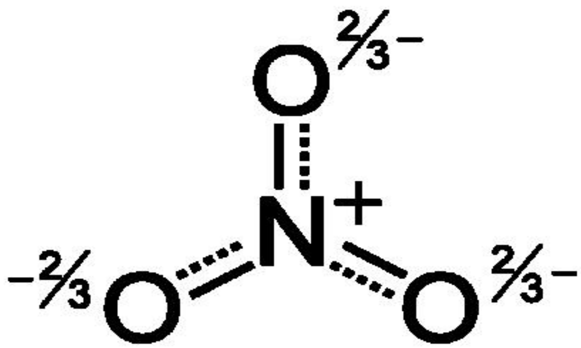
Nitrate



Schematic diagram of the nitrate ion. Source: Ben Mills. Creative Commons public domain

Nitrate is a polyatomic ion having a molecular formula NO_3^- and molecular mass of 62.0049 grams per mole. This ion is the conjugate base of HNO_3, its geometry consistng of one central nitrogen atom surrounded by three identically-bonded oxygen atoms in a trigonal planar arrangement. The nitrate ion carries an electrical charge of minus one, arising from a combination formal charge in which each of the three oxygen atoms carries a fractional two thirds charge, whereas the nitrogen atom carries a plus one charge, all these adding up to minus one formal charge of the polyatomic nitrate ion. This atomic arrangement is often invoked as a classic example of chemical resonance. Similar to the isoelectronic carbonate ion, the nitrate ion can be represented by resonance structures.

Nitrate is a very important chemical soil amendment responsible for a major portion of the agriculturalproductivity expansion from 1970 to 2012; however, the adverse unintended consequences of massive dosages of nitrate to soils have included ecosystem alteration and imbalances, including driving many plantspecies to extinction. In addition adverse impacts of groundwater and surface water contamination are widespread. In fact, more wells have been condemned due to nitrate contamination than from any other chemical substance. One of the reasons for this outcome is the high solubility of most nitrate salts, leading to rapid infiltration of nitrates to aquifers.

Chemical properties

Virtually all inorganic nitrate salts are readily soluble in aqueous media. An example of an inorganic nitrate salt is potassium nitrate, KNO_3. In organic chemistry, a nitrate is a functional group with generic chemical formula $RONO_2$, where R represents any organic residue. These compounds are esters of nitric acid and alcohols formed by nitroxylation. Examples are methyl nitrate produced by the chemical reaction of methanol, and nitric acid, the nitrate of tartaric acid and the inappropriately-termed nitroglycerin. Both organic and inorganic nitrates are employed as explosives and propellants. An example use of inorganic nitrate is classical gunpowder. In all these cases the thermal decomposition of the nitrate yields molecular nitrogen gas plus large amounts of chemical energy, due to the high energy content bond of molecular nitrogen. particularly in inorganic nitrate reactions, oxidation from the nitrate oxygens is also an important energy-releasing process. Free nitrate ions in solution can be detected by a nitrate ion selective electrode in the same way as the pH selective electrode reponds to free hydrogen ions.

Faunal toxicity

Nitrate exhibits toxicity to fauna, especially to amphibians; (Steenvoorden et al. 2002) moreover, nitrate toxicosis can occur through enterohepatic metabolism of nitrate to nitrite being an intermediate.(Merck Veterinary Manual. 2008) Nitrites oxidize the iron atoms in hemoglobin from ferrous (Fe^{2+}) to ferric (Fe^{3+}) iron, rendering it unable to transport oxygen. (Kim-Shapiro et al. 2005) This process can lead to generalized hypoxia in organ tissue and a hazardous condition called methemoglobinemia. Although nitrite converts to ammonia, if there is a greater quantity of nitrite than can be converted, the animal gradually suffers from oxygen deprivation.

Human health issues

Spinach, one of the leafy foods high in nitrates.

Humans are affected by nitrate toxicity, with very young individuals being particularly vulnerable to methemoglobinemia, due to nitrate metabolizing triglycerides present at higher concentrations than at other stages of human development. Methemoglobinemia in infants is known as *blue baby syndrome*, a condition currently thought to be the product of a number of factors, which can include factors which cause gastric distress, such as diarrheal infection, protein intolerance, or heavy metaltoxicity, with nitrates playing a lesser role. Nitrates are most often ingested by infants in the form of elevated nitrate drinking water. However, nitrate exposure may also occur when consuming vegetable food products containing high nitrate concentrations. Some lettuce varieties, for example, may have elevated nitrate in growth conditions such as reduced sunlight, undersupply of the essential micronutrients molybdenum and iron, or elevated concentrations of nitrate due to reduced nitrate uptake by theplant. High levels of nitrate fertilization also contribute to elevated levels of nitrate in the harvested plantbiomass.

