A PROJECT REPORT ON

" SOIL ANALYSIS "

DISSERTION SUBMITTED TO THE RANI CHANNAMMA UNIVERSITY BELAGAVI, ON THE PROJECT WORK FOR THE PARTIAL FULLFILLMENT OF THE DEGREE OF

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IN

CHEMISTRY

SUBMITTED BY :

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UNDER THE GUIDENCE OF

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CERTIFICATE

This is to certify that the dissertation entitled with the "STUDY OF SOIL ANALYSIS" for the award of the degree of the Bachelor of the science in Chemistry is based on research work carried out by ASHOK. B. HUNDEKAR under the Department of Chemistry.

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Learning Objectives

After Completing This Review, You Should be Able To Explain And/Or Describe:

1. The Overall Behaviour Of N, P, K, S And Micronutrients In Agricultural Soils.

2. How Soil Properties And Environmental Conditions Affect Nutrient Availability And Movement In The Soil.

3. How The Environment And Management Practices Affect The Utilization Of Manure Nutrients By Crops In Terms Of Agronomic Benefits And Environmental Risks.

4. Sources And Loadings Of Trace Elements In Manures And Potential Long Term Implications.

5. The Effect Of Manure On Soil Properties Such As Salinity, Sodicity, Ph, Organic Matter Content, And Microbial And Enzyme Activity.

Overview:-

The Effects Of Manure And Fertilizer On Soil Fertility And Soil Quality Focuses Primarily On The Behaviour Of Nitrogen (N) And Phosphorus (P) In Soil Because These Two Nutrients Are The Main Nutrients That Limit Crop Yields In Manitoba And They Are Also The Nutrients Of Particular Concern For Environmental Quality. In Addition, Potassium (K), Sulphur (S), Macronutrients And Other Trace Elements, Salts And Sodium, Soil Ph And Organic Matter And Microbial Activity Are Covered.

Nutrients in Crop Production

Nutrients are essential for crop production. All plants require nutrients to grow and a significant portion of these nutrients are removed and exported when a crop is harvested. Sustainable crop production requires the nutrients that are removed to be replaced with synthetic fertilizers, manures, municipal wastes or, in a few cases, the atmosphere.

Generally, plant nutrients are divided into two groups, according to the amount of each nutrient required for plant growth: **macronutrients** which are required in large amounts (generally measured in several or many pounds per acre) and **micronutrients** which are required in relatively small amounts (generally less than 1 lb per acre). This definition, based on requirement, does not always match up with the quantities actually found in soils or plants. For example, iron (Fe) is the most abundant mineral nutrient present in soil and chlorine (Cl) is often found in large quantities in plant tissue. However, the plant's true nutritional requirements for Fe and Cl are very small, so both of these elements are regarded as micronutrients.

Macronutrients that are generally derived from carbon dioxide (CO2) in the atmosphere and water (H2O) from soil, and are therefore not generally regarded as limiting for crop production, include:

C Carbon

H Hydrogen

O Oxygen

Macronutrients that are derived mainly from soil, and are therefore often referred to as "mineral" nutrients that might be limiting for crop production, include:

N Nitrogen (some N is also derived from the atmosphere)

P Phosphorus

K Potassium

S Sulphur (some S is also derived from the atmosphere)

Ca Calcium

Mg Magnesium

Micronutrients essential for plant growth that are derived mainly from soil include:

Mo Molybdenum

B Boron

Cl Chlorine (some Cl is also derived from the atmosphere)

Cu Copper

Zn Zinc

Mn Manganese

Fe Iron

There are also several additional elements that may be regarded as essential nutrients but which have little, if any, practical importance for crop nutrient management in the Canadian Prairies. These include nickel (Ni), sodium (Na), silicon (Si), vanadium (V), fluorine (F), iodine (1), strontium (Sr), barium (Ba), aluminium (Al), and cobalt (Co) which are sufficient in Manitoba soils for Manitoba crops.

Elements that are not essential for plant growth but are essential for animal nutrition, such as selenium (Se), are often added to livestock feeds in Manitoba.

Regardless of whether the nutrient is required in large or small quantities, if the plant does not have a sufficient supply, the growth of the plant will be limited by that nutrient. This principle is commonly referred to as Liebig's Law, which states that the level of plant growth can be no greater than that allowed by the most limiting of all essential plant growth factors (Figure 1).

Liebig's "Law of the Minimum"

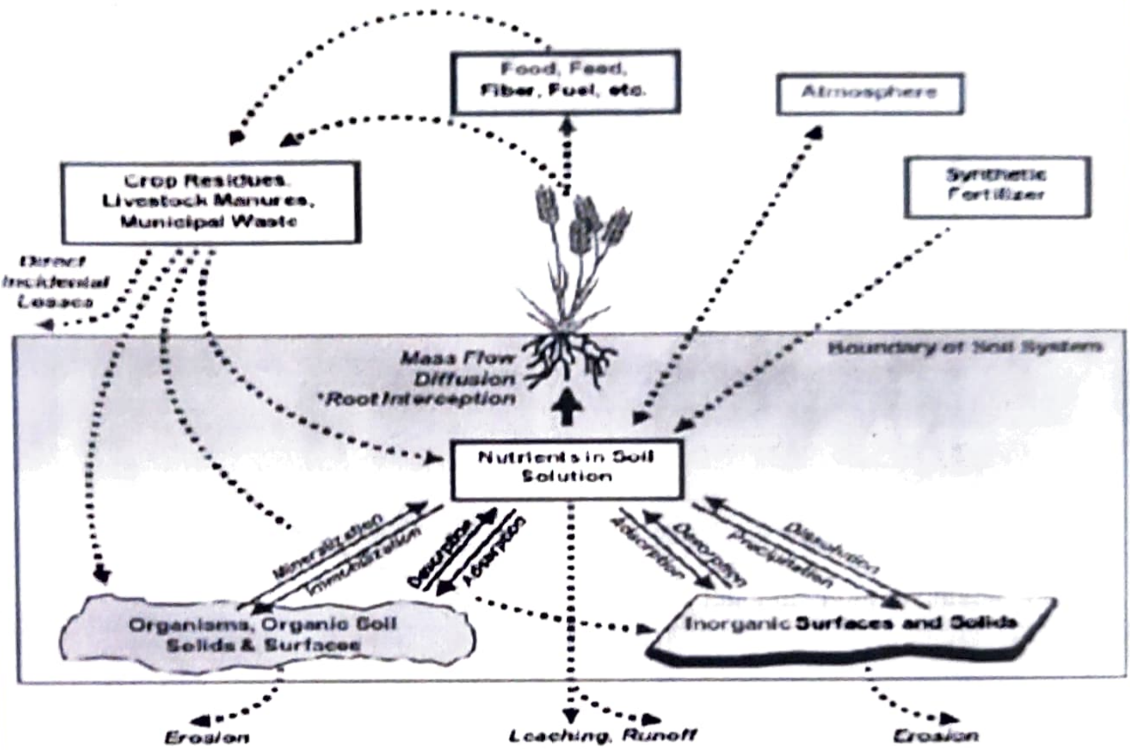
Liebig's "Law of the Minimum" for crop growth can be illustrated by a barrel. In this case, sulphur (S) is the most limiting nutrient (figure adapted from Saskatchewan Ministry of Agriculture).

