

Synthetic Fertilizers; Role and Hazards

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ABSTRACT

Agriculture has relied on the use of natural fertilizers (substances that increase the nutrient levels of soil) for most of human history. Synthetic fertilizers made an entrance at the end of the 19th century and paved the way for modern agricultural production. Their use increased crop yields and brought on an agricultural revolution, the likes of which the world had not seen before. Synthetic fertilizers continue to have far-reaching effects, both positive and negative, and are likely to remain a part of human life for some time to come. These are commonly used for growing all crops and play a great role in plants growth. The importance of synthetic fertilizers are supplying of consistent amounts of precise nutrients to the soil. They act on soil immediately unlike organic fertilizers that need to break down before absorption. This immediate efficacy is especially beneficial to dying or severely malnourished plants. Although of these benefits of synthetic fertilizers, there are some negative effects such as these fertilizers kill beneficial microorganisms in the soil that convert dead human and plant remains into nutrient-rich organic matter. Nitrogen, phosphate and potassium based synthetic fertilizers leach into groundwater and increase their toxicity, causing water pollution. Fertilizers that leach into streams, rivers, lakes and other bodies of water disrupt aquatic ecosystems. Synthetic fertilizers increase the nitrate levels of soil. These harmful nitrites react with the hemoglobin in the blood stream to cause methaeglobinaemia, which damages the vascular and respiratory systems, causing suffocation and even death in extreme cases (when blood methaemoglobin level is 80 percent or more). Plants that grow in overly fertilized soil are deficient in iron, zinc, carotene, vitamin C, copper and protein. Although synthetic fertilizers may produce impressively quick results in your garden, or at commercial farms where growth equals profit, the liberal and uncontrolled use of these synthetic compounds can lead to fertilizer pollution.

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INTRODUCTION

Fertilizer defined as any organic or inorganic material of natural or synthetic origin (other than liming materials) that is added to the soil to supply one or more plant nutrients essential to the growth of plants. Or, Fertilizer is either a chemical or organic compound that is applied to plant for the purpose of providing supplemental nutrition to enhance all or a number of the plants growth characteristics. Fertilizer also defined as any substance that contains one or more essential plant nutrient elements. On the other hand, it can be defined as plant nutrients existing naturally in the soil, atmosphere, and in animal manure. However, naturally occurring nutrients are not always available in the forms that plants can use, or in the quantities needed. So we add to them by applying fertilizer, to make plants grow to their maximum potential.

Plants absorb nitrogen from the soil as both NH_4 and NO_3 ions, but because nitrification is so pervasive in agricultural soils, most of the nitrogen is taken up as nitrate. Nitrate moves freely toward plant roots as they absorb water. Once inside the plant NO_3 is reduced to an NH_2 form and is assimilated to produce more complex compounds. Because plants require very large quantities of nitrogen, an extensive root system is essential to allowing unrestricted uptake. Plants with roots restricted by compaction may show signs of nitrogen deficiency even when adequate nitrogen is present in the soil. Today, virtually all nitrogen materials are manufactured, usually from ammonia. Such materials are less expensive; more concentrated, and are just as plant-available as the organics used in the past. The production of fertilizers demands much energy and generates considerable greenhouse gas (GHG) emissions. Kongshaug (1998) estimated that the fertilizer production consumes approximately 1.2% of the world's energy and is responsible for approximately 1.2% of the total GHG emissions. Ammonia (NH_3) is the primary input for the majority of worldwide nitrogen fertilizer production and all nitrogen fertilizers (DOE, 2000 and EFMA, 2000). According to Wood and Cowie (2004) Worldwide ammonia production is largely based on modifications of the Haber-Bosch process where NH_3 is synthesized from a 3:1 volume mixture of hydrogen and nitrogen at elevated temperature and pressure in the presence of an iron catalyst (Engelstad, 1985). All the nitrogen used is obtained from the air and the hydrogen may be by either of the following processes:

- (a) Steam reforming of natural gas or other light hydrocarbons (Natural Gas Liquids, Liquefied Petroleum Gas or Naphtha); or
- (b) Partial oxidation of heavy fuel oil or coal. About 85% of world ammonia production is based on steam reforming concepts (EFMA, 2000a). Natural gas is the preferred hydrocarbon feedstock (Engelstad, 1985) with

approximately 80% of world ammonia capacity being based on natural gas (EFMA, 2000 and Patyk, 1996).

Ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) is produced by reacting phosphoric acid (H_3PO_4) with anhydrous ammonia (NH_3). Ammoniated superphosphates are produced by adding normal superphosphate or triple superphosphate to the mixture.

Microbial degradation of petroleum hydrocarbon is a very important factor in the treatment of oil pollution both in aquatic and terrestrial environment (Ibe and Ibe, 1984).

THE DIFFERENCES BETWEEN ORGANIC AND INORGANIC FERTILIZERS

Fertilizers Can be Classified into two Groups: Organic or Inorganic.

1. Organic fertilizers are derived from living or once-living material, including animal wastes, crop residues, compost and numerous other by-products of living organisms. These fertilizers are the oldest known form of fertilizers and have been used for hundreds if not thousands of years to increase the yield or condition of agricultural and ornamental plants. Organic fertilizers, as the name suggests are derived from “organic” or naturally found materials and include such things as composted vegetable materials and decomposed animal waste. They are normally applied liberally as topdressing to agricultural fields or production areas. The material needs to be decomposed as to allow the release of the nutrients into the soil. Organics are normally “broad spectrum” fertilizers that provide a whole spectrum of nutrients to the plant with one application.
2. Inorganic fertilizers are derived from non-living sources and include most of our man-made, petroleum fertilizers and commercial fertilizers. Man-made and natural fertilizers contain the same elements, but man-made fertilizers act more quickly.

Although the distinction between the two types is not always clear-cut, urea, for example, is a naturally occurring organic compound, but chemically synthesized urea is generally grouped with inorganic fertilizers. According to the Minnesota Department of Agriculture, a natural organic fertilizer has to be derived from either plant or animal materials containing one or more elements (other than carbon, hydrogen, and oxygen) that are essential for plant growth. Plant roots absorb the majority of their nutrients from the soil solution as simple, inorganic ions (charged atoms or molecules). Larger molecules can also be absorbed, but their rate of absorption is slow. Most inorganic fertilizers dissolve readily in water and are immediately available to plants for uptake. When used according to recommendations, these types of fertilizers efficiently supply the required nutrients for plant growth and are safe for the environment.

Organic fertilizers are more complex chemical substances that take time to be broken down into forms usable by plants. They are slow-release type fertilizers, compared to the quick-release characteristics of most inorganic fertilizers. It is important to apply these organic fertilizers well before periods of rapid plant growth.

Organic fertilizers usually have a low salt index, so larger amounts can be applied at one time without causing injury to plant roots. With organic nitrogen sources (except urea), one application can be made without having to be concerned about losing most of the nitrogen to leaching. However, even organic fertilizers applied at excessive rates can cause environmental degradation due to nitrate leaching or runoff of soluble organic compounds.

The cost of organic fertilizers at garden centers per pound of nutrient basis is usually higher than quick-release inorganic fertilizers.

Organic matter can increase soil drainage, aeration, water holding capacity, and the ability of the soil to hold nutrients.

