

Background Information for Interpretation of Watershed Watch Parameters

This document provides background 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: Physical Parameters, Fecal Bacteria, Nutrient Parameters, Metal-Related Parameters, and Herbicides and Pesticides.

Text was compiled from the River Assessment Monitoring Project (RAMP) website of Kentucky Water Watch (<http://water.nr.state.ky.us/ww/ramp/> and subsidiary pages), Kentucky Water Watch's Water Resource Monitoring (WRM) web pages (<http://water.nr.state.ky.us/ww/waterres.htm> and subsidiary pages), 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.

PHYSICAL 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]

Methodology

In the laboratory, pH is an electrometric measurement. The computer aided titrimeter (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

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

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

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.

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

Solubility Of Oxygen in Fresh Water (100% Saturation)

Temperature (°C)	Dissolved Oxygen (PPM = mg/L)	Temperature (°C)	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
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]

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]

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 CaCO_3 (even though all the hardness may not be due to CaCO_3). [RAMP]

Classification of Water by Hardness Content

CaCO_3 (mg/L)	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 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 [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

Methodology

Although analysis can be performed by potentiometric titration using the computer aided titrimeter (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

Summary

Fluorides are compounds containing the element fluorine. Some of the most common of these compounds include the following: sodium fluoride (NaF), sodium silicofluoride (Na₂SiF₆), and calcium fluoride (CaF₂). 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 titrimeter (CAT) to measure fluoride. [RAMP]

Environmental Impact

Fluoride ions maybe 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.

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 $\mu\text{mho}/\text{cm}$. [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.

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 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]

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 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 signalled 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 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]

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 titrimer (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.

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.

NH_3 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: NO_3^- , NO_2^-

Units: milligrams per liter

Summary

Nitrogen is one of the most abundant elements. About 80 percent of the air we breath 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 N_2 , or as nitrate NO_3 , nitrite NO_2 or ammonia NH_3 . 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. 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, PO_4^{2-}

Units: milligrams per liter

Summary

Phosphorus is one of the key elements necessary for growth of plants and animals. Phosphates PO_4^{2-} 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]

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^-

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]

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 (SO_2), sulfate ions (SO_4^{2-}) and sulfides (S^-). 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. 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.

METAL-RELATED PARAMETERS

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]

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

Units: milligrams per liter or micrograms (μg) per liter

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]

Environmental Impact

See summary section.

Antimony Abbreviation: Sb

Units: milligrams per liter or micrograms (μg) per liter

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 $\mu\text{g}/\text{L}$, and the Kentucky domestic water supply source criterion (KDWSSC) for antimony is 146 $\mu\text{g}/\text{L}$. Kentucky acute and chronic aquatic life criteria for antimony are 9,000 $\mu\text{g}/\text{L}$ and 1,600 $\mu\text{g}/\text{L}$, 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

Units: milligrams per liter

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]

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

Units: milligrams per liter or micrograms (μg) per liter

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

Units: milligrams per liter or micrograms (μg) per liter

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

Units: milligrams per liter

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]

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

Units: milligrams per liter or micrograms (μg) per liter

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 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1991). The toxicity of chromium to aquatic life varies with the valence 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 $\mu\text{g/L}$ and 11 $\mu\text{g/L}$, whereas the criteria for trivalent chromium are 1,700 $\mu\text{g/L}$ and 210 $\mu\text{g/L}$, based on a total hardness concentration of 100 mg/L as CaCO_3 . [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.

Cobalt Abbreviation: Co

Units: milligrams per liter or micrograms (μg) per liter

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

Units: milligrams per liter or micrograms (μg) per liter

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

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 $\mu\text{g/L}$ and 12 $\mu\text{g/L}$, 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 $\mu\text{g/L}$, 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

Units: milligrams per liter

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]

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 Fe²⁺ and ferric Fe³⁺ 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 Fe²⁺ 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

Units: milligrams per liter or micrograms (µg) per liter

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 µg/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 µg/L and 3 µg/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

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

Units: milligrams per liter or micrograms (µg) per liter

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]

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

Units: milligrams per liter

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

Units: milligrams per liter

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]

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

Units: milligrams per liter or micrograms (μg) per liter

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]

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

Units: milligrams per liter or micrograms (µg) per liter

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

Units: milligrams per liter or micrograms (µg) per liter

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 powerplants 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 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

Units: milligrams per liter or micrograms (µg) per liter

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

Units: milligrams per liter or micrograms (µg) per liter

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]

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

Units: milligrams per liter

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

Units: milligrams per liter or micrograms (μg) per liter

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

Units: milligrams per liter or micrograms (μg) per liter

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]

Environmental Impact

See summary section.