If nutrients are supplied to crops at rates below crop requirements, yields will be reduced and the long term productivity of the land will decline. However, if nutrients are applied in excess of crop requirements and removal, they increase the risk of agronomic problems such as crop lodging (in the case of N), nutrient imbalances or toxicities and environmental problems such as nitrate leaching to groundwater, P runoff to surface water and release of greenhouse gases to the atmosphere.

The main challenge for managing nutrients in crop production systems is to provide sufficient nutrients for optimum plant growth without causing unacceptable risk to the environment. In order to meet this challenge successfully, nutrient management planners must understand the processes that control nutrient availability to crops and the environment and employ beneficial management practices accordingly.

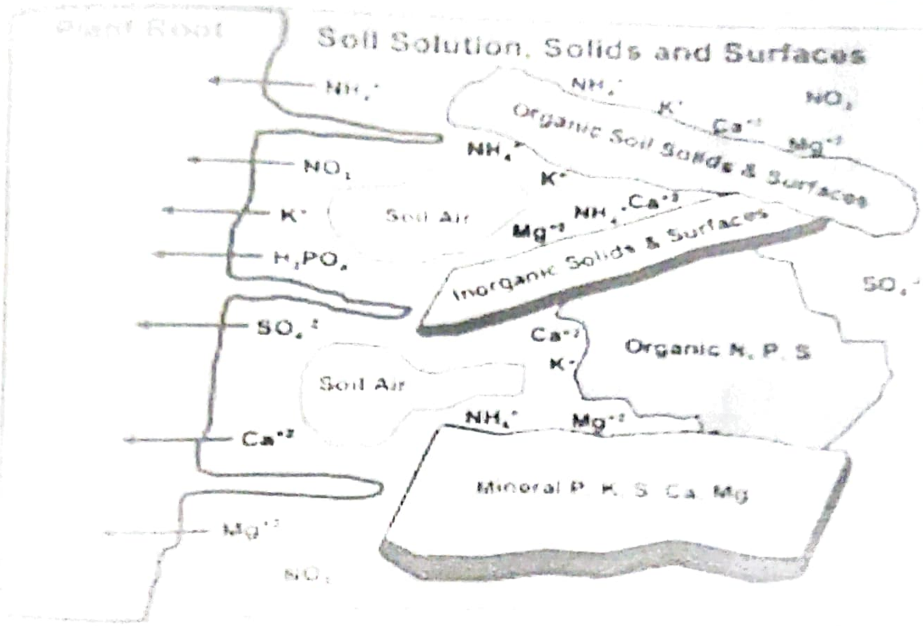
The Nutrient Cycle

From an agricultural perspective, the nutrient cycle can be thought of in terms of gains, removals, internal transformations and losses (Figure 2). Within the soil portion of the nutrient cycle, nutrient fate is controlled by interactions between nutrients in soil solution and plant roots, soil solids and soil surfaces (Figures 2 and 3). These complex interactions result in a relatively small proportion of the soil's nutrients (often only 1-2 per cent or less) being immediately available plants



*Root interception of nutrients directly from soil surfaces and solids is generally negligible for most nutrients.

Figure 2 | The nutrient cycle. Dashed lines represent nutrient gains or losses in the soil system; solid lines represent internal transformations within the soil system.



Soil portion of the nutrient cycle. Nutrient ions move from soil solution into plant roots and are replenished from reserves in soil solids and on soil surfaces.

• Nutrients in soil solution - At the heart of the nutrient cycle (Figure 2) are the nutrients in soil solution which are in the form of free ions (ex: cations such as NH4+ and anions such as NO3-) or in other soluble forms, such as chelates.

Chelates quickly convert to plant available forms near the root surface. - Some nutrients bond with soluble organic compounds in soil to form ring complexes called chelates. Chelation increases the solubility of nutrients, preventing the formation of insoluble precipitates and decreases the toxicity of some micronutrients. Although chelated nutrients may not be immediately available, they are mobile and can

• Gains of Nutrients to Soil

• Atmospheric deposition - Atmospheric deposition refers to nutrients that are deposited on land or water from the air.

• Biological fixation - Biological nitrogen (N) fixation is the conversion of biologically unavailable atmospheric N to plant available ammonium (NH4) by rhizobial bacteria.

• Application of synthetic fertilizers - Synthetic fertilizers are applied to agricultural soils to increase crop yields and quality in Manitoba.

Synthetic fertilizers can be formulated to provide more than one nutrient. A variety of fertilizers are available with nutrients in varying proportions. Fertilizers are most commonly granular but can also be in a liquid or gaseous state.

- **Plant residues** - Crop residues contain significant quantities of nutrients that are returned to the soil if the residues are not removed from the field at harvest.

V • **Livestock manures** - Manure is a by-product of livestock production and an excellent source of nutrients for crop production.

- **Municipal biosolids, industrial waste and other amendments** - Municipal and industrial wastes contain a variety of nutrients that enter the nutrient cycle when applied to soil.

• Losses of Nutrients from Soil

- **Atmospheric losses** - Nutrients can be lost to the atmosphere through chemical and biological processes. Volatile nutrients can be easily lost as gases when exposed to the atmosphere. As well, during anaerobic microbial respiration some nutrients are converted to gases and lost to the atmosphere.

- **Leaching-**Leaching is the downward movement of water and soluble substances in soil below the root zone. It is an environmental concern when it contributes to groundwater contamination. Leaching occurs during periods of wet weather, at certain times of year (most likely early spring and late fall) and in certain places in the landscape, especially in sandy soils. Depressions in the landscape where groundwater recharge occurs are more susceptible to leaching because they collect water from surrounding areas, particularly during heavy rainfall events or during snowmelt runoff over frozen soils, which then moves downward to groundwater.