The beneficial effects of organic matter on soil structure can have a greater effect on plant growth than the fertilizer value of some of these organic materials. Synthetic Fertilizers are “Man made” inorganic compounds-usually derived from by-products of the petroleum industry. Examples are:

SYNTHETIC FERTILIZERS OF NITROGEN (N)

Nitrogen is abundant in our atmosphere but rare in the soil—it is naturally “fixed” (converted to soil availability) by bacteria on the roots of leguminous plants, or by a strike of lightning. The Haber-Bosch process was developed in the early 20th century to combine nitrogen from the air with hydrogen at high temperature and pressure to make anhydrous ammonia (NH_3), the basis for all synthetic nitrogen fertilizers as well as munitions used in warfare. The hydrogen source for the process is natural gas, a non-renewable resource that currently accounts for 80 to 90 percent of the cost of fertilizer production. In the conventional system, our very ability to feed ourselves is dependent upon a non-renewable fossil fuel.

Synthetic nitrogen fertilizer became popular in the U.S. after World War II when large stocks of leftover ammonium nitrate munitions were marketed for agricultural use. However, the widespread adoption of synthetic fertilizer and associated agricultural practices had a host of unintended consequences to our environment, the quality of our foods, and the sustainability of our food system (Fig. 1).

Synthetic fertilizers are banned from USDA’s organic production standards, but were used in conventional food production on a massive scale. More than 21 million tons of synthetic fertilizers were spread over American

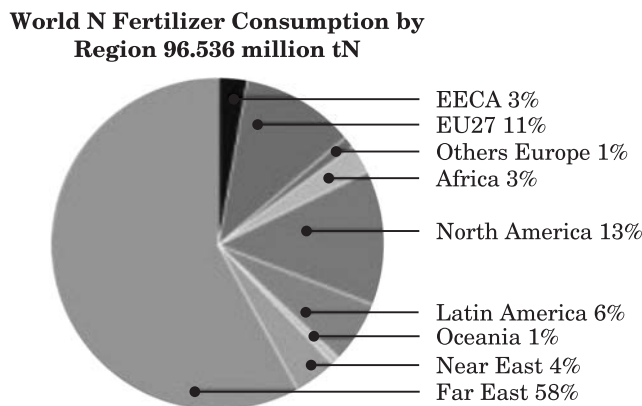


Fig. 1: World consumption of N fertilizer until 2012.

farmland in 2010 alone, covering about one-eighth of the continental land mass. Ammonium nitrate is a chemical compound with the formula NH_4NO_3 . It is composed of nitric acid and salt of ammonia. In room temperature, ammonium nitrate appears in a white crystalline form and it is also colorless. Its melting point is at 169.6 degrees Celsius or 337.3 degrees Fahrenheit. These crystals are rhombohedral in shape but when they are subjected to temperatures above 32 degrees Celsius, they change to monoclinic crystals. Ammonium nitrate is usually used as a solid material with an analysis of up to 34% nitrogen. It contains both NH_4^+ and NO_3^- forms of nitrogen, and is used as a source of nitrogen in many blends of liquid and dry fertilizers, as well as being applied directly. Pure ammonium nitrate is very hygroscopic and can be explosive under certain conditions; however, present fertilizer grades of the material are specially conditioned, and when stored and handled properly, pose no problem or hazard.

Ammonium nitrate was said to be developed Germans which they used as fertilizers instead of Chilean Nitrates since it is a lot cheaper. Commercially, it is prepared by mixing nitric acid and ammonia salt. The reaction from the two substances combined will form Ammonium Nitrate. The kind of ammonium nitrate sold in the market contains an average of 33.5 percent of nitrogen. This compound is very soluble in water; and if the water which ammonium nitrate was dissolved at is heated, the by-product will be nitrous oxide which is commonly referred to as laughing gas.

Role of Synthetic Nitrogen Fertilizer in Soil

Since the Green Revolution of the 1960s, substantial increases in cereal production have allowed an ongoing rise in world population, which has exceeded 6.5 billion (United Nations, 2006). The gain in agricultural productivity has been accomplished with the introduction of modern crop production practices that rely on high-yielding varieties and heavy inputs of fertilizers and pesticides.

This approach is solely directed toward maximizing grain yield, without regard to long-term impacts on the soil resource that is crucial for sustainable cereal production. Nitrogen is the most important mineral nutrient for cereal production, and an adequate supply is essential for high yields, especially with modern cultivars. Consequently, a dramatic escalation has occurred in global consumption of synthetic N, from 11.6 Tg in 1961 to 104 Tg in 2006 (FAO, 2009). This N is applied largely in the form of ammoniacal fertilizers produced via the Haber Bosch process, an energy-intensive conversion of highly inert N_2 to highly reactive NH_3 that relies on natural gas for process energy and as a source of H_2 (Smil, 2001). Faced with rising energy costs and concomitant price increases for N fertilizers, grain producers are under growing pressure to maximize fertilizer N uptake efficiency (FNUE), defined herein as $100 \times (\text{fertilized yield} - \text{unfertilized yield}) \times \text{grain N concentration} / \text{fertilizer N applied}$.

Ammonium nitrate (as an example for synthetic nitrogen fertilizer) is generally used as a fertilizer. It is actually sold in the form of pellets that are coated with clay. The reason why it is very popular in agriculture is because of the high nitrogen amount in this compound. Nitrogen is a very important plant nutrient that assists in the growth and metabolic processes that the plant undergoes. Agriculturists love using ammonium nitrate because it is a cheap alternative to expensive fertilizers. It can also yield rapid growth and may increase the fruit production capacity of a plant. It may also affect the quality of green leafy vegetables since the nitrogen which is used by the plants is actually very helpful in the process of photosynthesis. Another famous use of ammonium nitrate is as an additive in explosives. Ammonium nitrate is sensitive to heat and any application of this external factor can lead to explosion. It is a strong oxidizing agent. This means that it can actually remove certain electrons from other reactants when subjected to a redox chemical reaction. This is the reason why ammonium nitrates are paired and added in combustibles like TNT and others. Aside from that, ammonium nitrate is also the main component of an explosive called ANFO which stands for Ammonium Nitrate Fuel Oil. It is an explosive mixture which is used widely in mining. ANFO is composed of 94 percent ammonium nitrate and 6 percent fuel oil. The ammonium nitrate will serve as the oxidizing agent for the fuel. Another interesting fact about this compound is that it is actually hygroscopic. A hygroscopic substance is something that can easily collect water molecules from the environment where it is placed. Because of this reason, ammonium nitrates should not be stored in humid areas since water can easily affect the compound's explosive function. Ammonium nitrates are now regulated by the government since it is already used to create fertilizer bombs. These are improvised explosive devices that other people use in terrorism. Ammonium nitrate can be very helpful in agriculture but correct storage and handling should always be observed.

Nitrate fertilization generally, leads to higher levels of amino acids and protein and increased growth (Bernier *et al.*, 1993), and also to changes in

carbon metabolism including increased levels of organic acids and decreased levels of starch (Scheible *et al.*, 1997a), to changes in phytohormone levels (Crawford, 1995) and to changes in allocation and phenology including a decreased root: shoot ratio (Scheible *et al.*, 1997b), altered root architecture (Stitt and Feil, 1999).

