

Physicochemical Parameters of Natural Waters

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Introduction

All freshwater bodies are inter-connected to the oceans, the atmosphere, and aquifers via a complex hydrological cycle. Wetlands, icecaps and biopheric water also participate in the continuous conveyance of water on planet Earth. The Earth's hydrological cycle is driven by evaporation and gravity on which ecosystems and human societies depend. Growing populations may put stresses on natural waters by impairing both the quality of the water and the hydrological budget. The fate and transport of many anthropogenic pollutants are determined by not only hydrological cycles, but also physicochemical processes. In order to mitigate the impact human societies have on natural waters, it is becoming increasingly important to implement comprehensive monitoring regimes. Monitoring water resources will quantify water quality, identify impairments, and help policy makers make land use decisions that will not only preserve natural areas, but improve the quality of life. We discuss here in situ environmental parameters that can be measured remotely by deployable sensors.

pH

The pH of natural water can provide important information about many chemical and biological processes and provides indirect correlations to a number of different impairments. The pH is the measurement of the acid/base activity in solution, specifically it is the negative common logarithm of the activity/concentration of hydrogen ions,

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

In natural waters, the pH scale runs from 0 to 14. A pH value of 7 is neutral, a pH less than 7 is acidic and greater than 7 represents base saturation or alkalinity.

Pure water free of dissolved gases will naturally become ionized;



The actual number of water molecules that will ionize is relatively very small with the amount of hydrogen ions $[H^+]$ being equal to the amount hydroxide ion $[OH^-]$. At room temperature the concentration of $[H^+]$ in pure water will be 1×10^{-7} moles per liter. A pH of 7 is neutral because the $-\log(1 \times 10^{-7})$ is 7 by definition.

In unpolluted or pure waters, the pH is governed by the exchange of carbon dioxide with the atmosphere. Carbon dioxide is soluble in water and the amount of CO_2 that will dissolve in the water will be a function of temperature and the concentration of CO_2 in the air. As the gaseous CO_2 becomes aqueous, the CO_2 will be converted into H_2CO_3 which will acidify the water to a pH of about 6. If any alkaline earth metals such as sodium are present, the carbonates and bicarbonate formed from the solubilization of CO_2 will interact with sodium increasing the alkalinity shifting the pH up over 7.

Lower values in pH are indicative of high acidity, which can be caused by the deposition of acid forming substances in precipitation. A high organic content will tend to decrease the pH because of the carbonate chemistry. As microorganisms break down organic material, the by product will be CO_2 that will dissolve and equilibrate with the water forming carbonic acid (H_2CO_3). Other organic acids such as humic and fulvic acid can also result from organic decomposition.

In addition to organic acids and the carbonate chemistry, the acidity of natural waters could also be controlled by mineral acids produced by the hydrolyses of salts of metals such as aluminum and iron.

Most metals will become more soluble in water as the pH decreases. For example, sulfur in the atmosphere from the burning of coal will create acid rain. The acid rain will dissolve metals such as copper, lead, zinc and cadmium as the rain runs off of man made structures and into bodies of water. The excesses of dissolved metals in solution will negatively affect the health of the aquatic organisms.

The alkalinity of natural waters is controlled by the concentration of hydroxide and represented by a pH greater than 7. This is usually an indication of the amount of carbonates, and bicarbonates that shift the equilibrium producing $[OH^-]$. Other contributors to an alkaline pH include boron, phosphorous, nitrogen containing compounds and potassium

Changes in pH can be indicative of an industrial pollutant, photosynthesis or the respiration of algae that is feeding on a contaminant. Most ecosystems are sensitive to changes in pH and the monitoring of pH has been incorporated into the environmental laws of most industrialized countries.

pH is typically monitored for assessments of aquatic ecosystem health, recreational waters, irrigation sources and discharges, live stock, drinking water sources, industrial discharges, intakes, and storm water runoff.

Dissolved Oxygen

Dissolved oxygen (DO) is essential to all forms of aquatic life including the organisms that break down man-made pollutants. Oxygen is soluble in water and the oxygen that is dissolved in water will equilibrate with the oxygen in atmosphere. Oxygen tends to be less soluble as temperature increases. The DO of fresh water at sea level will range from 15 mg/l at 0° C to 8mg/l at 25° C. Concentrations of unpolluted fresh water will be close to 10 mg/l.