Groundwater Recharge areas occur where the net movement of water is downward. In these areas infiltration exceeds the storage capacity of the soil and moves downward to the zone of saturation (groundwater). The surface and subsoil are usually non calcareous and non-saline.
Groundwater Discharge areas occur where the net movement of water is upward. In these areas, the zone of saturation is at or near the surface and the net movement of water is towards the ground surface. Discharge may be focused in areas such as springs, weeping embankments and baseflow discharge, or it may be diffuse over larger areas of the landscape. These areas may be characterized by soils that are calcareous and often have a build-up of salts.

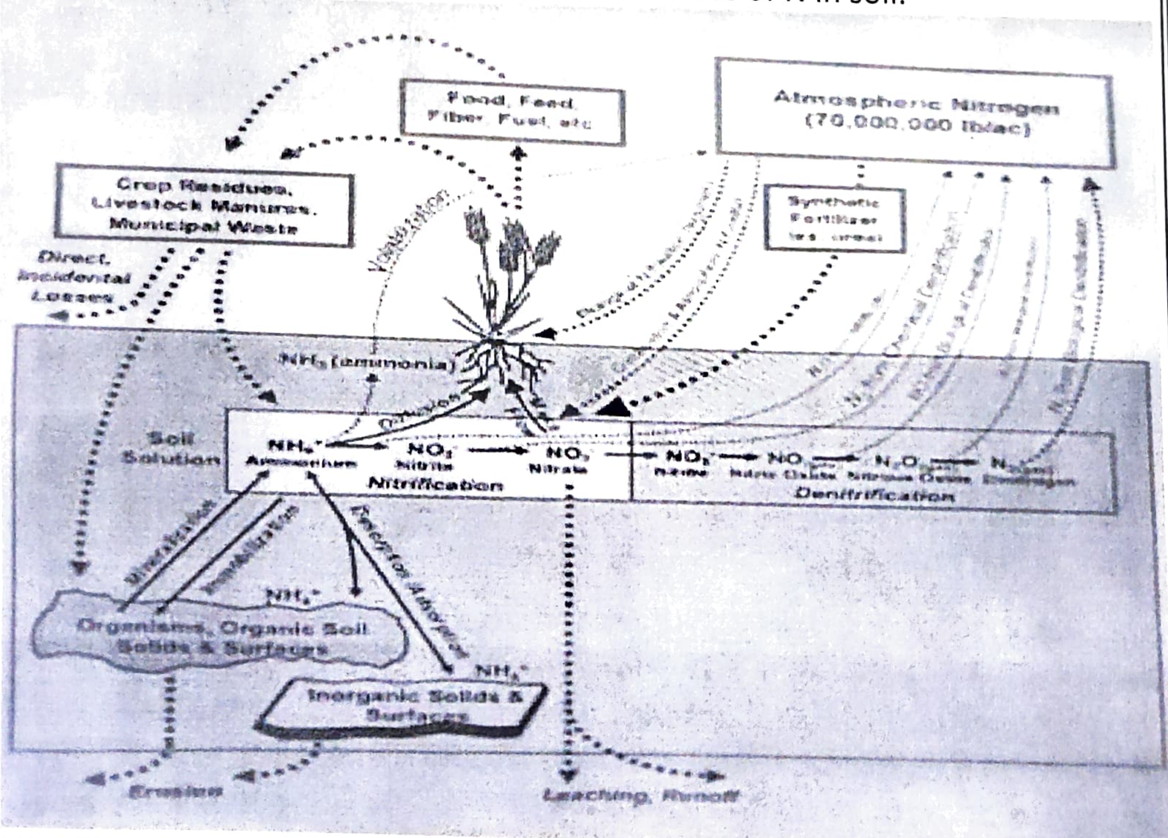
- **Runoff** - Runoff occurs when rainfall or snowmelt exceeds the infiltration rate of the soil. Runoff carries away dissolved nutrients.

- **Soil erosion** - Soil erosion is the movement and loss of soil by water, wind or tillage. Soil erosion carries away nutrients that are associated with the soil particles.

- **Soil erosion by water** - Water erosion is the detachment, movement and removal of soil from the land surface in runoff. Soil erosion by water carries away the dissolved nutrients in the runoff as well as the nutrients that are associated with the soil particles.

Nitrogen (N)

- **Nitrogen (N)** is a macronutrient that is required by crops in large amounts and is frequently deficient in agricultural soils, limiting crop production. Therefore, applications of N frequently increase yield and quality of crops in Manitoba. When fertilizer N and manure are applied to the soil, the N enters the soil N cycle. Similar to the nutrient cycle, the N cycle can be thought of in terms of gains, removals, internal transformations and losses of N in soil.



• **The N cycle**. Nitrogen behaviour in soil is complex and dynamic, with many forms, transformations and potential losses. Dashed lines represent N gains or losses in the soil system; solid lines represent internal transformations within the soil system. The amount of N in soil is very small, compared to the huge reservoir in the atmosphere, which is 78 per cent N2.

Gains of N to Soil

• **Atmospheric fixation and deposition** - Reactions between atmospheric N and lightning or sunlight generate small quantities of plant available ammonium (NH4) and nitrate (NO3) that is deposited onto soil.

• **Combustion fixation and deposition** - During the combustion process, diesel and gasoline engines convert small quantities of atmospheric N into plant available N that is eventually deposited onto the soil.

• **Biological N fixation** - Most of the biological fixation of N in agricultural soils is by Rhizobium bacteria in the nodules of legume crops such as alfalfa, beans, peas and lentils. In the case of green manures, legume crops are grown to fix N for the subsequent crop.

• **Application of synthetic N fertilizers** - Synthetic N fertilizers are applied to agricultural soils to increase crop yields and quality. A variety of N fertilizers are available with the N in specific proportions. Nitrogen fertilizer can be in a granular, liquid or gaseous state. Specialty products are also available that slow the release of N. Virtually all of the world's synthetic N fertilizer is manufactured using the "Haber-Bosch" process to make ammonia from natural gas and atmospheric N, under high pressures and temperatures (industrial fixation). The ammonia from this process is then either applied directly into soil as anhydrous ammonia (82-0-0) or converted into other N fertilizers such as urea (46-0-0) or urea-ammonium nitrate solution (28-0-0).

• **Plant residues** - Nitrogen that is contained in unharvested plant residue eventually returns to the soil N cycle. The amount of N that is returned to the soil depends on how much residue is left behind and the concentration of N in the residue.