Production of Ammonium Nitrate

Ammonia can be oxidized in air to produce nitric acid (HNO_3). This nitric acid can then be neutralized with more ammonia to produce a solution that is typically 83% ammonium nitrate and 17% water. This solution can be used to produce nitrogen fertilizer solutions or can be processed further to produce solid ammonium nitrate (Figs. 2 and 3).

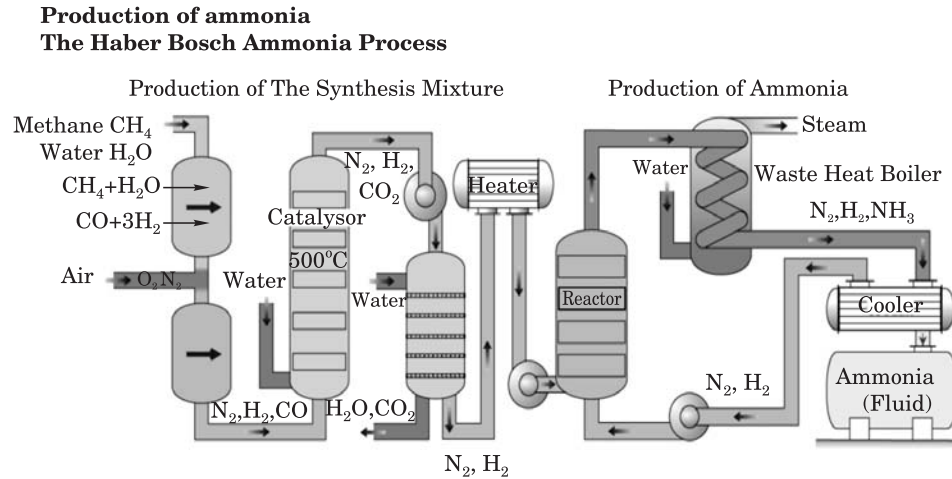


Fig. 2: Production of ammonia.

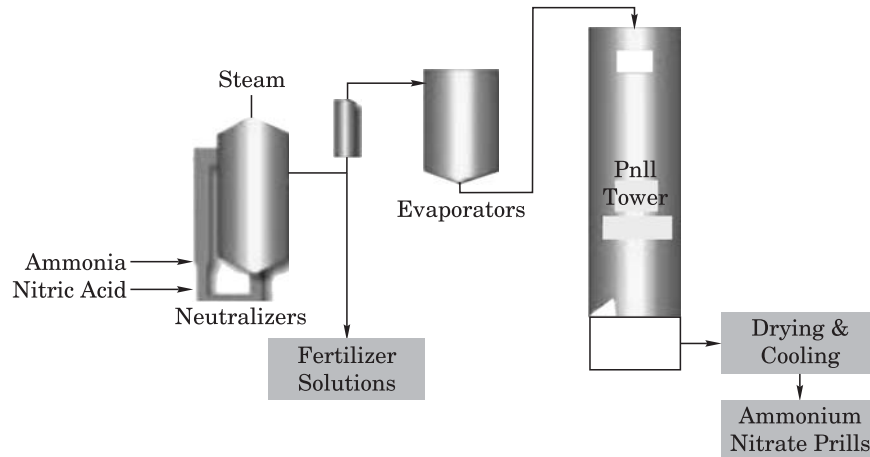
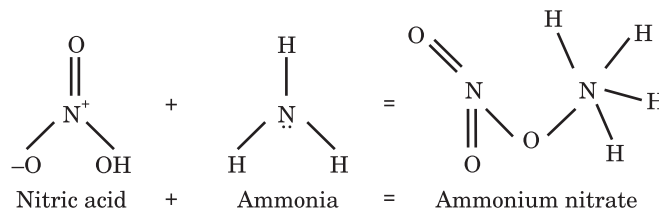


Fig. 3: Production of ammonium nitrate.

Production of Ammonium Nitrate Fertilizer



Metabolism of Ammonium Nitrate

Generally, NO_3^- occurs in a much higher concentration than NH_4^+ in the soil solution and is free to move to the roots by diffusion and mass-flow. Plants, however, tend to prefer NH_3 to NO_4^- the preference varying with ambient pH and temperature (Clarkson and Warner, 1979). It is therefore of interest to study to what extent the presence of a low ambient NH_4^+ concentration affects the above mentioned processes in NO_3^- -fed plants. Hedley *et al.* (1982) observed a steady decline in the uptake of NO_3^- by rape, when plants grown in small volumes of soil became extremely P deficient. They suggested that this, together with an increased uptake of Ca^{2+} was the cause of a higher uptake of cations than of anions in the P deficient plants.

Usry (2013) reported that the air is about 80% nitrogen. In nature, this is where the nitrogen nutrient originates. It can be brought into the soil by rain, other plants (such as legumes: alfalfa, clover, peas, *etc.*), other organisms (such as blue-green algae or microbes), the decay of other green plants, *etc.* There are about 50,000,000,000 (fifty billion) microbes in a tablespoon of healthy soil. Many more of these microbes are near the roots of plants. Their primary job is to breakdown organic matter and to also feed plants. You could have every element in its proper proportion available in the soil, but without the microbial action plants would not be able to utilize them. Synthetic chemical fertilizers actually inhibit, kill and alter this natural microbial activity which is so very important to healthy plants. In healthy soil there are herds of microbes near the roots of plants which out-compete pathogenic species and form a protective layer on the surface of living plant roots. Microbes are essential in making minerals available to plants and they also retain large quantities of nutrients (such as nitrogen, phosphorus, potassium, sulfur, *etc.*) in their bodies which help to prevent these nutrients from being leached or washed away. Some microbes eat the dead cells of other microbes thus retaining the nutrients within the soil. In the natural process, predator organisms which eat other microbes get too much nitrogen in relation to the carbon that they require. It takes 30 parts of carbon to assimilate one part of nitrogen in a normal soil. When the predator microbe consumes excessive amounts of nitrogen, it is released into the soil as nitrate. Plants can only use nitrogen in the nitrate form. (For example, ammonia nitrogen can not be accessed by plants until it is broken down into the nitrate form by microbial action). Nitrate is very, very, very water soluble. Remember this point when you read further down.

Hazards of Ammonium Nitrate

Nitrogen is an essential constituent of proteins. In humans, when our proteins (amino acids) breakdown, the nitrogen waste from the protein turns to ammonia (NH_3). Ammonia is very, very toxic, but the liver along with other body functions quickly convert the ammonia into a less toxic substance, urea [$(\text{NH}_2)_2\text{CO}$]. While urea has some toxicity, we excrete it when we go to the bathroom or sweat. However, the body is set up to process and handle nitrogen waste only at a constant rate. If there is too much nitrogen waste for the body to handle at one time, you will notice that you start to feel poorly. The highly toxic ammonia content starts to buildup in the body (and possibly the less toxic urea buildup if there are difficulties with the kidneys or other body systems). You might personally observe this at those times you eat too much in proteins, such as meat. A person will start to feel kind of lousy and kind of poisoned in an odd sort of way. Some bacteria and parasites in the body also can dump toxic ammonia into the system causing similar symptoms. So, you can imagine how stressful this is on a body's system when nitrogen from fertilizers enters the body through the air, skin, or ingestion. The body can only handle so much at a time. Also, ammonia can easily affect the brain which lacks the enzyme essential for changing it into urea.