In general, the concentration of dissolved oxygen will be the result of biological activity. Photosynthesis of some aquatic plants will increase the DO during day light hours and the DO levels will fall during the nighttime hours. In natural waters, man-made contamination, or natural organic material will be consumed by microorganisms. As this microbial activity increases, oxygen will be consumed out of the water by the organisms to facilitate their digestion process. The water that is near the sediment will be depleted of oxygen for this reason.

In waters contaminated with fertilizers, suspended material, or petroleum waste, microorganisms such as bacteria will break down the contaminants. The oxygen will be consumed and the water will become anaerobic. Typically DO levels less than 2 mg/l will kill fish.

In situ DO sensors are usually membrane electrodes while laboratory methods are titrations.

Other indirect laboratory tests for assessing the DO is the biological oxygen demand (BOD) and the chemical oxygen demand (COD). The BOD is the amount of oxygen required to biologically break down a contaminant and the COD is the amount of oxygen that will be consumed directly by an oxidizing chemical contaminant.

Electrical Conductivity

Electrical conductivity (EC) in natural waters is the normalized measure of the water's ability to conduct electric current. This is mostly influenced by dissolved salts such as sodium chloride and potassium chloride. The common unit for electrical conductivity is Siemens per meter (S/m). Most freshwater sources can range between 0.001 to 0.1 S/m.

The source of EC may be an abundance of dissolved salts due to poor irrigation management, minerals from rain water run off, or other discharges.

EC is also the measure of the water quality parameter "Total Dissolved Solids" (TDS) or salinity. At about 0.3 S/m is the point as which the health of some crops and fresh water aquatic organisms will to be affected by the salinity.

Field measurements of EC reflect the amount of total dissolved solids (TDS) in natural waters. The relationship between TDS and EC can be described by the equation;

$$\text{TDS (mg/L)} \approx \text{EC (mS/cm)} \times 640$$

Salinity refers to the presence of dissolved inorganic ions such as Mg^+ , Ca^{++} , K^+ , Na^+ , Cl^- , SO_4^{4-} , HCO_3^- and CO_3^{2-} in the aqueous solution or soil matrix. The salinity is quantified as the total concentration of soluble salts and is expressed in terms of electrical conductivity. There exists no in-situ salinity probe (based on EC alone) that can distinguish between the different ions that may be present. When salts such as sodium chloride are in their solid form, they exist as crystals. Within the salt crystal, the sodium and the chlorine atoms are joined together in what is called an ionic chemical bond. An ionic chemical bond holds the atoms tightly together because the sodium atom will give up an electron to the chlorine thus ionizing the atoms. If an atom like sodium gives up an electron, it is said to be a positively charged ion (also called a cation). If an atom such as chlorine receives an electron, it is said to be a negatively charged ion (also called an anion and is given the suffix ide, like chloride). The sodium and the chloride ions comfortably arrange themselves into a stacked like configuration called a crystal lattice. The sodium chloride crystal lattice has a zero net charge.

Water will dissolve the sodium chloride crystal lattice and physically separate the two ions. Once in solution, the sodium ion and the chloride ion will float around in the solution separately and randomly. This is generally true for all inorganic salts. Once in a solution, the ions will float apart and become two separate species dissolved in the water. Typical, charged ions exist separately in a solution. If the water dries up, the cations and the anions will find each other and fuse back into a crystal lattice with a zero net charge.

Temperature

Many aquatic organisms are sensitive to changes in water temperature. Temperature is an important water quality parameter and is relatively easy to measure. Water bodies will naturally show changes in temperature seasonally and daily; however, man made changes to stream water temperature will affect fish's ability to reproduce. Many lake and rivers will exhibit vertical temperature gradients as the sun will warm the upper water while deeper water will remain cooler.

Fish friendly dams will have selective water releases where the temperature of the stream can be controlled by the water depth of release. In the summer, the water could be released from the bottom of the dam and in the winter the water is released from the top. This selective release will mitigate the impact the dam will have on the water temperature.

