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NEWS FROM THE WONDERFUL WORLD OF SOIL AND PLANTS

MINERALS - The Elements and What They Do

Today we continue with our study of all the minerals (elements) in the human body, what they do. See previous newsletters (9/17/21 and 9/24/21) for a list of references and introduction to the Periodic Table.

Today we look at elements 40-47 which are zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, and silver.

40) Zirconium (Zr) - Zirconium is a hard silvery metal that is very resistant to corrosion due to an oxide layer that forms on its surface. It will burn in air like a few other metals and is unaffected my most acids. Zirconium is the 12th most abundant element in the earth's crust.

Zirconium is found in igneous rocks at 165 ppm, shale at 160 ppm, sandstone at 220 ppm, and limestone at 19 ppm. Fresh and seawater have very little zirconium at less than 1 ppm. Soils average around 300 ppm, marine plants at 20 ppm, and land plants at less than 1 ppm. Due to its low solubility, it does not tend to accumulate in living organisms with land animals at less than 1 ppm, and marine animals 0.1-1.0 ppm.

Zirconium occurs naturally in a combined state with other elements. It is not very soluble hence; we do not know as much about it as other elements in regards to living systems. The most common electrical state is +4 even though others do occur. The most common mineral is zircon ($ZrSiO_4$) which is zirconium silicate.

One of the first uses for zirconium was in the form of zirconium carbonate where it was used to treat poison ivy. The zirconium compound reacted with the irritant urushiol and rendered it inactive.

Several semi-precious gemstones have zirconium as a component (made from zirconium silicate and zirconium oxide). The most famous is the gemstone cubic zirconia that out sparkle's diamonds.

Zirconium is used in certain types of incendiary cluster bombs due to its burning in air. Zirconium compounds are very hard (8.5 Mohs) which is many times harder than quartz. When zirconium is combined with yttrium, it makes a coating that protects jet engines and turbines from the high temperatures (does not melt until 4,377^{0}C).

Zirconium is used in many products from televisions to ceramics (ex. ceramic knives). Zirconium oxide (ZrO_2) is very hard and often used as an abrasive.

Gardening and Landscaping Problems Associated with Zirconium (Zr)

Historically, zirconium was not considered essential to plants, however new research suggests that zirconium participates in several physiological processes (similar to titanium).

Growth of chlorella green algae is stimulated if exposed to trace amounts of zirconium ascorbate. In experiments with fungi (yeast) it was found that zirconium ascorbate or zirconium citrate increased protein synthesis.

Some plants have no measurable zirconium at all. However, the leaves of deciduous trees can have as much as 500 ppm (ex. Ash tree).

Organic acids from decaying organic matter and fungi help zirconium become more available.

Recent research has found zirconium in the nodules produced by nitrogen fixing bacteria and may be required for nitrogen fixation to occur. Zirconium tends to accumulate in the roots of some plants. Zirconium in Tomato roots have been found to range from 0.5-7.0 ppm.

In remediation of mine tailings and in some soils mycorrhizal fungi hyphae colonize mostly on zirconium and titanium mineral grains and would not colonize a soil if these minerals were missing.

Zirconium toxicity is extremely rare.

Sources: granite sand, basalt sand, compost made from deciduous leaves, re-mineralizer

41) Niobium (Nb) - It is 34th most common element in the earth's crust and is relatively common. It is a soft grayish ductile metal of group 4 on the Periodic table.

It is a component of the minerals pyrochlore and columbite. This element is named after Niobe the daughter of Tantalus (element tantalum) and son of Zeus of Greek mythology. The name reflects the great similarity between the two elements in their physical and chemical properties, making them difficult to distinguish. They are often found together in nature with the highest concentration in acidic igneous rocks.

Niobium is found in igneous rocks at 20 ppm, shale at 11 ppm, and limestone at 0.3 ppm. Very little is found in fresh or seawater. Land plants average 0.3 ppm and marine animals only 0.001 ppm.

Niobium has a +5 valence or electrical state and has a great affinity to associate with iron (Fe), titanium (Ti), and zirconium (Zr).