Some adults can be more susceptible to the effects of nitrate than others. The methemoglobin reductase enzyme may be under-produced or absent in certain individuals that have an inherited mutation. Such individuals are not able to break down methemoglobin as rapidly as people that have the enzyme, leading to increased circulating levels of methemoglobin (the implication being that the blood of such individuals is less oxygen-rich). Those with insufficient stomach acid (including many vegetarians) may also be at risk. It is the increased consumption of green, leafy vegetables that typically accompany vegetarian style diets may lead to increased nitrate intake. A wide variety of medical conditions, including food allergies, asthma, hepatitis, and gallstones may be linked to low stomach acid; these individuals may also be highly sensitive to the effects of nitrate.

Since approximately 1960, inorganic nitrate has been associated with adverse human health effects, but some evidence of the contrary has mounted. In the 1990s, a research group at Karolinska Institutet demonstrated how the body can convert nitrate to nitric oxide, a molecule involved in numerous keymetabolic functions, such as blood pressure regulation, immune defense and cellular metabolism. Nitric oxide can mitigate against mitochondrial dysfunction related diseases, These results are of sports-medicine interest, since they demonstrate that nitrate reduces oxygen consumption during physical exercise; however, they are also of potential significance to diseases involving mitochondrial dysfunction, such as diabetes and cardiovascular disease. Methylene blue can be used to treat methemoglobinemia, via reduction of ferric iron in affected blood cells to ferrous iron.

Livestock toxicity

Nitrate poisoning is a concern chiefly for cattle producers, but also takes place in other ruminants. Nitrate is taken up from soil whenever plants increase in biomass; however when growth is interrupted, the roots of vascular plants continue to pump nitrate from soil; when such plant growth is halted, the nitrate then accumulates and concentrates in the plant stems and leaves. Thus, harvesting after such nitrate buildup results in a crop that is high in nitrates. Factors that can cause nitrate accumulation in flora are frost, hail, drought, hot arid winds, pesticide damage, herbicide damage and any other plant stunting environmental causes. Metabolic symptoms of nitrate poisoning include amplified heart and respiration rates; in advanced situations, livestock blood and tissue may turn a blue or brown color. Feed can be tested for nitrate; moreover, compensatory treatment consists of supplementing existing feed supplies with lower nitrate substances.

Aquatic system effects

In freshwater or coastal estuarine systems, nitrate concentrations can attain sufficiently high levels to causefish mortality. Although nitrate is less toxic than ammonia or nitrite, (Romano & Zeng.) nitrate levels over 30 parts per million can inhibit faunal growth, impair the immune system and cause stress in some aquaticspecies. In most cases of excess nitrate concentrations in aquatic systems, the primary source is surface runoff from agricultural or landscaped areas that have received excess nitrate fertilizer. The ensuing process is termed eutrophication and often produces algae blooms. As well as leading to aquatic anoxia and*dead zones*, these blooms may alter ecosystem function, favoring some groups of organisms over others. As a result, nitrate is widely utilized as a chief indicator of water quality. Nitrate is additionally found in septic systems for treating domestic wastewater. Water quality may thus be affected through groundwaterresources that have a high density of septic systems within a drainage basin. Ponds or lakes that rely on subsurface water for recharge can then be adversely altered by nitrates via this process.

Agriculture

A great expansion of nitrates began in the 20th century, amending soils in order to promote higher crop yields. The expansion was particularly intense starting in the 1970s as part of the much heralded *green gevolution*. Unfortunately the adverse ecological effects were not realized until decades later after massive disturbances to both terrestrial and aquatic systems, including large numbers of species extinctions to both fauna and flora. Faunal toxicity is particularly high for amphibians. In the case of plants, the effects are ostensibly more subtle in phenomenology, but even more damaging in a total ecosystem impact. When nitrogen content of soil is elevated, the competitive balance amongst various plant species is shifted, generally to favor non-native invasives that thrive on the elevated nitrogen. In many habitats, as much as one half of the native forbs and grasses are eliminated when significant dosages of ntirate are added to enhance crop fertility. It should be noted that many crop types, such as orchards and vineyards, are capable of growing compatibly with an abundance of native flora, provided soil chemistry is not altered.

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