Some streams will increase in temperature as the stream water moves down stream through urban, industrial and agricultural areas. This man made temperature loading can be characterized by the Total Maximum Daily Load (TMDL). For example, a stream in forested head waters will be at a suitable temperature for the native aquatic life. As the stream meanders through pasture land, the riparian vegetation will not be abundant enough to effectively shade the stream. Once the stream makes in to urban area, the stream may become channeled to make room for housing. Removing the natural meander from a stream will increase the velocity of the water which will cause erosion further degrading the quality of the water. Impervious structures such as parking lots, roads and

buildings will prevent the infiltration of rainwater into the groundwater. Instead of being fed from cool groundwater, the stream will receive run off after rain events further degrading the quality of the water and increasing the temperature.

Environmental policies require the monitoring of stream water temperature. In most urban and industrial locations, environmental permits are required to help minimize the temperature loading to streams.

Turbidity

Turbidity or Total Suspended Solids (TSS) is the material in water that affects the transparency or light scattering of the water. The measurement unit used to describe turbidity is Nephelometric Turbidity Unit (NTU). The range for natural water is 1 to 2000 NTU. There are a number of manual field methods for measuring TSS, such as Secchi discs where a metal disc is lowered in the water with a calibration line. The depth at which the disc disappears is directly correlated to TSS. In situ electronic turbidity sensors measure the backscatter of infrared light to determine the NTU of the water.

TSS is typically composed of fine clay or silt particles, plankton, organic compounds, inorganic compounds or other microorganisms. These suspended particles range in size from 10 nm to 0.1 mm although in standardized laboratory tests, TSS is defined as the material that cannot pass through a 45 μm diameter filter. TSS as well as TDS can be influenced by changes in pH. Changes in the pH will cause some of the solutes to precipitate or will affect the solubility of the suspended matter.

The manmade sources of TSS include erosion, stormwater runoff, industrial discharges, microorganisms, and eutrophication. Many fish species are sensitive to prolonged exposure to TSS and monitoring of TSS is an important criteria for assessing the quality of water.

Total Nitrogen

Nitrogen (N_2) is essential to life on Earth and is the most abundant element in Earth's atmosphere. Biological compounds such as proteins, amino acids, and nucleic acids contain nitrogen. In the environment, plants and micro organisms convert N_2 into a different oxidation states where it becomes part of the nitrogen cycle. The major inorganic oxidation states include nitrate ion (NO_3^-), nitrite ion (NO_2^-), ammonia (NH_3), and ammonium ion (NH_4^+). Total nitrogen in natural waters refers to the sum of organic nitrogen containing compounds, and the inorganic nitrogen oxidation states present in solution. Total nitrogen can be calculated from the sum of the total kjeldahl nitrogen (organic and reduced nitrogen) ammonia, nitrate and nitrite. Acceptable ranges of total nitrogen are 2 to 6 mg/L.

There are many sources of total nitrogen in the environment. Automobile exhaust contains nitrous oxide which will enter surface water through precipitation processes. Storm water runoff, livestock, sewage discharge, fertilizers and waste water discharges all contribute to the abundance of total nitrogen in the environment. Natural sources are the natural break down of plant and animal material.

Nitrate

Nitrate ion (NO_3^-) is the common form of nitrogen in natural waters. Nitrite (NO_2^-) will oxidize into nitrate after entering an aerobic regime.



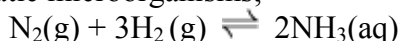
Similarly, plants and microorganisms will reduce nitrate into nitrite but nitrite ion will quickly oxidizes back into nitrate once it reenters the water. Natural sources of nitrate are igneous rock, plant decay and animal debris. Nitrate levels over 5 mg/L in natural waters normally indicates man made pollution, 200 mg/L is an extreme level. Man made sources of include, fertilizers, livestock, urban runoff, septic tanks, and waste water discharges. In general, nitrates are less toxic to people than ammonia or nitrite however at high levels, nitrate will become toxic especially to infants. Methemoglobinemia is nitrate poisoning where high levels of nitrate enter in hemoglobin will oxidize the ferric iron II into ferrous iron III inhibiting the blood's ability to carry oxygen.

