Mineral Nutrients in Water: Quality Variation of Rainwater, Surface Water, and Ground Water[®]

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BACKGROUND

Water normally used for irrigation in agriculture and horticulture is from streams, lakes, and ground water from deep wells. In addition for different reasons, rainwater has become more popular. The nutritional value of water from different sources can vary strongly, depending on:

- Different emissions and their local and regional impact on deposition and water;
- Soil and bedrock mineral chemistry, soil texture, and structure;
- Climatic conditions (rainfall and temperature) that determines the weathering rate of soil particles;
- The combined effect of deposition and bedrock on runoff water;
- Soil management (agriculture or forestry, fertilisation or no fertilisation) that has a determining impact on surface water.

Below is presented some examples of the normal variation in water chemistry, together with some evaluating aspects on the chemical variables of interest from an ecological point of view. The input to these results are mainly from Sweden and my own experiences from analysis of rainwater, stream and lake water, and soil and ground water. The Swedish Environmental Agency has also collected a lot of experimental results in two books (Naturvardsverket 1999 a,b).

NORMAL VARIATION IN WATER CHEMISTRY FORM DIFFERENT WATER SOURCES

Rainwater. The rainwater values described below all refer to measurements in open field situations. Inside, e.g., forests, the values on through fall and stem flow are strongly affected by dry deposition, leaching, or uptake of some elements by leaves/needles. In Central Europe the rainwater is strongly enriched in NH₄-N and NO₃-N, showing values around 10 to 30 mg N per litre of each element, while in clean regions the values are about 100 to 1000 times lower. Rainwater in Europe is commonly somewhat acid (pH<5), but close to agricultural land and coal burning emissions pH is normal (pH 5.3 to 5.6) or even neutral or slightly basic (6.5 to 8.0). A pH value around 5.5 is in balance with CO₂ in the air and is normal in unpolluted areas. Rain water usually has very low potassium concentrations and almost no PO₄³⁻, while sodium, calcium, and magnesium vary in concentration depending on how close to the sea the rain is collected.

Lake and Stream Water. In these types of water the soil and bedrock conditions together with soil management are absolutely determining the water chemistry. In addition, local water emissions, e.g., from industries or wastewater treatment sites, can strongly affect the situation. The variation in NH_4^+ and NO_3^- content is depending mostly on the appearance of agricultural land, but also on eventual

wastewater emissions. The latter will increase both ions, and usually also PO_4^{3-} . Leaching from agriculture sites varies within Europe but is usually in the range of 30 to 50 kg N per ha per year, which give values in the drainage water of about 20 to 30 mg litre⁻¹, that is similar to deposition in strongly nitrogen-polluted areas.

Ground Water. The bedrock and the impact from weathering of small mineral particles become more important in determining water chemistry the deeper the ground water is in the soil. The pH values are usually relatively high (6.5 to 8), except in acidified regions, where pH might go down to below 6 and even reach below 5 in strongly acidified areas. Total N values are usually low, and in the range of 0.01 to 1 mg litre⁻¹. In agricultural areas, however, NO₃-N can reach toxic values (10 to 50 mg litre⁻¹), which can be strongly negative for small children to drink.

Some Water Chemical Variables.

Conductivity. Conductivity $(mS \cdot m^{-1})$ reflects the net amount of ions in the water and is often used as a rough indicator of the nutritional value of the water. However, one cannot identify specific ion values, e.g., nitrogen ions that are the most important for plant growth. In rainwater the conductivity frequently is around 1 to $2 mS \cdot m^{-1}$, in lakes and streams it is around 5 to $20 mS \cdot m^{-1}$, and in ground water similarly 5 to $30 mS \cdot m^{-1}$. When pH values are below 5.5 there is a strong increase in conductivity due to the high specific ion conductivity of hydrogen ions. At pH values below 5 it is necessary to correct for this high conductivity of the hydrogen ions, based on pH, in order to obtain a more reliable nutritional indication.

pH. Normal values are 6.5 to 8.5 in ground water, streams, and lakes. Values of 6.0 to 6.5 are still good for organisms, but below 6 ecological problems might appear. Below 5.5 there is no buffering capacity against acidification, especially if the humus content is low and these low pH values cause severe problems for fish and other gillbreathing organisms. Above pH 8.5 there is an increasing risk of ammonia formation in ammonium-enriched waters, which also is deleterious for most water organisms breathing through gills (Fig. 1).

Alkalinity. Normal alkalinity values (HCO_3^- , above pH 5.5) in surface and ground waters in balance with carbon dioxide are >500 µeq·litre⁻¹ (corresponding to >30 mg·litre⁻¹ of HCO_3^-). Such values also counteract corrosion in drinking water tubes. Below 500 µeq·liter⁻¹ liming is considered positive in surface waters, and below 200 µeq·liter⁻¹ liming is recommended to maintain fish populations in streams and lakes. Some ground water may go below 500 µeq·litre⁻¹, but satisfactory values are usually above 1000 µeq·litre⁻¹ or >60 mg·litre⁻¹ of HCO_3^- .

Aluminium. Total content of aluminium is commonly analysed, but it is not the best variable from a toxicity point of view. Inorganic aluminium ions (free or labile Al^{3+}) is then the best but expensive to analyse for. It appears in concentrations of about 0.02 to 0.2 µg-litre⁻¹ in acidified streams and lakes. In total aluminium, some, or most of the aluminium, may be bound to organic humus particles and not toxic to gill-breathing organisms or plants. However, total aluminium is a good indicator of the acidification impact and mineral soil water intrusion into streams and lakes. For drinking water a values below 0.1 mg-litre⁻¹ is recommended, and for irrigation a similar level should be recommended.



