentration of insecticide is not as rapid for granules and controlled release formulations in the water, but the resulting concentration persists longer [50]. Volatilization is probably the primary route of loss of chlorpyrifos from water. Volatility half-lives of 3.5 and 20 days have been estimated for pond water [51]. The photolysis half-life of chlorpyrifos is 3 to 4 weeks during midsummer in the U.S. Its change into other natural forms is slow [52]. Research suggests that this insecticide is unstable in water, and the rate at which it is hydrolyzed increases with temperature, decreasing by 2.5- to 3-fold with each 10 C drop in temperature. The rate of hydrolysis is constant in acidic to neutral waters, but increases in alkaline waters. In water at pH 7.0 and 25 C, it had a half-life of 35 to 78 days [12].

[EXTOXNET]

For more information, see the complete profile for chlorpyrifos on the EXTOXNET site.

(2,4-Dichlorophenoxy)Acetic Acid

Abbreviation: 2,4-D Units: milligrams per kilogram (of body weight) or milligrams per liter or parts per million

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Summary

There are many forms or derivatives of 2,4-D including esters, amines, and salts. Unless otherwise specified, this document will refer to the acid form of 2,4-D. 2,4-D, a chlorinated phenoxy compound, functions as a systemic herbicide and is used to control many types of broadleaf weeds. It is used in cultivated agriculture, in pasture and rangeland applications, forest management, home, garden, and to control aquatic vegetation. It may be found in emulsion form, in aqueous solutions (salts), and as a dry compound. The product Agent Orange, used extensively throughout Vietnam, was about 50% 2,4-D. However, the controversies associated with the use of Agent Orange were associated with a contaminant (dioxin) in the 2,4,5-T component of the defoliant. The acid form is of slight to moderate toxicity. [EXTOXNET]

Methodology

KRWW grab samples were analyzed by the contract laboratory.

Environmental Impact

Effects on aquatic organisms: Some formulations of 2,4-D are highly toxic to fish while others are less so. For example, the LC50 ranges between 1.0 and 100 mg/L in cutthroat trout, depending on the formulation used. Channel catfish had less than 10% mortality when exposed to 10 mg/L for 48 hours [1,9]. Green sunfish, when exposed to 110 mg/L for 41 hours, showed no effect on swimming response. Limited studies indicate a half-life of less than 2 days in fish and oysters [24]. Concentrations of 10 mg/L for 85 days did not adversely affect the survival of adult Dungeness crabs. For immature crabs, the 96-hour LC50 is greater than 10 mg/L, indicating that 2,4-D is only slightly toxic. Brown shrimp showed a small increase in mortality at exposures of 2 mg/L for 48 hours [7,20]. [EXTOXNET]

Breakdown in soil and groundwater: 2,4-D has low soil persistence. The half-life in soil is less than 7 days [21]. Soil microbes are primarily responsible for its disappearance [20]. Despite its short half-life in soil and in aquatic environments, the compound has been detected in groundwater supplies in at least five States and in Canada [20]. Very low concentrations have also been detected in surface waters throughout the U.S. [23].

Breakdown in water: In aquatic environments, microorganisms readily degrade 2,4-D. Rates of breakdown increase with increased nutrients, sediment load, and dissolved organic carbon. Under oxygenated conditions the half-life is 1 week to several weeks [20]. [EXTOXNET]