In the environment, nitrate will become toxic to fish at about 30 mg/L. Nitrate pollution will cause eutrophication of a stream where algae and aquatic plant growth will consume the oxygen and increase the TSS of the water. Eutrophication is usually the result of nitrate and phosphate contamination and is a significant reduction of water quality.

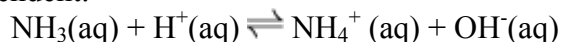
Nitrate can exist naturally in groundwater but can increase dramatically on irrigated lands if the irrigation operation is not managed properly. Groundwater contaminated with nitrate can contaminate sources of drinking water in wells, and will contaminate the surface water as the ground water recharges streams and lakes. As more land is converted into agricultural land and as urban areas expand, nitrate monitoring is an important tool in accessing locating and mitigating man made sources of nitrate.

Ammonia

In unpolluted water, trace amounts of ammonia (NH_3) are present from the reduction of atmospheric nitrogen by aquatic microorganisms;



Ammonia also occurs naturally from the breakdown of nitrogenous organic compounds in water and soil and the breakdown of biota. Ammonia is at equilibrium with ammonium ion (NH_4^+) and the equilibrium reaction between ammonia and ammonium ion (see ammonium) is pH dependent.



At a higher pH, ammonia will be the predominate form and at a lower pH the ammonia ion will be predominate. Total ammonia is the sum of the two forms. Unionized ammonia is much more volatile than the ionized form, as the pH increases, NH_3 will leave the aqueous solution by volatilization. Natural seasonal fluctuations can occur from the death and decay of phytoplankton, bacteria and other aquatic organisms. The bottom anoxic waters of lakes may contain higher levels of ammonia as the decay material settles to the bottom.

Natural unpolluted waters can be 0 to 3 mg/L. Higher concentrations correspond to pollution and can be toxic to aquatic organisms. Man made sources of ammonia can come from industrial discharges, particularly from the pulp and paper industry. Other man made sources of ammonia include fertilizer runoff, sewage releases into natural waters, and industrial releases.

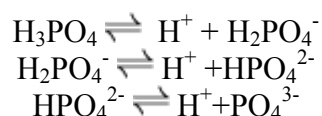
Ammonium

Ammonium (NH_4^+) is the ionized form of ammonia and will equilibrate with ammonia in solution (see ammonia). The source of ammonium in the environment mirror that of ammonia. At a pH of less 8, over 95% of the total ammonia is in the ammonium ion form at 15 degrees Celsius. Most vertebrates including mammals will convert ammonium into urea where it can be excreted or bioaccumulated.

Ammonium can be measured in situ with an ion selective electrode. Ammonium ion is less toxic than ammonia and because it is the most abundant form at the typical pH of surface water. Ammonium ion will however become toxic at higher concentrations.

Phosphate

Phosphate (orthophosphate or total reactive phosphorus (TRP) is the ionized form of Orthophosphoric acid. In solution and in natural waters, phosphate ion will have many forms and will be at a pH dependent equilibrium;



The higher the pH, the more PO_4^{3-} will form from the deprotonation of HPO_4^{2-} . Unlike total ammonia, phosphates are less soluble and less volatile, therefore, phosphates will form salts with sodium and calcium and fall out of solution to accumulate in the sediment. Phosphates ions in natural waters will exist in solution in its ionized form, as salts, in organic form or as a particulate species. Higher concentrations rarely occur, because after it enters a water system, it will be rapidly up taken by plants.

In general, phosphorous is an essential nutrient to living organisms (see total phosphorus). In unpolluted waters, phosphorous can enter a water system from the weathering of phosphorous bearing rocks and minerals. In areas of high volcanic activity, phosphorous may be naturally abundant in the soils.

Man made sources of phosphate in the environment include domestic and industrial discharges, agricultural runoff where fertilizers are used, and changes in land use in areas where phosphorous is naturally abundant in the soil.

In general, phosphates are not very toxic to people or other living organisms. Like nitrogen containing compounds, the main environmental impact associated with phosphate pollution is eutrophication. High levels of phosphorus will be quickly consumed by plant and microorganisms, impairing the water by depleting the dissolved

oxygen and increasing the turbidities. These impairments will kill or harm fish and other aquatic organisms.