Vanadium Abbreviation: V

Units: milligrams per liter or micrograms (μg) per liter

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 $\mu\text{g/L}$. Smoot and others (1991) reported a maximum dissolved vanadium concentration of 67 $\mu\text{g/L}$. [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]

Environmental Impact

See summary section.

Zinc Abbreviation: Zn

Units: milligrams per liter or micrograms (μg) per liter

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]

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 $\mu\text{g/L}$ and 106 $\mu\text{g/L}$, respectively. The SMCL for zinc is 5,000 $\mu\text{g/L}$. [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]

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]

HERBICIDES AND PESTICIDES

Atrazine 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. It is available as dry flowable, flowable liquid, liquid, water dispersible granular, and wettable powder formulations.

Trade Names: Aatrex, Aktikon, Alazine, Atred, Atranex, Atrataf, Atratol, Azinotox, Crisazina, Farmco Atrazine, G-30027, Gesaprim, Giffex 4L, Malermais, Primatol, Simazat, and Zeapos.

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. Atrazine is toxicity class III - slightly toxic. In November, 1994, the EPA initiated a Special Review which could result in use restrictions or cancellation of atrazine if health data warrant such action. Products containing atrazine must use the Signal Word CAUTION.

Chemical Class: triazine [EXTOXNET]

Toxicology

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 abdominal pain, diarrhea and vomiting, eye irritation, irritation of mucous membranes, and skin reactions [3]. At very high doses, rats show excitation followed by depression, slowed breathing, incoordination, muscle spasms, and hypothermia [3]. After consuming a large oral dose, rats exhibit muscular weakness, hypoactivity, breathing difficulty, prostration, convulsions, and death [16]. Atrazine is

a mild skin irritant. Rashes associated with exposure have been reported. The oral LD50 for atrazine is 3090 mg/kg in rats, 1750 mg/kg in mice, 750 mg/kg in rabbits, and 1000 mg/kg in hamsters. The dermal LD50 in rabbits is 7500 mg/kg and greater than 3000 mg/kg in rats [15,16]. The 1-hour inhalation LC50 is greater than 0.7 mg/L in rats. The 4-hour inhalation LC50 is 5.2 mg/L in rats [3,6]. Chronic toxicity: Some 40% of rats receiving oral doses of 20 mg/kg/day for 6 months died with signs of respiratory distress and paralysis of the limbs. Structural and chemical changes in the brain, heart, liver, lungs, kidney, ovaries, and endocrine organs were observed [3,16]. Rats fed 5 or 25 mg/kg/day of atrazine for 6 months exhibited growth retardation. In a 2-year study with dogs, 7.5 mg/kg/day caused decreased food intake and increased heart and liver weights. At 75 mg/kg/day, there were decreases in food intake and body weight gain, increased adrenal weight, lowered blood cell counts, and occasional tremors or stiffness in the rear limbs [3]. Reproductive effects: Dietary doses of atrazine given to rats on days 3, 6 and 9 of gestation up to about 50 mg/kg/day caused no adverse reproductive effects [3]. Teratogenic effects: Atrazine does not appear to be teratogenic. In mice, atrazine did not cause abnormalities in fetuses whose dams were given doses of 46.4 mg/kg/day during days 6 through 14 of gestation [3]. Mutagenic effects: The weight of evidence from more than 50 studies indicates that atrazine is not mutagenic [3]. Carcinogenic effects: Atrazine did not cause tumors when mice were given oral doses of 21.5 mg/kg/day from age 1 to 4 weeks, followed by dietary doses of 82 mg/kg for an additional 17 months. However, mammary tumors were observed in rats after lifetime administration of high doses of atrazine [3]. Thus, available data regarding atrazine's carcinogenic potential are inconclusive.