• **Livestock manures** - Livestock manure is an excellent source of organic and inorganic N. Unlike synthetic fertilizer, manure is a heterogeneous mix of micro and macro nutrients and organic matter making it more challenging to manage well. In Manitoba, livestock manure must be land applied as a fertilizer for crop production. Manure application rates are most often applied to meet the N requirements of the crop. Municipal biosolids, industrial waste and other.

• **amendments** - Municipal biosolids, solid municipal waste and some industrial wastes contain N in a variety of organic and inorganic forms.

Losses of N from Soil

• **Losses of N from soil include:** Gaseous losses to the atmosphere due to volatilization, nitrification and denitrification; nitrate leaching to groundwater; and loss to surface water through runoff and erosion.

• **Ammonia (NH3) volatilization** - Most synthetic fertilizers and livestock manures contain or can form NH3 gas. This form of N is easily lost if exposed to the atmosphere. If urea or manure is surface-applied, volatilization can result in a substantial loss of agronomically available and economically valuable N. In addition, subsequent deposition of NH3 causes environmental problems such as NH3 toxicity in sensitive plants, plant species shifts in natural areas and eutrophication if deposited on surface water. Ammonia can also combine with other compounds in the atmosphere to form particulate matter in the air that is linked to respiratory problems in humans or can contribute to the formation of haze. Ammonia is also an indirect source of N2O, a strong greenhouse gas. Factors that affect the formation of NH3 and loss by volatilization include:

• **Soil coverage** - Volatilization of NH3 is reduced if the manure or NH4-based fertilizer is properly covered by soil. Volatilization losses from surface applied manure can be minimized if manure is immediately and well incorporated into soil. Losses are negligible from manure that is injected into soil with proper closure of injection furrows.

• **Soil pH** - Volatilization is greater on high pH (alkaline) soils than on low pH (acidic) soils because the low concentration of H+ in high pH soils favours the formation of NH3 instead of NH4.

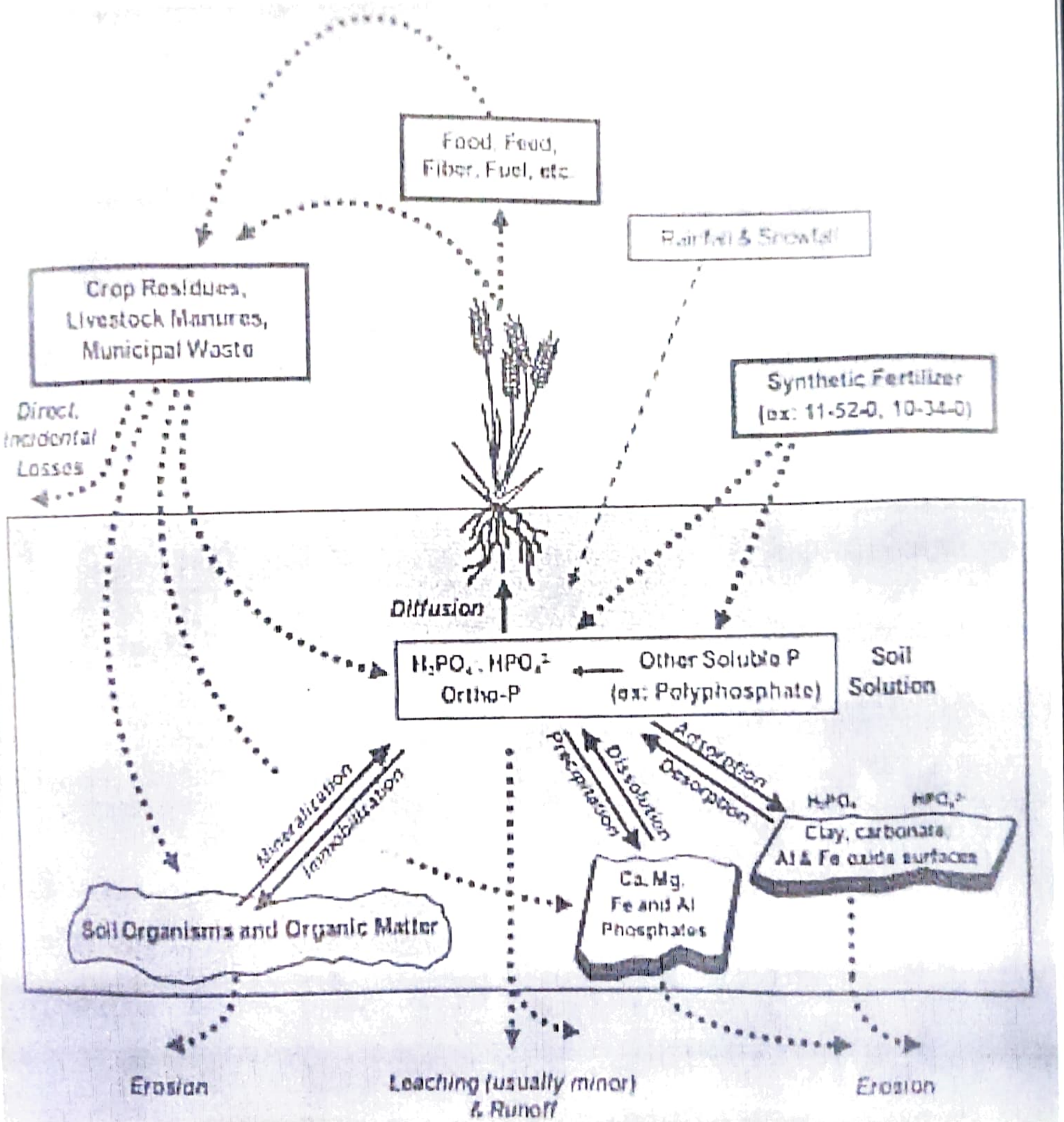
• **Weather**- Warm weather increases the rate of NH3 formation and the risk of loss. Wind increases the rate of air exchange and the rate of NH3 loss to the atmosphere. In addition, warm temperatures and wind also encourage drying of moist soil, which concentrates the NH3 in soil solution and forces it into the air.

• **Soil texture and organic matter** - Sandy soils with low clay and soils with low organic matter contents have low cation exchange capacity, resulting in a low capacity to retain NH4 and a higher risk of losing NH3 through volatilization.

• **Denitrification** - Denitrification is the conversion of NO3 or NO2 to gaseous forms of N, including dinitrogen gas (N2), N2O and NO, which are then lost to the atmosphere. The conversion may be a biological or simply a chemical process. N2O is a powerful greenhouse gas with approximately 300 times the warming potential of carbon dioxide (CO2).