In the late 1970's, phosphates were phased out of domestic detergents. Prior to the removal of phosphates, domestic sewerage would cause very large algal blooms in lakes, rivers and streams.

Total Phosphorus

The term “total phosphorus” corresponds to the total dissolved and filterable phosphorus in all of its forms in solution including organic phosphorus. Like phosphates, the major environmental impact associated with the total phosphorus parameter is eutrophication of surface water (see phosphate). The total phosphorus parameter may be chosen over phosphates because in most water systems, the total phosphorus concentration correlates well to other water quality parameters particularly algae growth and chlorophyll.

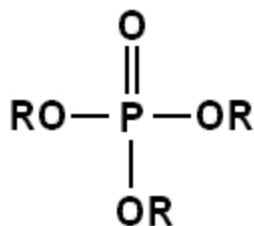
Some organic forms of phosphorus are relatively unreactive and would not be detected by an analyses from phosphates. Organic phosphorus can dramatically affect the algal growth, therefore, it may be more appropriate to evaluate total phosphorus as opposed to the reactive phosphates. Some microorganisms will uptake only inorganic phosphates, in this case, measurement of reactive phosphates may be a better indicator of water quality than total phosphorus. Ideally, phosphates and total phosphorus should both be evaluated when assessing a water system.



Eutrophication from phosphorus contamination, (photo provided by the US EPA).

The fate and transport of phosphorus and phosphorus containing compounds in the environment is driven by the phosphorus cycle. The phosphorus cycle is primary driven by the uptake of phosphorus by living organisms. Phosphorus and phosphorus containing compounds act as energy conveyers for living organisms. Once the organism dies,

phosphorus will be reintroduced to the soil and water where it is up taken again by another organism. The residence time in any particular body of water will be a function of pH, temperature, and climate. The most common source of phosphate pollution is poor management of agricultural irrigation and run off.



Orthophosphate ester (organic phosphate). Where R can be an organic radical or H.

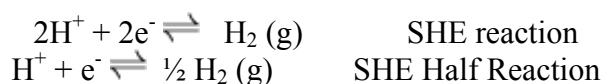
Oxidation Reduction Potential.

Oxidation reduction potential (ORP) or redox is the activity or strength of oxidizers or reducers in solution. ORP measurements are used to quantify water disinfection procedures and access breakdown of pollutants. Like pH, ORP is not the direct concentration measurement of the analyte, but the activity. The common unit for ORP is millivolts. If the potential is positive, than the solution is oxidizing where as a negative ORP is a reducing solution. The more positive, the greater the affinity for electrons.

Reduction/oxidation (redox) reactions are electrochemical reactions that involve the migration of electrons from one species to another. An oxidizer is a chemical species that receive electrons, and reducers are the chemical species that donate electrons. The table below may provide some useful insight by summarizing the terminology.

<u>Reducers</u>	<u>Oxidizers</u>
Donate electrons	Accept electrons
Reductants	Oxidants
Gets Oxidized	Gets Reduced
Negative Voltage (or neutral)	Positive Voltage (or neutral)
Reducing Agent	Oxidizing Agent
Sodium sulfite	Chlorine
Sodium bisulfate	Ozone
Hydrogen Sulfide	Hydrogen Peroxide

Like alkalinity and bassisity, one is at the expense of the other. ORP is not measured by an absolute direct measurement, but rather it is measured by the comparison to a reference Redox reaction. By convention, most ORP measurements are based on the comparison to a Standard Hydrogen Electrode (SHE) which is arbitrarily assigned to be “0” Volts ORP.



In the process of photosynthesis, organic compounds that contain carbon, nitrogen

and sulfur, will be reduced. Chemical energy is stored in the reduced species which also includes organic pollutants. Microorganisms will catalyze the reduced chemical species to obtain energy for their metabolism and other cellular processes. Oxygen is the most favorable oxidant used by many organisms. To obtain chemical energy, the organism will take the electrons away from the reduced chemical species, give it the electron accepting O_2 reducing it to H_2O . Other oxidants in natural waters include NO_3^- and SO_4^{2-} . The dominant organism in a micro-environment will be the organism that can utilize the best oxidant available. The best oxidant for the organism will be the one that has the highest ORP.