Ammonium nitrate (NH_3NO_3): Ammonia, a base, is extremely toxic to humans. It has a sharp penetrating odor. Nitric acid is mixed with ammonia to form a salt, ammonium nitrate. Ammonium nitrate can easily have reactions if exposed to a variety of metals (*e.g.*, iron, zinc, copper), acids, alkalis, solvents, oil, grease, *etc.* You will notice that bags of fertilizer are often plastic coated and sealed in order to keep contaminants out and gases in. Storage alone will give off ammonia. Introduce heat to fertilizer and there will be further instability. The release of toxic fumes is one of the main hazards associated with the decomposition of Ammonium nitrate. Exposure to ammonium nitrate can cause eye and skin irritation and burns. Inhalation exposure can result in irritation of the nose, throat, and lungs. One can also experience nausea, vomiting, flushing of the face and neck, headache, nervousness, uncontrolled muscle movements, faintness and collapse. Because ammonia or nitrates combine rapidly with water, feeling dehydrated is common. Lips will become dry. The next time you handle or are exposed to chemical fertilizer, you will probably notice some of these symptoms. Because the accumulation of ammonia in the body can quickly lead to death, the urea cycle in humans is extremely important.

Usry (2013) stated that nitrate is converted to a very toxic substance (nitrite) within the digestive systems of human infants and also different livestock and poultry and birds. During the first few months of an infants life or in some baby animals or in some adult animals there exists a bacteria in the stomach which changes the nitrate to nitrite. Nitrite is extremely toxic and reacts with the hemoglobin in the blood to cut out the oxygen supply. It does

not take a whole lot of substance to start producing toxic reactions. A baby will suffocate if not given immediate medical attention. Signs are parts of the body turning blue or the blood turning chocolate brown. These signs occur with both humans and animals. Some livestock will go into convulsions and then die. Pregnant mothers should also dramatically avoid fertilizers. Also, you certainly would not want to expose any of your young pets (or some adult species) to fertilizer. As a baby gets older, the hydrochloric acid in the stomach kills off the bacteria which change the nitrate to nitrite. It should be noted that the bacteria which convert the nitrate into the deadly nitrite can exist in adults to various degrees

According to Department of Mines and Petroleum (2012) fires are avoided by rigorously eliminating and reducing the amount of potential fuel, combustible materials and dangerous contaminants in and around the ammonium nitrate store. Fires involving ammonium nitrate cannot be extinguished by oxygen deprivation because of the provision of oxygen from ammonium nitrate. Water is the most effective means of fire fighting—attempts to smother fires with dry chemical, carbon dioxide or foam extinguishers will not succeed. Suitably designed, constructed and maintained ammonium nitrate storage facilities and ammonium nitrate transfer equipment play a vital role in minimizing the risk of fire—as does appropriate training of all relevant persons.

The risk of an explosion is decreased by reducing the potential for the AN to be:

- Heated, such as in a fire
- Contaminated
- Confined.

Given the nature of modern formulations of AN, explosions of solid AN (excluding those initiated by explosives) without prior fire are very unlikely. If all potential sources of fuel can be eliminated, the chance of an accidental explosion is remote. However, such explosions can and have occurred with concentrated hot solutions, particularly during manufacture.

Toxicity of Ammonium Nitrate to Human

- There is limited information about the toxicity of ammonium nitrate; unless otherwise stated the information is about nitrates in general.
- Ammonium nitrate is well absorbed after ingestion, potentially absorbed by inhalation; dermal absorption of nitrates may occur through abraded areas (Mozingo *et al.*, 1988).
- The main mode of toxicity of nitrates is the induction of methemoglobinaemia.
- The primary systemic toxicity of nitrates is due to *in vivo* conversion to nitrites.

- The minimum lethal human exposure has not been established.
- Inhalation exposure to 200 $\mu\text{g. m}^{-3}$ for 2 hours caused no adverse health effects (Hall and Rumack, 1999).
- Five patients who ingested 6 to 234 g (from cold packs) suffered no severe symptoms; three developed mild gastritis and two had mild hypotension (Ellenhorn *et al.*, 1997).
- Occupational Exposure Standards: no data available.
- A relatively small amount of the nitrogen contained in fertilizers applied to the soil is actually absorbed by plants. The rest runs off into waterways, where it creates massive “algal blooms.” The overgrown nitrate-fed algae starve water of oxygen, suffocating fish and other aquatic life and creating huge “dead zones” in lakes and oceans. The number of identified oceanic dead zones has grown from 60 in 1995 to 405 in 2008. The Mississippi River fertilizes a dead zone in the Gulf of Mexico that fluctuates in size from 3,000 to 8,000 square miles.
- Runoff nitrogen also leaches into groundwater, contaminating drinking water and creating widespread health hazards.
- Soil bacteria convert excess nitrates into nitrite ions, which, if ingested, get into the bloodstream where they attach to hemoglobin molecules, reducing their ability to carry oxygen and starving the body of oxygen. Nitrates in drinking water used for infant formula can cause potentially fatal blue-baby syndrome, and can cause serious health problems for adults and children alike. High levels of nitrates and nitrites were found in 25,000 community wells that provided drinking water to two thirds of the nation’s population.
- Excess nitrates in the soil sometimes convert to nitrosamines, which have been shown to cause tumors in laboratory animals. Nitrate-contaminated water is also linked to reproductive problems, urinary and kidney disorders, and bladder and ovarian cancer.
- Applying fertilizer releases oxidized nitrates, which contribute to the formation of smog, act as greenhouse gases, and destroy protective ozone. Nitrogen oxides also react with water in the atmosphere to form acid rain.

SYNTHETIC FERTILIZERS OF PHOSPHATE (P)

Phosphate is an essential element needed in living organisms, and it is also a non-renewable resource dependent exclusively on mined rock phosphates. An input of phosphorus is crucial for food production since all plants need an adequate supply of it for successful growth. A shortfall in phosphorus will result in a reduction of crop yield (Fig. 4). Agriculture is by far the main user of mined phosphorus globally, accounting for between 80–90% of the total world demand (Childers *et al.*, 2011).

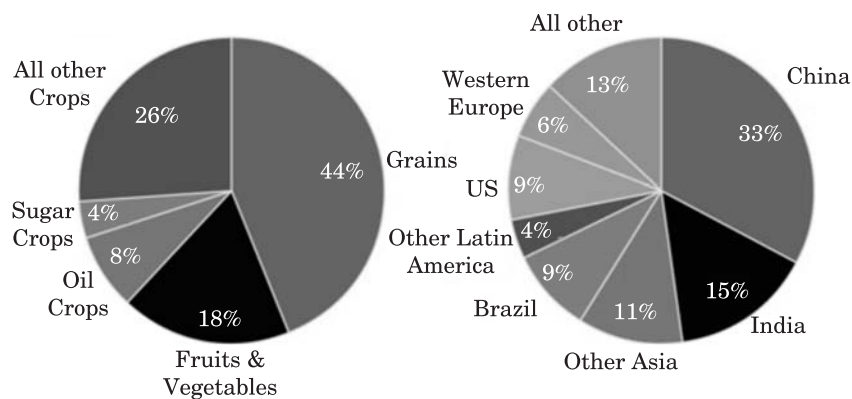


Fig. 4: World consumption of phosphate fertilizers

According to FAO data up to 2009, China, India and Europe already consume about 60% of the global use of phosphate fertilizer. China is the largest consumer of phosphorus fertilizers in the world with 34% of world total and India is second with 19% of global consumption. Phosphorus consumption in China and India show increasing trends (20% and 80% increase from 2002 to 2009, respectively), while in Europe consumption decreased by about 20% in the same period (reflecting price increases and environmental restrictions). On a worldwide scale, population growth, changes towards meat-rich diets and growing demands for bioenergy crops will push an increasing demand for phosphorus fertilizers in the future.