Organ toxicity: Lethal doses of atrazine in test animals have caused congestion and/or hemorrhaging to the lungs, kidneys, liver, spleen, brain, and heart [3]. Long-term consumption of high levels of atrazine has caused tremors, changes in organ weights, and damage to the liver and heart [3].

Fate in humans and animals: Atrazine is readily absorbed through the gastrointestinal tract. When a single dose of 0.53 mg atrazine was administered to rats by gavage, 20% of the dose was excreted in the feces within 72 hours. The other 80% was absorbed across the lining of the gastrointestinal tract into the bloodstream. After 72 hours, 65% was eliminated in the urine and 15% was retained in body tissues, mainly in the liver, kidneys, and lungs [3]. [EXTOXNET]

Methodology

KRWW grab samples were analyzed by the contract laboratory.

Environmental Impact

Ecological Effects:

Effects on birds: Atrazine is practically nontoxic to birds. The LD50 is greater than 2000 mg/kg in mallard ducks. At dietary doses of 5000 ppm, no effect was observed in bobwhite quail and ring-necked pheasants [15,16]. Effects on aquatic organisms: 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 [16].

Effects on other organisms: Atrazine is not toxic to bees [16].

Environmental Fate:

Breakdown in soil and groundwater: Atrazine is highly persistent in soil. Chemical hydrolysis, followed by degradation by soil microorganisms, accounts for most of the breakdown of atrazine. Hydrolysis is rapid in acidic or basic environments, but is slower at neutral pHs. Addition of organic material increases the rate of hydrolysis. Atrazine can persist for longer than 1 year under dry or cold conditions [21]. 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 [23]. 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) [24].

Breakdown in vegetation: Atrazine is absorbed by plants mainly through the roots, but also through the foliage. Once absorbed, it is translocated upward and accumulates in the growing tips and the new leaves of the plant. In susceptible plant species, atrazine inhibits photosynthesis. In tolerant plants, it is metabolized [6]. Most crops can be planted 1 year after application of atrazine. Atrazine increases the uptake of arsenic by treated plants [16].
[EXTOXNET]

Chlorpyrifos Abbreviation: -----

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

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. It is available as granules, wettable powder, dustable powder and emulsifiable concentrate.

Trade Names: Brodan, Detmol UA, Dowco 179, Dursban, Empire, Eradex, Lorsban, Paqeant, Piridane, Scout, and Stipend.

Regulatory Status: The EPA has established a 24-hour reentry interval for crop areas treated

with emulsifiable concentrate or wettable powder formulations of chlorpyrifos unless workers wear protective clothing. Chlorpyrifos is toxicity class II - moderately toxic. Products containing chlorpyrifos bear the Signal Word WARNING or CAUTION, depending on the toxicity of the formulation. It is classified as a General Use Pesticide (GUP).

Chemical Class: organophosphate. [EXTOXNET]

Toxicology

Acute toxicity: 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]. Symptoms of acute exposure to organophosphate or cholinesterase-inhibiting compounds may include the following: numbness, tingling sensations, incoordination, headache, dizziness, tremor, nausea, abdominal cramps, sweating, blurred vision, difficulty breathing or respiratory depression, and slow heartbeat. Very high doses may result in unconsciousness, incontinence, and convulsions or fatality. Persons with respiratory ailments, recent exposure to cholinesterase inhibitors, cholinesterase impairment, or liver malfunction are at increased risk from exposure to chlorpyrifos. Some organophosphates may cause delayed symptoms beginning 1 to 4 weeks after an acute exposure which may or may not have produced immediate symptoms [2]. In such cases, numbness, tingling, weakness, and cramping may appear in the lower limbs and progress to incoordination and paralysis. Improvement may occur over months or years, and in some cases residual impairment will remain [2]. Plasma cholinesterase levels activity have been shown to be inhibited when chlorpyrifos particles are inhaled [8]. The oral LD50 for chlorpyrifos in rats is 95 to 270 mg/kg [2,13]. The LD50 for chlorpyrifos is 60 mg/kg in mice, 1000 mg/kg in rabbits, 32 mg/kg in chickens, 500 to 504 mg/kg in guinea pigs, and 800 mg/kg in sheep [2,13,44]. The dermal LD50 is greater than 2000 mg/kg in rats, and 1000 to 2000 mg/kg in rabbits [2,13,45]. The 4-hour inhalation LC50 for chlorpyrifos in rats is greater than 0.2 mg/L [46].