Niobium is used mostly in alloys, the largest part in special steel such as that used in gas pipelines. Although these alloys contain a maximum of 0.1%, the small percentage of niobium enhances the strength of the steel. The temperature stability of niobium-containing super alloys is important for its use in jet and rocket engines as it resists corrosion at high temperatures. It is also used in surgical implants, coins, and jewelry. At room temperature, it is very resistant to most acids.

Niobium is used in various superconducting materials. These superconducting alloys, also containing titanium and tin, are widely used in the superconducting magnets of MRI scanners.

In soils, the weathering of the various niobium containing minerals determines its mobility and availability in soils. Increased levels of organic matter in the soil increase the availability of niobium.

We find small amounts of niobium in human blood, kidneys, lungs, muscle, and testes. Metallic niobium has low toxicity since it is poorly absorbed in our digestive system.

Gardening and Landscaping Problems Associated with Niobium (Nb)

Niobium is relatively mobile under humid conditions and therefore available to plants. It is relatively common in most all plants at very low levels.

Some plants that are members of the *Rubis* family (blackberries, dewberries, raspberries, etc.) can have 10 ppm in their tissues. Mosses and lichens often accumulate 0.5 ppm although the role is unknown.

In some banana fruits, 320 ppm has been found.

Sources: granite sand, basalt sand, re-mineralizer

42) Molybdenum (Mo) - This little-known trace element is essential to nearly every life form on Earth. The amount that is in our food is directly related to how much is in the soil in which the plants grow.

Molybdenum is a lustrous silvery metal that is soft when pure. It occurs in nature at the +6 or +2 electrical or oxidation state. It occurs in igneous rocks at 1.5 ppm, shale at 2.6 ppm, sandstone at 0.02 ppm, limestone at 0.4 ppm, and very little in fresh or seawater. In soils, it averages 2 ppm where it is strongly concentrated by humus. Marine plants have 0.45 ppm, land plants have 0.9 ppm, marine animals from 0.6-2.5 ppm, and land animals at 0.2 ppm.

Molybdenum is different from many other nutrients as its solubility (availability) decreases as the pH becomes lower or more acidic. It is more available in alkaline soils hence its availability is very sensitive to pH, oxygen, and drainage issues.

When molybdenum is added to steel, it produces an alloy that can be used to make tools from drills to armor for military tanks. If combined with sulfur (S) it forms a lubricant that can withstand very high temperatures. Molybdenum is used in many types of electronic products and in automobile to aircraft parts.

Small amounts of molybdenum are essential for all life but the function and requirements not fully understood by scientists.

Over 50 enzymes require molybdenum to work properly where it functions as a co-factor, a few of these are:

Sulfite oxiase - helps build proteins
Xanthine oxidase - multiple functions
Aldehyde oxidase - helps metabolize drugs and toxins
Mitochondrial amidoxime (helps body remove toxic substances)

It is also used as a catalyst for enzymes that breakdown fats, carbohydrates and certain amino acids.

A deficiency of molybdenum can lead to headaches, rapid heartbeat, mental health issues, and even coma, problems with uric acid production, and decreased metabolism of sulfur containing amino acids.

Tooth enamel contains high amounts of molybdenum that suggests it might help prevent tooth decay.

In areas where there is low molybdenum in the soils (and hence the foods), the lack of molybdenum has been associated with cancer of the esophagus and stomach (10X higher rates). The Linus Pauling Institute has found that sufficient molybdenum helps in the treatment of certain forms of cancer.

When molybdenum is present in the soil it prevents the production of cancer-causing agents known as nitrosamines in plant foods. In animal studies, it prevents pulmonary and liver fibrosis and reduces damage to liver and the heart from antibiotics.

Though rare, too much molybdenum in our system (mammals) can cause a copper (Cu) deficiency known as *molybdenosis,* while low molybdenum intake can cause copper toxicity.

These effects vary with species, breed, and sex. There is also a molybdenum-sulfur relationship although not as strong.

Molybdenum is generally not stored in body as it is easily absorbed and excreted via urination.