The phosphorous in synthetic fertilizer is usually triple super phosphate 0-46-0 (N-P-K) made by treating rock phosphate with phosphoric acid. Years ago the phosphorous source was 0-20-0 or super phosphate. It was pretty darn good even though it was created by a synthetic process. Rock phosphate was made by treatment with sulfuric acid. It was a more balanced phosphate and did not tie up trace minerals.

Ammonium phosphate is the salt of ammonia and phosphoric acid. It has the formula $(\text{NH}_4)_3\text{PO}_4$ and consists of ammonium cations and phosphate anion. It is obtained as a crystalline powder upon mixing concentrated solutions of ammonia and phosphoric acid. It is soluble in water, and the aqueous solution on boiling loses ammonia.

According to Nyers *et al.* (1979) ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) is produced by reacting phosphoric acid (H_3PO_4) with anhydrous ammonia (NH_3). Ammoniated superphosphates are produced by adding normal superphosphate or triple superphosphate to the mixture. The production of liquid ammonium phosphate and ammoniated superphosphates in fertilizer mixing plants is considered a separate process. Both solid and liquid ammonium phosphate fertilizers are produced in the U.S. This discussion covers only the granulation of phosphoric acid with anhydrous ammonia to produce granular fertilizer.

Total ammonium phosphate production in the U.S. in 1992 was estimated to be 7.7 million megagrams (Mg) (8.5 million tons).

Production of Ammonium Phosphate

Ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) is produced by reacting phosphoric acid (H_3PO_4) with anhydrous ammonia (NH_3). Ammoniated superphosphates are produced by adding normal superphosphate or triple superphosphate to the mixture. The production of liquid ammonium phosphate and ammoniated superphosphates in fertilizer mixing plants is considered a separate process. Two basic mixer designs are used by ammoniation-granulation plants: the pugmill ammoniator and the rotary drum ammoniator. Approximately 95 percent of ammoniation-granulation plants in the US. use a rotary drum mixer developed and patented by the Tennessee Valley Authority (TVA). The basic rotary drum ammoniator-granulator consists of a slightly inclined open-end rotary cylinder with retaining rings at each end, and a scrapper or cutter mounted inside the drum shell. A rolling bed of recycled solids is maintained in the unit. In the TVA process, phosphoric acid is mixed in an acid surge tank with 93 percent sulfuric acid (H_2SO_4), which is used for product analysis control, and with recycled acid from wet scrubbers. Mixed acids are then partially neutralized with liquid or gaseous anhydrous ammonia in a brick-lined acid reactor. All of the phosphoric acid and approximately 70 percent of the ammonia are introduced into this vessel. Slurry of ammonium phosphate and 22 percent water are produced and sent through steam-traced lines to the ammoniator-granulator. Slurry from the reactor is distributed on the bed; the remaining ammonia (approximately 30 percent) is sparged underneath. Granulation, by agglomeration and by coating particulate with slurry, takes place in the rotating drum and is completed in the dryer. Ammonia-rich off gases pass through a wet scrubber before exhausting to the atmosphere. Primary scrubbers use raw materials mixed with acid (such as scrubbing liquor), and secondary scrubbers use pond water. Moist ammonium phosphate granules are transferred to a rotary concurrent dryer and then to a cooler. Before being exhausted to the atmosphere, these off gases pass through cyclones and wet scrubbers. Cooled granules pass to a double-deck screen, in which oversize and undersize particles are separated from product particles. The product ranges in granule size from 1 to 4 millimeters. The oversized granules are crushed, mixed with the undersized, and recycled back to the ammoniator-granulator.

Triple Super Phosphate

This is produced by treating phosphate rock (apatite) with either sulfuric acid or phosphoric acid, making it extremely acidifying (EPA, 2006). When applied to the soil it reacts with calcium to form tri-calcium phosphate, which is water insoluble, *i.e.* requiring microbial action for breakdown (Anderson, 2004). Even in a soil with healthy microbial activity only about 15–20% of this phosphorous

is easily available to plants, considerably less in soil which does not have good microbial diversity (Wheeler and Ward, 1998). The production of each ton of phosphoric acid is accompanied by the production of 4½ tons of calcium sulfate, also known as phosphogypsum. This is a highly radioactive product and also contains heavy metals and other impurities. By 1989 phosphogypsum waste covered a total of 8500 acres, stacked between 3 and 60 meters high, causing serious land, air and water pollution (Skorovarov *et al.*, 1988).

Role of Synthetic Phosphates Fertilizers in Plants

When phosphorus fertilizers are applied, only a small proportion of it is immediately available to plants. The rest is stored in soils in varying degrees of availability. It is common for farmers to apply phosphorus in excess to make it more available to crop plants, although this also increases the risk of most phosphorus being lost via run-off, leaching or soil erosion, finally ending up in lakes, rivers and oceans. This represents a financial loss and environmental damage (Tirado and Allsopp, 2012). The authors stated also, Arable land losses are due to inefficiencies in farm management: 33% of the phosphorus entering the soil is lost by erosion (both wind and water). Only between 15–30% of the applied phosphorus fertilizer is actually taken up by harvested crops. Losses at the livestock production level are mostly due to improper management of manure, about half of the phosphorus entering the livestock system is lost into the environment instead of reapplied to farm soil where it could be used by subsequent crops. Overall, about 90% of the phosphorus entering the system is lost into the environment. Because of the increasing scarcity of high-grade phosphate reserves, and the huge problem of losses to surface waters and subsequent nutrient pollution and eutrophication, it is imperative that we “close the loop” on the losses of phosphorus. In order to achieve a sustainable use of phosphorus, two main strategies should be apply to any system:

1. Stop or minimise losses, by increasing efficiency in the use of phosphorus, mostly in arable land and the food chain. Additionally, sustainable phosphorus-use will benefit from shifting to plant-rich diets that are more efficient users of phosphorus (and other resources) than meat-rich diets, and from minimising food waste.
2. Maximise recovery and reuse of phosphorus, mostly of animal and human excreta, and thus minimise the need for mined phosphorus.

Scientists describe phosphorus in soils as existing in four different “pools” on the basis of their accessibility to plants (Syers *et al.*, 2008):

1. The first pool of phosphorus is that which is in the soil solution and is immediately available for uptake by plants.
2. The second pool is that phosphorus which is held on sites on the surface of soil particles. This phosphorus can be readily transferred into soil solution for uptake by plants if the concentration of phosphorus in the

soil solution is lowered by plants uptaking the phosphorus already in solution.

3. The third pool of phosphorus is more strongly adsorbed to the soil particles and is less readily extractable by plants but it can become available to plants over time.
4. The phosphorus in the fourth pool is very strongly bonded to the soil components and is only very slowly available to plants for uptake, often over a period of many years.