Chronic toxicity: Repeated or prolonged exposure to organophosphates may result in the same effects as acute exposure including the delayed symptoms. Other effects reported in workers repeatedly exposed include impaired memory and concentration, disorientation, severe depressions, irritability, confusion, headache, speech difficulties, delayed reaction times, nightmares, sleepwalking, and drowsiness or insomnia. An influenza-like condition with headache, nausea, weakness, loss of appetite, and malaise has also been reported [8]. When technical chlorpyrifos was fed to dogs for 2 years, increased liver weight occurred at 3.0 mg/kg/day. Signs of cholinesterase inhibition occurred at 1 mg/kg/day. Rats and mice given technical chlorpyrifos in the diet for 104 weeks showed no adverse effects other than cholinesterase inhibition [43]. Two-year feeding studies using doses of 1 and 3 mg/kg/day of chlorpyrifos in rats showed moderate depression of cholinesterase. Cholinesterase levels recovered when the experimental feeding was discontinued [2]. Identical results occurred in a 2-year feeding study with dogs. No long term health effects were seen in either the dog or rat study [2,47]. A measurable change in plasma and red blood cell cholinesterase levels was seen in workers exposed to chlorpyrifos spray. Human volunteers who ingested 0.1 mg/kg/day of chlorpyrifos for 4 weeks showed significant plasma cholinesterase inhibition [47].

Reproductive effects: Current evidence indicates that chlorpyrifos does not adversely affect reproduction. In two studies, no effects were seen in animals tested at dose levels up to 1.2 mg/kg/day [8]. No effects on reproduction occurred in a three-generation study with rats fed

dietary doses as high as 1 mg/kg/day [43,47]. In another study in which rats were fed 1.0 mg/kg/day for two generations, the only effect observed was a slight increase in the number of deaths of newborn offspring [2]. Teratogenic effects: Available evidence suggests that chlorpyrifos is not teratogenic. No teratogenic effects in offspring were found when pregnant rats were fed doses as high as 15 mg/kg/day for 10 days. When pregnant mice were given doses of 25 mg/kg/day for 10 days, minor skeletal variations and a decrease in fetal length occurred [43,45]. No birth defects were seen in the offspring of male and female rats fed 1.0 mg/kg/day during a three-generation reproduction and fertility study [2,47].

Mutagenic effects: There is no evidence that chlorpyrifos is mutagenic. No evidence of mutagenicity was found in any of four tests performed [43].

Carcinogenic effects: There is no evidence that chlorpyrifos is carcinogenic. There was no increase in the incidence of tumors when rats were fed 10 mg/kg/day for 104 weeks, nor when mice were fed 2.25 mg/kg/day for 105 weeks [43]. Organ toxicity: Chlorpyrifos primarily affects the nervous system through inhibition of cholinesterase, an enzyme required for proper nerve functioning. Fate in humans and animals: Chlorpyrifos is readily absorbed into the bloodstream through the gastrointestinal tract if it is ingested, through the lungs if it is inhaled, or through the skin if there is dermal exposure [8]. In humans, chlorpyrifos and its principal metabolites are eliminated rapidly [2]. After a single oral dose, the half-life of chlorpyrifos in the blood appears to be about 1 day [41]. Chlorpyrifos is eliminated primarily through the kidneys [8]. Following oral intake of chlorpyrifos by rats, 90% is removed in the urine and 10% is excreted in the feces [13]. It is detoxified quickly in rats, dogs, and other animals [8]. The major metabolite found in rat urine after a single oral dose is trichloropyridinol (TCP). TCP does not inhibit cholinesterase and it is not mutagenic [8]. Chlorpyrifos does not have a significant bioaccumulation potential [8]. Following intake, a portion is stored in fat tissues but it is eliminated in humans, with a half-life of about 62 hours [2]. When chlorpyrifos (Dursban) was fed to cows, unchanged pesticide was found in the feces, but not in the urine or milk [48]. However, it was detected in the milk of cows for 4 days following spray dipping with a 0.15% emulsion. The maximum concentration in the milk was 0.304 ppm [2]. In a rat study, chlorpyrifos did not accumulate in any tissue except fat [49]. [EXTOXNET]