Phosphorus (P)

Similar to N, P is a macronutrient that is required by crops in large amounts and it is frequently deficient in Manitoba's agricultural soils. Therefore, applications of P fertilizer and manure frequently increase yields and quality of crops in Manitoba. When P fertilizer and manure are applied to the soil, the P enters the soil P cycle. From an agricultural perspective, the P cycle can be thought of in terms of gains, removals, internal transformations and losses (Figure 8).



Gains of P to Soil

- **Atmospheric deposition** - From an agricultural perspective, the small amounts of P deposited by rainfall, snowfall and phosphine gas (0.2 to 0.4 lb/acre) to soil are not significant. However, over the long term, these rates of P addition can be an important source of P loading to lakes and natural areas.

- **Application of synthetic P fertilizers** - Most of the P applied onto agricultural land in Manitoba is applied as synthetic fertilizer such as monoammonium phosphate (11-52-0) or ammonium polyphosphate (10-34-0). These fertilizers contain P in readily soluble, inorganic forms that are immediately or quickly available for uptake by plant roots. By convention, the amount of P in fertilizers is expressed as diphosphorus pentoxide or P205, even though this form of P is not found in fertilizers.

- **Livestock manures** - In contrast to synthetic fertilizers, the P concentration in livestock manures is much lower. Therefore, the amounts of manure that must be applied to match crop requirements are much greater than for synthetic fertilizer. Annual manure application rates, however, are most often applied to meet the N requirements of the crop.

- **Municipal biosolids, industrial waste and other amendments** - Municipal biosolids, solid municipal waste and some industrial wastes contain P in a variety of organic and inorganic forms.

- **Plant residues** - Phosphorus that is contained in unharvested plant residue eventually returns to the soil P cycle. The amount of P that is returned to the soil depends on how much residue is left behind and the concentration of P in the residue.

Losses of P from Soil

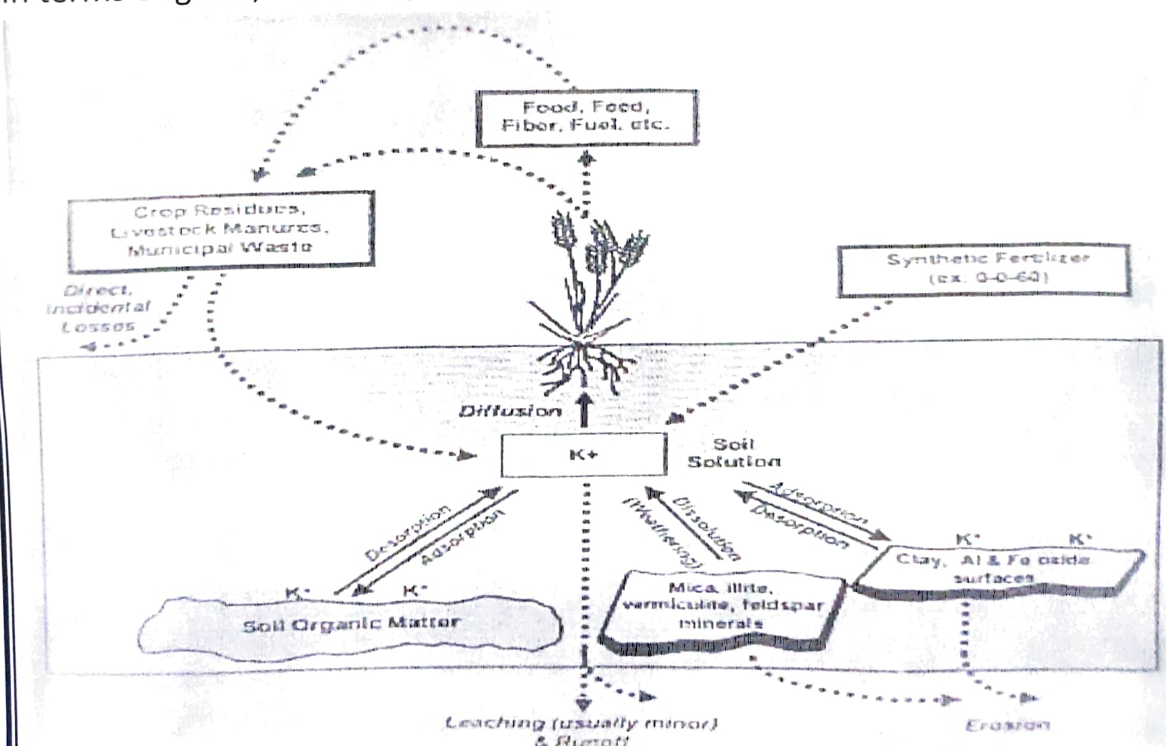
Three transport mechanisms account for the loss of P from soil: erosion of P on soil particles, runoff of dissolved P and leaching of P to groundwater (Figure 10). In addition to these losses from soil, manure P can also be lost directly, as incidental loss.

- **Runoff** - Runoff occurs when rainfall or snowmelt exceeds the infiltration rate of the soil. Runoff will carry away dissolved P. In Manitoba, most of the P lost from agricultural land to surface water is in the dissolved form (Glozier et al. 2006; Sheppard et al. 2006; Tiessen et al. 2010) because the majority of agricultural land. Once dissolved P enters a surface water pathway, it can be transported for long distances and is very difficult to intercept, compared to particulate P.

- **Soil erosion by water** - Water erosion is the detachment, movement and removal of soil from the land surface in runoff. Soil erosion by water carries away the dissolved P in the runoff as well as the organic P and P that is associated with the soil particles (particulate P). Soil erosion by water is an important pathway for P loss where land is steeply sloped and rainfall is the dominant cause of runoff (ex: in the Eastern and Southern U.S. and most of Europe). Transport distances for particulate forms of P are relatively short and losses of this form of P can be reduced with erosion control beneficial management practices.

Potassium (K)

Similar to N and P, K is a macronutrient that is required by crops in large amounts. Crops require nearly as much K as N. Unlike N and P, K is abundant in most of Manitoba's clay and loam soils. Therefore, crop responses to fertilizer or manure K are unlikely to occur except in sandy or organic (peat) soils. When K is added to soil, it enters the soil K cycle (Figure 12). The K cycle can be thought of in terms of gains, removals, internal transformations and losses of K in soil.