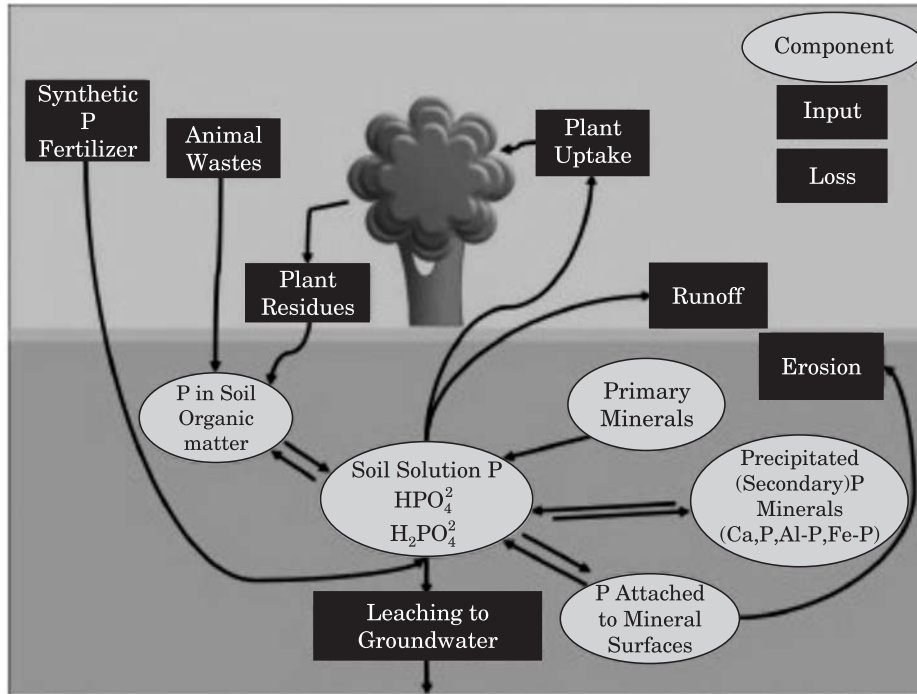


Fig. 5: Role of synthetic phosphate in soil.

According to Shober (2012) the role of phosphate in soil is Phosphorus must be dissolved in the soil solution in order to be taken up by plant roots. The dissolved forms of plant-available P in the soil solution are called orthophosphates (H_2PO_4^- or HPO_4^{2-} , depending on the soil pH) (Fig. 5). The amount of P dissolved in the soil solution at any particular time is usually very small. Once plant roots remove P from the soil solution, it is replenished by the residual P in the soil. We previously discussed how soil microbes transform organic forms of P in plant residues or organic soil amendments into plant-available P. This process is called mineralization, and the end products are soluble orthophosphates. Once in the soil solution, the orthophosphate form of P can be taken up by plant roots. The soil solution can also be replenished from several pools of inorganic (mineral) P in the soil. Solid P minerals in the soil

can dissolve in the soil solution when concentrations of soluble P diminish. This process, called dissolution can be compared with adding sugar to a glass of iced tea. When solid sugar is added to tea, it will dissolve in the liquid. Phosphorus can be attached to soil particles such as clay or specific minerals that contain iron or aluminum. Phosphorus can detach from these soil particles, thereby supplying P to the soil solution via a process called desorption. Finally, solid rocks can be a source of P as they break down into soil over a long period of time by a process called weathering. Just as soil solution P can be replenished when the concentration of P becomes low, P can be removed from the soil solution if the amount of P in the soil solution gets too high. Consider the iced tea example again. If too much sugar is added to the tea, some of it will not dissolve and will remain in solid form at the bottom of the glass. Similarly, when concentrations of P in the soil solution are too high, some of the dissolved P will form solid P minerals by a process called precipitation. Depending on soil pH, precipitation can result in the formation of solid calcium phosphate minerals (high soil pH) or aluminum and iron phosphate minerals (low soil pH). Alternatively, P can be removed from the soil solution and attach to soil particles like clays or iron and aluminum-bearing minerals via a process called adsorption.

The Hazards of Synthetic Fertilizers of Phosphates

According to Tirado and Allsopp (2012) some phosphate contain low levels of radionuclides, and some studies show increased radioactivity around phosphate mining areas. Phosphogypsum is a by-product of phosphate rock processing, and contains appreciable quantities of uranium. Phosphogypsum stockpiles present a serious environmental problem, with potential hazard for human health and pollution of the groundwater. Levels of radioactivity in phosphate fertilizers vary widely worldwide, but they might represent a concern because of their potential contribution to increased natural radioactivity in agriculture soils in the long term. Some rock phosphate fertilizers contain small amounts of the heavy metal cadmium. Because cadmium is highly toxic to humans, there are concerns about its accumulation in agriculture soils and transfer through the food chain. The EU is currently reviewing permitted levels of cadmium in phosphorus fertilizers, with a view of lowering and harmonizing safe levels. In Western countries, 54–58% of the cadmium found in the environment comes from the application of mineral phosphate fertilisers to agricultural land. In China, for example, recent analysis shows that high intensity use of phosphate fertilisers in the Yangtze-Huaihe region lead to elevated levels of cadmium in pond sediments of the watershed.

SYNTHETIC FERTILIZERS OF POTASSIUM (K)

Potassium fertilizers, like all chemical fertilizers, work by replacing lost nutrients in soil that are depleted of essential minerals from repeated harvesting

activities. Commonly known as potash (element K), potassium was originally discovered by farmers centuries ago when they found that wood ash in metal pots was useful in aiding plant growth. Commercially produced potassium comes in two types, muriate of potash and sulphate of potash. Both are salts that make up part of the waters of the oceans and inland seas as well as inland saline deposits (Fig. 6). Potassium chloride is bad on specific types of crops—especially fruit crops. It's also harsh on the soil. What we like as a potassium source is potassium sulfate. It's made from the salt of The Great Salt Lake. Potassium fertilizers are an easy way to replace potassium deficient soil with an essential nutrient for growth.

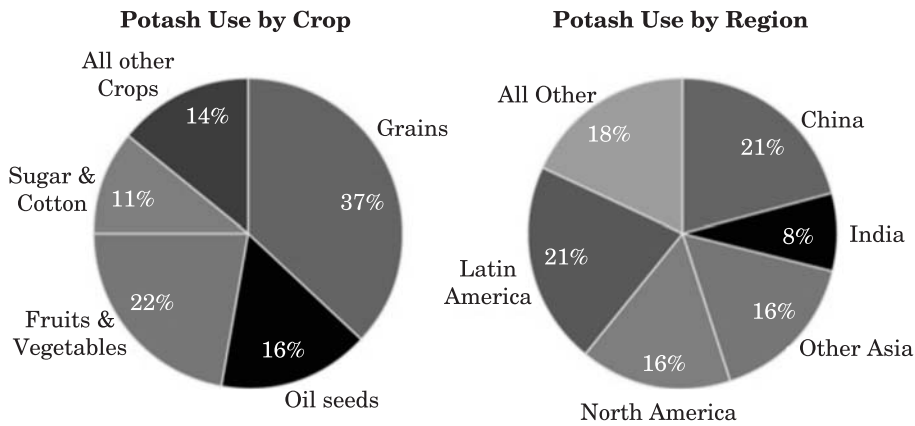


Fig. 6: World consumption of synthetic potassium fertilizer.