Methodology

KRWW grab samples were analyzed by the contract laboratory.

Environmental Impact

Ecological Effects:

Effects on birds: Chlorpyrifos is moderately to very highly toxic to birds [43]. Its oral LD50 is 8.41 mg/kg in pheasants, 112 mg/kg in mallard ducks, 21.0 mg/kg in house sparrows, and 32 mg/kg in chickens [8,13,43]. The LD50 for a granular product (15G) in bobwhite quail is 108 mg/kg [13,43]. At 125 ppm, mallards laid significantly fewer eggs [43]. There was no evidence of changes in weight gain, or in the number, weight, and quality of eggs produced by hens fed dietary levels of 50 ppm of chlorpyrifos [8].

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].

Effects on other organisms: Aquatic and general agricultural uses of chlorpyrifos pose a serious hazard to wildlife and honeybees [13,48].

Environmental Fate:

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].

Breakdown in vegetation: Chlorpyrifos may be toxic to some plants, such as lettuce [36]. Residues remain on plant surfaces for approximately 10 to 14 days. Data indicate that this insecticide and its soil metabolites can accumulate in certain crops [8]. [EXTOXNET]

(2,4-Dichlorophenoxy)Acetic Acid Abbreviation: 2,4-D

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

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.

Formulation: It may be found in emulsion form, in aqueous solutions (salts), and as a dry compound.

Commercial Names for Products Containing 2,4-D: Aqua-Kleen, Barrage, Lawn-Keep, Malerbane, Planotox, Plantgard, Savage, Salvo, Weedone, and Weedtrine-II.

Regulatory Status: 2,4-D is a General Use Pesticide (GUP) in the U.S. The diethylamine salt is toxicity class III-slightly toxic orally, but toxicity class I- highly toxic by eye exposure. It bears the Signal Word DANGER B POISON because 2,4-D has produced serious eye and skin irritation among agricultural workers.

Chemical Class: phenoxy compound [EXTOXNET]

Toxicology

Toxicological Effects:

Acute toxicity: The acid form is of slight to moderate toxicity. The oral LD50 of 2,4-D ranges from 375 to 666 mg/kg in the rat, 370 mg/kg in mice, and from less than 320 to 1000 mg/kg in guinea pigs. The dermal LD50 values are 1500 mg/kg in rats and 1400 mg/kg in rabbits, respectively [1,5,7]. In humans, prolonged breathing of 2,4-D causes coughing, burning, dizziness, and temporary loss of muscle coordination [1]. Other symptoms of poisoning can be fatigue and weakness with possible nausea. On rare occasions following high levels of exposure, there can be inflammation of the nerve endings with muscular effects [25].

Chronic toxicity: Rats given high amounts, 50 mg/kg/day, of 2,4-D in the diet for 2 years showed no adverse effects. Dogs fed lower amounts in their food for 2 years died, probably because dogs do not excrete organic acids efficiently. A human given a total of 16.3 g in 32 days therapeutically, lapsed into a stupor and showed signs of incoordination, weak reflexes, and loss of bladder control [1,5,7].