Many environmental pollutants biodegrade in this fashion and need strong oxidizing agents to facilitate the process. For example, injecting oxygen or an oxygen releasing compound into the groundwater will chemically breakdown subsurface pollutants such as petroleum products and other organic pollutants. In groundwater remediation operations involving organic pollutant, aerobic and a strongly positive ORP conditions need to be achieved.

Up until the 1970's, it was common practice for dry cleaners to dump the spent dry cleaning solvent on the ground to get rid of it. Dry cleaning solvents contain chlorinated solvent that can be extremely toxic to aquatic life and people. Because the chlorinated solvents are more dense than water, they will quickly migrate downward to the bedrock. The solvent will slowly solublize into water where it is then transported to the surface water. In some cases, groundwater contaminate plumes will travel many miles over the course of many decades before it seeps into a river or lake. Most of the chlorinated solvents seeping into water bodies today, were dumped in the 1940s and 50s.

In chlorinated solvents, the chlorine-carbon chemical bond is very strong and resistant to break down. New remediation techniques for chlorinated compounds involve anaerobic process with negative ORPs species such as reduced iron (Fe^0 or Fe^{II}) These reducing agents will donate electrons to the chlorine atom thus breaking the chlorine carbon chemical bond. Once the chemical bond is broken, the chlorinated solvent will chemically degrade into more benign species.

ORP measurements are useful for drinking water, swimming pools, fruit and vegetable disinfection, metal etching, waste water treatment and other applications. ORP targets in mV can be set to eliminate pathogens such as E. Coli, and other harmful bacteria and viruses. An oxidizing chemical species pulls electrons away from cell membranes oxidizing the cell quickly causing death to the pathogen.

The higher the ORP, the faster the organism will die. For example an ORP of 665 mV will kill E. Coli within a few seconds, where as an ORP of 485 will eliminate the E. Coli within a day.

Consequences of Water Quality Problems and Poor Policies

Ohio's Cuyahoga River first caught on fire in the 1930's and would catch on fire every few of years until the late 1960s. In 1969, levels of oil sheen and floating debris got so bad that when the river caught on fire it caused damage to bridges and boats. This event led to environmental reforms in the United States which included the Clean Water Act, and the formation of the US Environmental Protection Agency.



The 1952 burning of the Cuyahoga River, Cleveland Ohio. Photo provided by the US EPA.

Between 1942 and 1952, the Hooker Chemical Company buried more than 21,000 tons of chlorinated benzenes, dioxin tricholophenols and other chemicals into a land fill near Love Canal, New York. In 1952, as a gift to the school system, Hooker sold 16 acres of the land fill to the local school system for the new elementary school and new homes at a reduced price. By 1958 the fumes coming up from the ground were so toxic that it caused severe burns, illness, blisters and death. Eventually, the US Federal Government spent millions of dollars relocating the residents and hundreds of millions of dollars cleaning up the site. This environmental disaster ignited many law suits and the creation of "Superfund" regulations.

Perhaps one of the worst environmental events occurred in 1984 in Bhopal, India when 42 tons of methyl isocyanate was released into the environment, killing over 2,000 people and injuring several thousands more. This incident led to the Right to Know Laws and improved emergency responses in the US and in Europe.

Conclusion

By the late 1970s, many industrialized countries adopted environmental laws prohibiting the release of toxic chemicals into the environment. While rivers catching on fire and toxic chemicals oozing into elementary schools are largely a thing of the past, the water quality of natural waters are still being impacted by land use. As populations grow, natural lands are diminishing and are being converted into urbanized land and

agricultural land. The change in land use from a forest to urbanized land will threaten the water quality of natural waters and the ecosystem which is dependent on it.

One of the most important tools for mitigating human impact to streams, rivers and lakes is water monitoring. Monitoring solutions help prevent the introduction of contaminants, indentifies impaired reaches, and helps enforce environmental policies. Monitoring regimes, along with progressive environmental policies, are helping to mitigate the human impact to natural waters and natural ecosystems to improve the quality of life.

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