Role of Potassium in Plants

The main role of potassium in plants is helps plants maintain salt balance and aids in uptake of nutrients, promotes development of thick cell walls for improved winter hardiness and heat resistance, reduces damage due to drought and disease, aids in water uptake, influences enzyme performance and enhances overall health and vigor of plants. So, the role of potassium can be summarized in few points:

1. Stimulates early growth,
2. Increases protein production,
3. Improves the efficiency of water use,
4. Is vital for stand persistence, longevity, and winter hardiness of alfalfa, and
5. Improves resistance to diseases and insects.

The total K content of soils frequently exceeds 20,000 ppm (parts per million). Nearly all of this is in the structural component of soil minerals and

is not available for plant growth. Because of large differences in soil parent materials and the effect of weathering of these materials in the United States, the amount of K supplied by soils varies. Therefore, the need for K in a fertilizer program varies across the United States. Three forms of K (unavailable, slowly available or fixed, readily available or exchangeable) exist in soils. A description of these forms and their relationship to each other is provided in the paragraphs that follow. The general relationships of these forms to each other are illustrated in (Fig. 7).

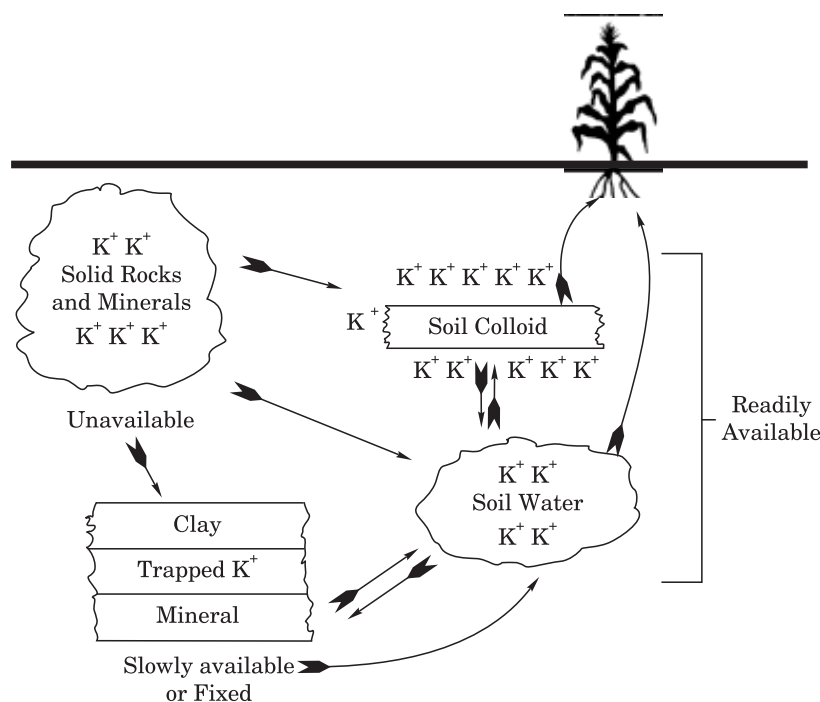


Fig. 7: Role of potassium in plants.

Potassium fertilizer production in Canada began before the 19th century with the manufacture of POTASH from wood ashes. The industry expanded until the late 19th century, when Germany became the world's major potash supplier by mining potash (potassium chloride) deposits. Potash deposits were found in Saskatchewan in 1943 but development did not begin until 1954, when the Potash Corporation of America sank the first shaft at Patience Lake. There are presently numerous potash mines, mostly in Saskatchewan and to a lesser extent in New Brunswick. The Saskatchewan potash deposits are approximately 1000 m below the earth's surface in central Saskatchewan, and consist of a mineral deposit called sylvinite that contains both sodium chloride and potassium chloride. The potash reserves in Saskatchewan and eastern Manitoba are considered some of the premium world reserves of potash and

are estimated to contribute to world potassium production over the next number of centuries. Commercially, potash fertilizers can be purchased in bulk in the form of small fractions of crushed material. Rack Petroleum makes all kinds of blends at its Fertilizer Plant.

Production of Potassium Fertilizer

The majority of mined KCl is used for obtaining various grade fertilizers based on the particle size (granular, standard, fine, soluble). Granular KCl is often applied in mixtures with other N and P based fertilizers to provide, in one application, the nutrients required by the crops.

Another potassium fertilizer is potassium sulfate, which is frequently used for crops where additional chloride from more common KCl fertilizer is undesirable. Potassium sulfate can be extracted from the mineral langbeinite or it can be synthesized by treating potassium chloride with sulfuric acid at high temperature. By adding magnesium salts to potassium sulfate, a granular potassium-magnesium compound fertilizer can also be produced (Fig. 8).

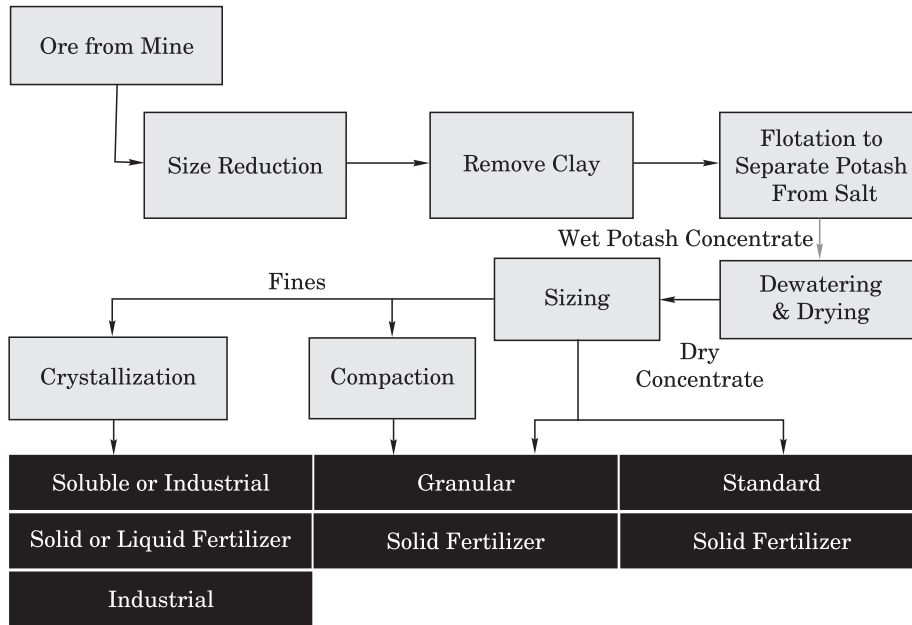


Fig. 8: Production of potassium fertilizer

The Hazards of Synthetic Fertilizers of Potassium

1. This product contains about 50% potassium and 50% chloride. In the soil the chloride combines with nitrates to form chlorine gas. This kills

microbes. Applying 1 pound of potassium chloride to the soil is equivalent to applying 1 gallon of Clorox bleach. Or in other words: 2 ppm chlorine are generally thought to be sufficient to sterilize drinking water—potassium chloride application typically results in chloride levels as high as 50–200 ppm.