Gains of K to Soil

- **Synthetic K fertilizer** - Potassium is applied to some Manitoba soils as potash fertilizer (0-0-60). However, the amounts of K fertilizer applied in Manitoba are very small, compared to N and P fertilizer because of substantial reserves of K in most clay and loam soils.

- **Livestock manures** - Most manures contain substantial amounts of K. The K in manure is in an inorganic, highly soluble form and is considered to be 90-100 per cent as available to crops as synthetic fertilizer K (Schoenau and Davis 2006). Repeated applications of livestock manure increase plant available K in soil. High concentrations of plant available K can suppress plant uptake of divalent cations such as Ca^{2+} or Mg^{2+}. Feeding high K forages to cattle or sheep increases the risk of dietary imbalances, such as grass tetany, milk fever and udder oedema. Testing to determine the risk of dietary imbalances should be considered for all feeds grown on heavily manured soils.

- **Municipal biosolid, industrial waste and other amendments -** Municipal biosolids, industrial waste and other amendments are a source of K.

- **Plant residues** - Potassium that is contained in unharvested plant residue returns to the soil K cycle. The amount of K that is returned to the soil depends on how much residue is left behind and the concentration of K in the residue. The K in mature plants is highly soluble; therefore, it leaches readily out of the residue and into soil with rainfall (Lupwayi et al. 2006).

Losses of K from Soil

Three transport mechanisms account for the loss of K from soil: leaching of K to groundwater, runoff of dissolved K and erosion of K associated with soil particles. In addition to these losses from soil, manure K can also be lost directly, as incidental loss. The environmental concerns related to K loss are regarded as minor, compared to N and P losses.

- **Leaching of K to ground water** - Leaching losses of K are generally negligible, except in very sandy soils, and are regarded as being of minor concern from an environmental or human health perspective. Continuous application of high rates of manure K in excess of crop removal, however, can saturate the soil's K retention capacity, resulting in small amounts of downward movement (Olson and Papworth 2006).

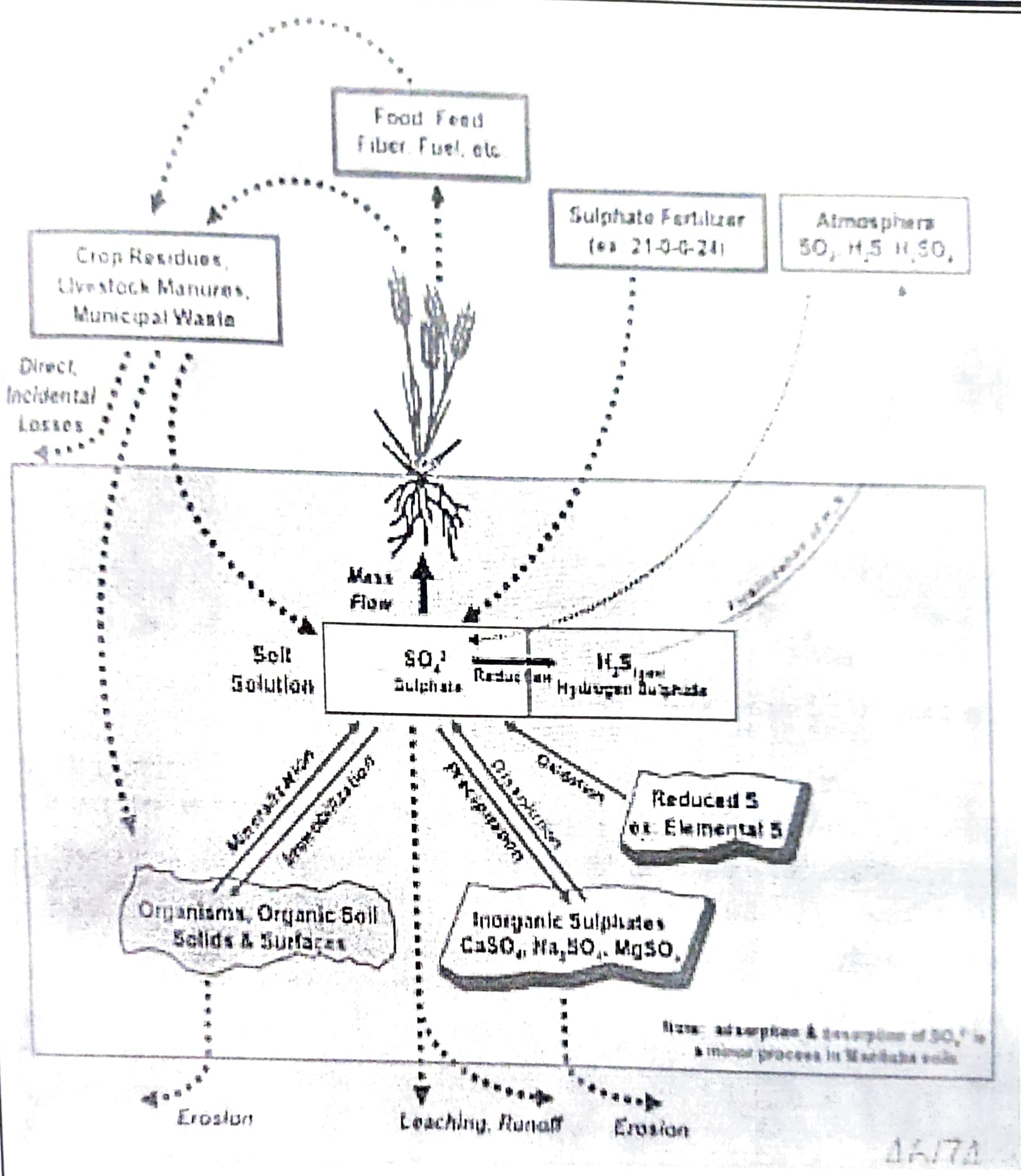
- **Runoff** - Runoff occurs when rainfall or snowmelt exceeds the infiltration rate of the soil. Losses of dissolved soil K in runoff are very small, due to adsorption processes that keep K attached to the surfaces of soil particles in most soils. Losses of K from plant residues may be significant during spring runoff. Soil Erosion by Water - Water erosion is the detachment, movement and removal of soil from the land surface in runoff. Soil erosion by water carries away the dissolved K in the runoff as well as the organic K and K that is associated with the soil particles (particulate K).

In Manitoba, loss of particulate K is not a common transport pathway for our relatively flat agricultural landscapes and dry, cold climate where snowmelt over frozen soils is the dominant form of runoff.