Certain beneficial microorganisms that are involved with nutrient uptake require molybdenum where it is used in electron transfer reactions. Molybdenum availability is related to other nutrients and the chemical complexing of those nutrients. As in mammals, it is required for certain physiological processes such as enzyme and co-enzyme systems (i.e., nitrate reductase enzyme and sulfite oxidase).

Good food sources are grass fed pork, lamb, and beef liver. Of the vegetables and fruits, legumes have the most molybdenum. Bananas and potatoes also contain some.

Gardening and Landscaping Problems Associated with Molybdenum (Mo)

Molybdenum is a trace nutrient and most plants require 0.01-10 ppm. Molybdenum is involved with nitrogen (N) metabolism of plants where it is essential for the conversion of the ammonium (NH_4^+) cation to the nitrate (NO_3^-) anion. Nitrogenase is involved with converting the nitrate (NO_3^-) anion into the ammonium (NH_4^+) cation.

It is a structural component of the enzyme nitrogenase which has significant effects on pollen formation (used in reduction of nitrates for the formation of proteins). It also helps plants use nitrogen, and a shortage of molybdenum leads to inefficient utilization of nitrogen leading to increased risk of nitrate (NO_3^-) leaching and the polluting of ground water.

As in plants, molybdenum is involved with nitrogen fixation by azotobacteria and non-symbiotic nitrogen fixing bacteria. In 2009, it was recognized that molybdenum was the limiting factor in forest growth, not phosphorous (P) as previously believed. Nitrogen uptake by trees depends on soil bacteria converting atmospheric nitrogen to ammonia and these bacteria require

molybdenum to work! Most phosphate fertilizers contain molybdenum hence researchers were confused.

Recently it was discovered that some species of algae could also fix nitrogen from the air if molybdenum was present in the soil.

If deficient in molybdenum, plants often appear as if they are nitrogen deficient.
The earliest symptoms occur on the youngest leaves and stems, where it is more common on acid sandy soils, and in humid regions. On some plants, there is an irregular artistic pattern of leaf yellowing, where the veins remain green, and the area in between turns yellow.

Legumes are more susceptible with marginal scorching and cupping or rolling of leaves, and irregular leaf blade formation known as whiptail in brassicas crops. Legume plants tend to have more molybdenum than other plants with levels up to 350 ppm without any toxicity symptoms.

Most artificial fertilizers tend to acidify the soil preventing molybdenum from being absorbed which then leads to an antagonistic relation with manganese. To correct the problem the soil needs to have lime applied to raise the pH.

Molybdenum is critical for "grasses" and other crops requiring little potash. Molybdenum like boron (B) is absorbed by plants as an anion not as a cation as most other nutrients.

The amount in plants tends to increase as the soil pH increases. The primary form of molybdenum in the soil is the soluble form called molybdate $(MoO_4)^{-2}$ anion, where the absorbability is increased 10X for each unit increase in pH.

Sources: compost, native mulches, most organic fertilizers, rock dusts, Biosolids (sewage sludge), some coal ash, re-mineralizer

43) Technetium (Tc) - Technetium is a silvery-grey, radioactive transition metal in-group 7 of the periodic table. Considered an artificial metal used in metal processing. It is mainly used in alloys of molybdenum (Mo) and niobium (Nb) where it exhibits super conductivity and is very resistant to oxidation.

This element is produced by the spontaneous fission of uranium (235) in nature. Hence, it is often found in uranium ores. It was also deposited in soils from fallout from worldwide nuclear testing. The most stable electrical or oxidation states are +7 and +4. It is absorbed in significant quantities only in soils high in organic matter. The chemical properties of technetium are very similar to manganese (Mn) since it is located directly below manganese on the periodic table.

Technetium has no biological role, as it does not occur naturally in the biosphere. Almost all technetium is created artificially as very little is found in nature. It is only considered toxic due to its radioactive properties. In rodent studies, it was not found to accumulate in their bodies even though they were fed large doses. In humans, it is poorly absorbed and we rapidly excrete it in our urine.

Isotopes of technetium are widely used in medicine for the diagnostic of thyroid disorders and other medical x-ray diagnostics (isotopes have the same numbers of protons and electrons but different numbers of neutrons in the nucleus of the atom).