Figure 1. The pH in water types from clean and affected areas.



Figure 2. Nitrate in water from clean and affected areas.

Acid-Neutralising Capacity. Acid-neutralising capacity (ANC) is calculated based on the knowledge of alkalinity, total organic carbon (see below), pH, and hydrogen-binding anions. There is usually a relatively good similarity to alkalinity and pH, but ANC is regarded as the best variable for determining the need for liming in acid lakes or streams.

Nitrogen. Total nitrogen (N) includes organic N, NH_4^+ , and NO_3^- (+eq. NO_2^-). These different fractions may be analysed separately, but total N is a good indicator of the total nitrogen status (productivity potential) of the water. Ammonium is a good indicator of animal/human disturbances, and NO_3^- is a good indicator of leaching from soils due to nitrification (formation of nitric acid in the soils by soil bacteria). Values on inorganic N in runoff water should normally be below 0.1 mg·litre⁻¹. Values above 0.5 mg·litre⁻¹ indicate some kind of disturbance/eutrophication. Drinking water should be recommended to be below 1 mg·litre⁻¹. Above 10 mg litre⁻¹ of NO_3^- N the water should not be used for drinking by small children (Fig. 2).

Phosphorus. Usually phosphorus (P) is analysed as total P as an indicator of mass balance in relation to total N. Total P values are usually around 10 to 15 μ g·litre⁻¹ in streams, lake, and ground water. Inorganic phosphate is a good indicator during the winter period of the potential productivity effect in streams and lakes. Inorganic



Figure 3. Phosphorus in water from clean and affected areas.

phosphate at values above 5 μ g·litre⁻¹ during summertime usually indicates pollution. This is very common in European streams and lakes today, and many have shown increased inorganic phosphate concentrations that may reach values around 100 μ g·litre⁻¹ (Fig. 3).

Total Nitrogen/Total Phosphorus. This ratio is used as the best indicator of which element, nitrogen or phosphorus, is limiting productivity especially in lake water. A value in the range of 10 to 15 is normal and indicates a good balance. Below 10 nitrogen is limiting and nitrogen-fixing organisms start working, above 20 indicates phosphorus is limiting and N is in abundance, which might start cyanobacteria blooming (ratio 20 to 30) in stream and lake water.



Figure 4. Calcium in water from clean and affected areas.

Calcium. Normal values in rain are around 0.1 to 0.2 mg·litre⁻¹, while in streams, lakes, and ground water values varies around 10 to 100 mg·litre⁻¹. Calcareous regions, though, might have even higher values. In acidified regions stream water concentrations of calcium may go below 0.5 mg·litre⁻¹, which is reported to cause negative effects on water organisms, probably due to calcium deficiency (Fig. 4).

Magnesium. Normal values in rainwater are around 0.05 to 0.1 mg·litre⁻¹, and in streams, lakes, and ground water around 1 to 10 mg·litre⁻¹.



Figure 5. Potassium in water from clean and affected areas.

Potassium. Normal values in rain are around 0.01 to 0.05 mg·litre⁻¹, and in streams, lakes, and ground water they vary around 0.1 to 10 mg·litre⁻¹ (Fig 5).

Manganese. Values in rainwater are usually below 2 μ g·litre⁻¹, and in normal streams, lakes, and ground water there is a variation from 0.5 to 10 μ g·litre⁻¹. In acidified areas 20 to 100 μ g·litre⁻¹ may appear.

Zinc. In rainwater the variation is from 1 to $100 \,\mu g$ ·litre⁻¹, and in most streams, lakes, and ground water the variation is very similar, but may reach up to $1000 \,\mu g$ ·litre⁻¹.

Copper. In rainwater the variation is from 0.05 to $1 \mu g$ -litre⁻¹, and in most streams, lakes, and ground water the variation is very similar, but may reach also $10 \mu g$ -litre⁻¹. In houses the corrosion of copper from copper tubes is depending on pH and how much total organic carbon (TOC) there is in the water. TOC values above 2



Figure 6. Copper in water from clean and affected areas.

mg·litre⁻¹ will release Cu ions from the tubes, and then the Cu values might strongly increase up to >1000 μ g·litre⁻¹. In drinking water even10,000 μ g·litre⁻¹ has been reported, which is toxic (Fig. 6).

Chloride. In soft water this depends mostly on the input by rain water, that varies from 0.05 mg·litre⁻¹ in areas far away from the coast to 1.0 mg·litre⁻¹ coastal locations. Normal values are 10 to 50 mg·litre⁻¹. Higher values might come from pollution (road salt or intrusion of sea water, etc.). Above 100 mg·litre⁻¹ there is an increasing risk for corrosion of drinking water pipes.

Sulphate. In rainwater sulphate (SO₄-S) depends strongly on the emissions of sulphur dioxide from coal burning, that since 1970 has decreased very much in Europe. Concentrations vary from 0.005 mg·litre⁻¹ in clean areas and far from the coast, to 0.5 to 1 mg·litre⁻¹ in most areas. Normal values in streams, lakes, and groundwater are 2 to 20 mg·litre⁻¹.

Total Organic Carbon. The TOC variable is little studied and in rainwater the values are close to 0 or detection limits for ordinary instruments. In humic surface water the concentrations may on the other hand reach >50 mg·litre⁻¹. In ordinary surface water the concentrations are reported to be around 1 to 10 mg·litre⁻¹, and in deep ground water usually below 1 mg·litre⁻¹. Values around 2 mg litre⁻¹ or higher seem to have a strong dissolution effect on Cu in copper pipes.

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