- **Direct loss** - Direct or incidental loss is the loss of fertilizer or manure to water before interacting significantly with soil. It can result from over-application, heavy rainfall immediately following application or application directly into a waterway (including ditches). Direct losses of manure can also be substantial if manure is applied onto frozen soils or snow in the winter, where the manure can be directly transported to surface water during snowmelt runoff.

Sulphur (S)

Sulphur is a macronutrient, however, it is required by crops in much smaller quantities than N and K. Ensuring adequate S nutrition is important, especially for crops with high S demand. Sulphur is abundant in most of Manitoba's agricultural soils, mainly due to large reserves of calcium sulphate (gypsum, $CaSO_4$) in subsoils. However, well drained sandy soils, highly leached soils and some well drained areas of loam soils may be deficient in S. These soils require routine S fertilization, especially for crops that have large S requirements such as canola and alfalfa. When S is applied to land, it enters the soil S cycle (Figure 13). The soil S cycle can be described in terms of gains, removals, internal transformations and losses.



Gains of S to Soil

- **Atmospheric deposition** - Similar to N, significant amounts of S can be deposited onto agricultural land from the atmosphere, especially near industrialized areas where S emissions result in deposition of sulphuric acid (H2SO4) as "acid rain." Atmospheric deposition can be substantial near coal-fired power plants, smelters, etc. However, atmospheric deposition of S in agricultural areas of Manitoba is very small and of little or no agronomic significance.

• **Synthetic S fertilizers** - Sulphur is frequently applied as synthetic fertilizer (ex: ammonium sulphate (21-0-0-24)) to avoid the risk of S deficiency in crops such as canola, which have a large requirement for S. However, most soils in Manitoba contain sufficient amounts of S for most crops. Therefore, responses to S fertilizer are much rarer than responses to N and P on Manitoba soils.

• **Plant residues** - The concentration of S relative to C in crop residues is sufficiently high that decomposition of crop residues releases more S than soil microbes require, resulting in net mineralization of S for the next crop. Therefore, crop residues are an important source of S in annual cropping systems.

• **Livestock manures** - Sulphur is present in livestock manures in both organic and inorganic forms. However, as much as 95 per cent of the total S in manure is not readily available to plants (Eriksen 2009). The concentrations of plant available S in typical livestock manures are often low relative to the concentrations of N, P and K, especially in liquid manures. Therefore, application of manure to meet crop requirements for N may not supply sufficient amounts of S for crops that require large amounts of S (ex: canola and alfalfa).

Alberta studies have measured N:S ratios from 7:1 to 17:1 for cattle manure and from 13:1 to 25:1 for pig slurry (Alberta Agriculture 2001). The majority of these N:S ratios are too large to ensure that canola will have sufficient S, since canola requires an N:S ratio of ~7:1. Saskatchewan studies have shown crop responses to supplemental S fertilizer on manured soils in field trials where S deficiencies exist (Schoenau and Davis 2006). So, although livestock manures can provide S to crops, supplemental fertilizer S on S deficient soils that receive manure may also be required to meet crop needs.

• **Municipal biosolids, industrial waste and other amendments-** Municipal biosolids, industrial waste and other amendments are sources of S.

Losses of S from Soil

Losses of S from soil include volatilization, leaching, runoff, erosion and direct loss. Compared to N and P, the environmental risks associated with S losses are regarded as minor.

• **Volatilization of H2S** - Similar to NH3, if liquid manure is surface-applied H2S can be volatilized. Hydrogen sulphide contributes to the odours generated during manure agitation and application. Hydrogen sulfide (H2S) is a colorless gas that smells like rotten eggs. It is extremely poisonous and can be deadly at low concentrations in poorly ventilated spaces.

- **Leaching** - Sulphate S is moderately soluble and is not adsorbed to the surfaces of soil particles in Manitoba's agricultural soils. Therefore, SO4 is regarded as reasonably mobile in soil and susceptible to leaching. However, SO4 leaching is of negligible agronomic or environmental concern. For example, concencentrations of SO4-S at depths below 15 cm were unaffected even after applying very high rates of cattle manure for 5 and 25 consecutive years (Hao and Chang 2003; Olson and Papworth 2006).

- **Runoff** - Runoff occurs when rainfall or snowmelt exceeds the infiltration rate of the soil. The loss of dissolved S in runoff is generally not a concern for water quality, compared to losses of P and N.

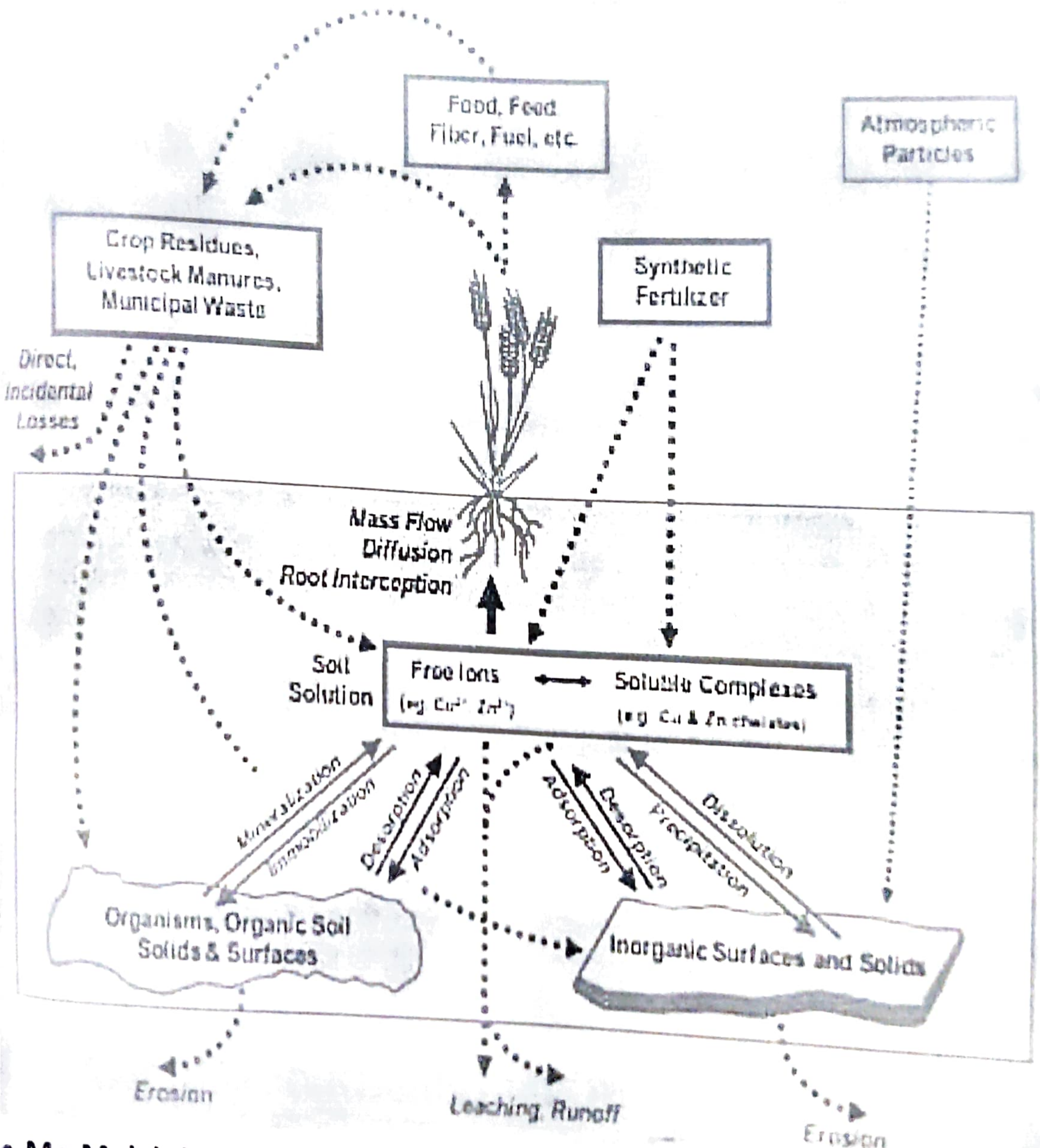
- **Soil Erosion by Water** - Water erosion is the detachment, movement and removal of soil from the land surface in runoff. Soil erosion by water carries away the dissolved S in the runoff as well as the organic S that is associated with the soil particles. However, erosion is not a common transport pathway for our relatively flat agricultural landscapes and dry, cold climate, where snowmelt over frozen soils is the dominant form of runoff.