Gardening and Landscaping Problems Associated with Technetium (Tc)

Technetium is easily absorbed by plants as the anion $(TcO_4)^-$ though extremely rare. In plants, technetium does not move around with the highest concentrations occurring in older plant tissues.

Organic fertilizers inhibit its phytoavailability.

Sources: radioactive fall-out, uranium ores

44) Ruthenium (Ru) - It is a hard lustrous silvery-white metal in the platinum group. It is found in igneous rocks at 0.001 ppm, and plants at 0.005 ppm, and land animals at 0.002 ppm and is one of the rarest metals on earth and is considered a precious metal. Ruthenium oxide (RuO_4) is highly toxic.

Used in various electrical components due to its ability to resist corrosion. It is used in some types of solar cells. A few radioactive isotopes are also used in medicine.

The most common usage is in jewelry along with platinum.

It has no known biological role and the amount in the human body is so small to be almost immeasurable.

Gardening and Landscaping Problems Associated with Ruthenium (Ru)

The amount of ruthenium in most plants is less than 5 ppb, but some species of algae concentrate it.

Sources: Ores of platinum metals, some nuclear reactors

45) Rhodium (Rh) - Rhodium is a shiny slivery white, very hard metal of group 9 on the periodic table and is the least common of the platinum group metals. As one of the rarest, it is also one of the most valuable of these metals. It is produced most often as a byproduct of refining platinum bearing ores.

In a few ferromanganese minerals, it can be concentrated to 44 ppm. A few animals like crustaceans easily bioaccumulate this element up to 12 ppm.

Rhodium is found on average in the Earth's crust at 6 ppb and in igneous rocks at 1-20 ppb. In fresh and saltwater, it only occurs only in a few parts per billion (ppb).

The most common electrical or oxidation state is +3 even though it has others depending on how it is combined. There are very few rhodium-containing minerals.

European studies have found it higher along highways as rhodium is used in catalytic convertors found in automobiles; in Sweden, the soils now have 40 ppb in some areas.

Rhodium is used in production of jewelry, as it is shinier than platinum and more valuable. In special tools, it is used as an alloying agent with other metals. It is often used in catalytic convertors to increase their efficiency. Because of its high reflectivity, and its ability to form extremely thin layers, it is used to coat optical fibers to make them more efficient.

Recently rhodium has been found to be an effective catalyst to remove nitrite and nitrate from contaminated water and at higher pH levels produced mostly ammonium and smaller amount of hydrazine.

For years, it was thought that rhodium did not play any biologic role as the amounts in human bodies are almost below detection limits. In its elemental form, the metal is very inert and is considered harmless.

Recent research has suggested that it plays a role in the absorption, utilization, and excretion of several metallic elements. Chemists at the University of Purdue have found that rhodium-based compounds that when exposed to light can kill tumor cells and deactivate several viruses.

We still have much to learn about this element.

Gardening and Landscaping Problems Associated with Rhodium (Rh)

Plants contain 1-2 ppb, and almost all food plants contain 1 ppb of this element.

Sources: coal, coal ash, re-mineralizer

46) Palladium (Pd) - Palladium is another member of the platinum group of metals and is a shiny, silvery-white metal which is malleable and ductile. It is found in igneous rocks at 0.01 ppm, and land animals at 0.002 ppm where it accumulates in mammalian livers and kidneys. Palladium is not very soluble hence very little is found in fresh or seawater.

Palladium is regarded as having low toxicity to humans as it is poorly absorbed and has no known biological role. Palladium chloride ($PdCl_2$), was once used as a treatment for tuberculosis. However, tests on rodents have shown it to be carcinogenic to them.

Palladium's main use is in catalytic convertors for car exhausts; however, it is used in electronic devices from computers to cell phones. It is also used in jewelry and coinage.

Recently palladium has been found to be an effective catalyst to remove nitrite and nitrate from contaminated water and at higher pH levels produced mostly dinitrogen (gas).

In Eastern Europe where they burn sewage sludge as a disposal method, the ash has been measured to have 100-600 ppm.