Reproductive effects: High levels of 2,4-D (about 50 mg/kg/day) administered orally to pregnant rats did not cause any adverse effects on birth weights or litter size. Higher doses (188 mg/kg/day) resulted in fetuses with abdominal cavity bleeding and increased mortality [1,5,7]. DNA synthesis in the testes was significantly inhibited when mice were fed large amounts (200 mg/kg/day) of 2,4-D [7]. The evidence suggests that if 2,4-D causes reproductive effects in

animals, this only occurs at very high doses. Thus reproductive problems associated with 2,4-D are unlikely in humans under normal circumstances. Teratogenic effects: 2,4-D may cause birth defects at high doses. Rats fed 150 mg/kg/day on days 6 to 15 of pregnancy had offspring with increased skeletal abnormalities, such as delayed bone development and wavy ribs [7].

This suggests that 2,4-D exposure is unlikely to be teratogenic in humans at expected exposure levels. Mutagenic effects: 2,4-D has been very extensively tested and was found to be nonmutagenic in most systems. 2,4-D did not damage DNA in human lung cells. However, in one study, significant effects occurred in chromosomes in cultured human cells at low exposure levels [26]. The data suggest that 2,4-D is not mutagenic or has low mutagenic potential.

Carcinogenic effects: 2,4-D fed to rats for 2 years caused an increase in malignant tumors [7]. Female mice given a single injection of 2,4-D developed cancer (reticulum-cell sarcomas) [7]. Another study in rodents shows a low incidence of brain tumors at moderate exposure levels (45 mg/kg/day) over a lifetime [1,7]. However, a number of questions have been raised about the validity of this evidence and thus about the carcinogenic potential of 2,4-D. In humans, a variety of studies give conflicting results. Several studies suggest an association of 2,4-D exposure with cancer. An increased occurrence of non-Hodgkin's lymphoma was found among a Kansas and Nebraska farm population associated with the spraying of 2,4-D [25,27]. Other studies done in New Zealand, Washington, New York, Australia, and on Vietnam veterans from the U.S. were all negative. There remains considerable controversy about the methods used in the various studies and their results [28]. Thus, the carcinogenic status of 2,4-D is not clear. Organ toxicity: Most symptoms of 2,4-D exposure disappear within a few days, but there is a report of liver dysfunction from long-term exposure [1,25].

Fate in humans and animals: The absorption of 2,4-D is almost complete in mammals after ingestion and nearly all of the dose is excreted in the urine. The compound is readily absorbed through the skin and lungs. Men given 5 mg/kg excreted about 82% of the dose as unchanged 2,4-D. The half-life is between 10 and 20 hours in living organisms. There is no evidence that 2,4-D accumulates to significant level in mammals or in other organisms [20]. Between 6 and 8 hours after doses of 1 mg/kg, peak concentrations of 2,4-D were found in the blood, liver, kidney, lungs, and spleen of rats. There were lower levels in muscle and brain. After 24 hours, there were no detectable tissue residues. Only traces of the compound have been found in the milk of lactating animals for 6 days following exposure. 2,4-D passes through the placenta in pigs and rats. In rats, about 20% was detected in the uterus, placenta, fetus, and amniotic fluid [27]. Chickens given moderate amounts of 2,4-D in drinking water from birth to maturity had very low levels of the compound in eggs [7]. [EXTOXNET]

Methodology

KRWW grab samples were analyzed by the contract laboratory.

Environmental Impact

Ecological Effects:

Effects on birds: 2,4-D is slightly toxic to wildfowl and slightly to moderately toxic to birds. The LD50 is 1000 mg/kg in mallards, 272 mg/kg in pheasants, and 668 mg/kg in quail and pigeons [5-7]. 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].

Effects on other organisms: Moderate doses of 2,4-D severely impaired honeybees brood production. At lower levels of exposure, exposed bees lived significantly longer than the controls. The honeybee LD50 is 0.0115 mg/bee [6,7].

Environmental Fate:

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].

Breakdown in vegetation: 2,4-D interferes with normal plant growth processes. Uptake of the compound is through leaves, stems, and roots. Breakdown in plants is by a variety of biological and chemical pathways [10]. 2,4-D is toxic to most broad leaf crops, especially cotton, tomatoes, beets, and fruit trees [7]. [EXTOXNET]