2. Potassium chloride contains very high amounts of potassium, which can result in an unbalanced phosphate: potash ratio. This ratio ideally ranges from 2:1 (most soils) to 4:1 (grasses).
3. Excess potassium in the soil can lead to a calcium deficiency in plants, since plants absorb calcium, magnesium and potassium largely in the ratio in which they are present in the soil.
4. In the soil excess potassium causes a loss of structure. Reduced soil air levels result in reduced root respiration and the production of toxic compounds in plants. Reduced soil air and insufficient calcium each also result in the reduction of soil microbes and the corresponding reduced breakdown of organic matter/nutrient availability to plants.
5. In drilling potassium is used to “close” the soil, because it disintegrates the clay particles (“ages” the clay) and effectively seals the soil.
6. Potassium is a soluble and highly leachable plant nutrient and it must be supplied at a constant rate. Once applied it is taken up by the plant rapidly. Although not necessarily harmful, over-application is of no added benefit to plants and therefore is an unnecessary added cost to the grower. Most plant experts discourage application of potassium to soil unless tests reflect it is needed.

Hazards of Synthetic Fertilizers in General

According to Usry (2013) synthetic fertilizers can seriously deplete the nutritional content of foods. Direct contact or exposure to synthetic chemical fertilizers can kill babies or cause health problems in many people. Also, if you have any type of urinary or kidney or liver or allergy or health difficulties, you should especially avoid any type of exposure. The adverse effects of synthetic chemical fertilizers are often underplayed and ignored despite their damage being far reaching. Synthetic fertilizers can cause a vast array of symptoms, some immediate, some signs showing up later, some effects on people and animals are direct, and some effects are indirect. In the U.S., generally there are three hyphenated numbers (for example: 15-5-10) on the front label of fertilizer bags representing the percentage of each element by weight in the bag. The elements represented are N, P, and K. Nitrogen, Phosphorus, and Potassium. For example, the expression “15-5-10” means: 15% of the bags weight contains Nitrogen, 5% of the bags weight contains phosphorous, and 10% of the bags weight contains Potassium. Upon further reading on a bag, you will see an analysis of the types of chemical compounds used in order to reach these percentages. In other words, you will see a listing of the chemicals used

to reach those percentages of 15-5-10. The synthetic chemicals used to reach these percentages of 15-5-10 can be different in different fertilizers. Some chemicals are harsher than others, but they all end up being harmful to plants and animals. These components written on the bag are “guaranteed” to be in the bag by law. What is written on the bag must be in the bag. Some states have slightly different regulations. These synthetic chemical compounds can be directly and indirectly harmful in a number of ways. There are about 92 naturally occurring mineral elements. These are three of them (NPK). These are essential for plant cell growth. There are about 10 other minerals which are also essential for plant cell growth, but many other minerals are also very important for healthy soil and plants. Oxygen, Carbon and Hydrogen are three essential nutrients for plants (*i.e.*, derived from water and carbon dioxide). Their respective percentages in a whole plant are roughly 45%, 44%, 6%. Compared to the percentages of these nutrients and the percentages of all the other minerals; Nitrogen, Phosphorus, and Potassium actually have relatively low percentages. However, these three elements have been over-played and over-emphasized with the commercial, synthetic fertilizers for a variety of reasons. It should be noted that there is a natural balance for healthy soil and healthy plants which includes microbes and the environment. When the synthetic and unnatural force feeding of chemicals occurs, the balance gets out of wack and problems occur. So, adding just these three elements is as nutty as feeding your children only cheerios, milk and juice. In fact, these three elements added synthetically can dramatically upset how plants can absorb other necessary mineral elements. These are only 3 of 13 essential elements, but there are many other important ones also. It is not a natural, balanced diet for plants.

Of the 29 fertilizers tested some were major and popular brands. Lead, mercury, arsenic, cadmium, barium, chromium, nickel, beryllium, dioxin, *etc.* can be pretty potent stuff. You can have kids and pets playing on the stuff, people breathing the dust, these toxins getting into the water runoff, agricultural accumulation in soils, plants and vegetables uptake many of these, *etc.* The metals found in these fertilizers are known or suspected carcinogens, reproductive and developmental, liver, and blood toxicants. In about a five year period, 270,000,000 (270 million) pounds of toxic waste was sent to fertilizer companies and farms according to reports from 44 different states. Regulations are extremely strict if industry wishes to dispose of toxic waste in lined landfills. However, regulations are relatively lax if they transfer the waste or resale it. In other words, the simplest method of getting rid of toxic waste is just to resale it. So, unwittingly we become the consumers who purchase toxic waste to dump on our yards and parks and food crops and feed crops. Also, conventional agriculture is a big culprit in taking all kinds of industrial waste, sludge, and/or sewage sludge and dumping it onto fields as fertilization. To give you an idea of how nutty this can go you can look at a relatively safe fertilizer: manure (when it is composted). Conventional farmers are not required to delay harvesting after applying fresh manure. Organic farmers must wait 90–

120 days between application of raw manure and the harvest of any organic crop which may be eaten raw, which allows the fresh manure time to compost and thus, prevent the spread of any potentially dangerous bacteria. From talking with different farmers and ranchers, I was amazed at how gross the dumping of masses of chemicals onto fields really was.

The Fertilizer consumption (% of fertilizer production) in world was 94.67 in 2009, according to a World Bank report, published in 2010. Fertilizer consumption measures the quantity of plant nutrients used per unit of arable land. Fertilizer products cover nitrogenous, potash, and phosphate fertilizers (including ground rock phosphate). Traditional nutrients—animal and plant manures—are not included. For the purpose of data dissemination, FAO has adopted the concept of a calendar year (January to December). Some countries compile fertilizer data on a calendar year basis, while others are on a split-year basis. This page includes a historical data chart, news and forecasts for Fertilizer consumption (% of fertilizer production) in World (Fig. 9).

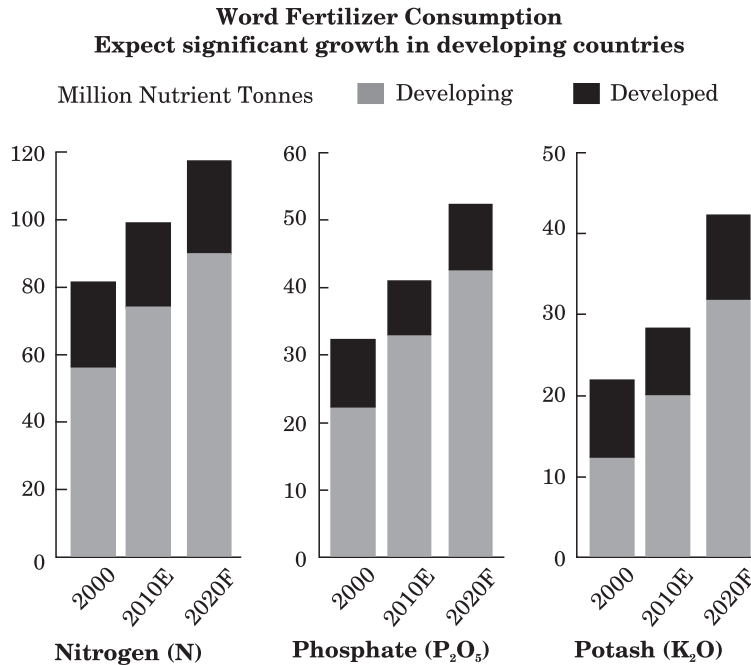


Fig. 9: World consumption of synthetic fertilizers.

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