Gardening and Landscaping Problems Associated with Palladium (Pd)

Plants do not absorb palladium as a pure element; however, some palladium compounds are absorbed where they accumulate in the roots.

Palladium is found in the leaves of some trees at 0.4 ppm. However, some Birch trees in Canada growing near mineral deposits containing palladium have over 4,000 ppm.

Very low levels of palladium salts will kill some plants like water hyacinth; while it does not bother most plants until 3 ppm then it affects growth.

Sources: coal, black shales, sewage sludge and its ash, Biosolids

47) Silver (Ag) - Silver is a soft lustrous metal of group 11 in the periodic table and is part of the group called the "Nobel Metals".

Silver is most often found with igneous rocks; in sedimentary rocks it is found at 0.07 ppm and in soils around the world at 0.1 ppm. There is very little silver in fresh or seawater. In marine animals, silver is 3-11 ppm and less than 1 ppm in land animals.

Silver forms many silver bearing minerals as it is easily combined with other elements and is produced as a by-product of refining other metal ores. Most silver produced is a by-product of the mining of gold, copper, lead and zinc.

The most common electrical or valence state for silver is +1 and readily combines with other elements to form various minerals. Argentite, which is silver sulfide (Ag_2S), cerargite which is silver chloride (AgCl), arsenide which is silver arsenide (Ag_3As) and many more, with sulfur minerals being the most common.

Silver has very high electrical and thermal conductivity (best of any metal) and is used in many electrical devices. Silver in the form of nano-particles has antibacterial properties.

Silver is used in mirrors (highest reflectivity of any metal), catalytic chemistry (since silver oxidizes easily), jewelry and much more.

Most soils range from 0.05 to 0.4 ppm with some organic soils reaching 5 ppm. Silver occurs in the soil most often as compounds of sulfide and chloride.

Silver can be found in soils as both a cation such as silver oxide (AgO^+) or an anion species like silver chloride ($AgCl_2^-$). Silver does not exist in soils as an element but is very mobile in the soil when combined with other elements. Bacteria, Achaea, and cyanobacteria control the solubility and precipitation of silver compounds. Some bacteria hyper accumulate silver in their spores up to 1,100 ppm.

Humic substances in the soil tend to absorb and complex silver. Humic and fulmic acids limit silvers phytoavailability. Hence, silver is more toxic in soils of low organic matter content.

Some feel that silver is not known to provide any essential function in humans as 90% of ingested silver is excreted. Others feel that silver is essential, as it is systemic disinfectant and involved with immune system support. Silver compounds are absorbed more readily as proteins like those of DNA and RNA that tend to bind to silver. Silver has anti-bacterial, anti-fungal, and anti-metabolite properties; hence a deficiency would result in an impaired immune system. A paper in the 1978 Science Digest found that silver kills over 650 disease organisms.

Silver sulfadiazine is used in most burn centers to treat injuries. It is also used to treat syphilis, cholera, herpes, and malaria.

The acid in our stomach causes silver to form a compound that precipitates out of solution where it is eliminated in our stool. As a result, silver accumulates in sewage sludge where over 360 tons of silver is dumped into our streams every year. Sewage sludge and compost made from Biosolids is a major source of silver contamination when applied to soils.

Gardening and Landscaping Problems Associated with Silver (Ag)

Plants can absorb silver in its soluble forms, which then enters the roots vascular systems where it is transported to other parts of the plant.

The amount of silver in plants varies greatly where most plants have 1 ppm silver or less in their tissues. However, there are some accumulator plants where the level of silver can reach 100 ppm. Root exudates of cyanogenic plants are known to dissolve silver from soil minerals.

For most plants, the amount of silver in them is closely related to the amount of silver in the soil.

Some fungi (ectomycorrhizal and saprobes) can accumulate silver to 20-30 ppm and up to 235 ppm have been measured.

Too much silver in the soil leads to toxicity like necrosis, wilting in the leaves by loss of turbidity. Often yields and growth are reduced, without any visible symptoms. Excess silver can also prevent plants from absorbing other cations, like potassium, cobalt, copper, iron, calcium, etc.

Sources: sewage sludge, composted Biosolids, wastewater from sewage treatment plants.