- **Direct loss** - Similar to any other component of manure, direct, incidental losses of manure S can occur if manure is applied onto frozen soils or snow, or immediately prior to heavy rainfall.

Micronutrients and Other Trace Elements

A trace element is a chemical element that is present in minute quantities in the environment or is required by plants or animals in minute quantities to maintain normal function. Micronutrients are trace elements that are required by plants or animals in small amounts (generally less than 1 lb per acre in the case of crops). Each micronutrient has a range of safe and sufficient intake. Intake in excess of this range may be toxic and intake below this range may cause deficiency problems. The range of optimal intake for each micronutrient is specific to each plant or animal. Excessive concentrations of trace elements in soil can cause problems for plant, animal and microbial life. For example, sheep are particularly sensitive to copper (Cu). In general, sheep need between 5-25ppm Cu in their total diet depending upon the interaction of Cu with molybdenum (Mo) and sulphur (S) coming from other sources. More than 25 ppm of Cu in total sheep diet can cause toxicity. In contrast to sheep, cattle can tolerate concentrations of Cu 10 times higher in their diet. Pigs and chickens can tolerate even higher levels.

Micronutrients essential for plant growth that are derived mainly from soil include:



• **Mo Molybdenum B Boron Cl Chlorine (some Cl is also derived from the atmosphere) Cu Copper Zn Zinc Mn Manganese Fe Iron** Where micronutrient concentrations in soil are deficient, application can improve crop growth. However, repeated or heavy applications of micronutrients can lead to accumulations of these elements in soil that may pose a risk to soil, plant, animal or human health. There are also several elements that may be regarded as essential but which have little, if any, practical importance for crop nutrient management in the Canadian Prairies.

These include nickel (Ni), sodium (Na), silicon (Si), vanadium (V), fluorine (F), iodine (1), strontium (Sr), barium (Ba), aluminum (Al), and cobalt (Co) which are sufficient in Manitoba soils for Manitoba crops. Elements that are not essential for plant growth but are essential for animal nutrition, such as selenium (Se), are often added to livestock feeds in Manitoba. Trace elements that are not essential for plant or animal growth have very little or no effect on growth when present at normal or low concentrations. Again however, when the concentration of these elements is high, soil, plant, animal or human health may be adversely affected.

Some potentially toxic trace metals such as cadmium (Cd), lead (Pb) and mercury (Hg) have no beneficial role in plants and animals. Application of these metals can have negative effects on crop yield and/or crop quality when added in excess. Consumption of food or feed with a high concentration of metals, particularly over a long period of time, can lead to health problems in animals and humans. In addition, microbial processes and the activity of soil organisms are negatively affected at very high metal concentrations, reducing soil respiration, nutrient cycling, and enzymatic processes. Also, metals at very high concentrations may move to groundwater and or to surface waters thus reducing water quality and limiting use. When micronutrients and other trace elements are applied to the soil, they enter the soil nutrient cycle which can be thought of in terms of gains, removals, internal transformations and losses.

Gains of Micronutrients and Other Trace Elements

To Soil Parent Material - In their natural condition, soils contain highly variable concentrations of trace elements. Total concentrations of trace elements depend, in part, on parent material and soil forming processes, particularly weathering of rock fragments. Generally soils with shale parent material (clay soils) have higher trace element content than soils formed from granitic materials. Soils developed on limestone parent material generally have the lowest trace element contents.

• **Atmospheric Deposition** - Atmospheric deposition of micronutrients and other trace elements onto agricultural soils can be from natural sources or pollution. Natural Sources - Dust from soil and volcanic ash are sources of trace elements. **Combustion Processes**-Combustion of coal, gasoline and other oil products results in atmospheric emission and deposition of trace elements.

- **Industrial Activities** - Mining, smelting and some manufacturing processes are significant sources of trace elements.

- **Synthetic Fertilizers** - Where micronutrient concentrations in soil are deficient, application of synthetic fertilizers containing these micronutrients can improve crop growth. Some fertilizers also contain trace elements that are not required by plants or animals including potentially toxic trace metals. Phosphorus fertilizers, for example, often contain Cd. The concentration of Cd in the fertilizer depends on how much Cd was in the rock from which the fertilizer was made. Long term use of fertilizers containing micronutrients and other trace elements may result in increased concentrations of these elements in soil.

- **Pesticides** - Trace elements have been added to land in pesticides. For example, elevated lead and arsenic have been found in orchard soils where lead arsenate was used as a pesticide in the 1960s.
- **Irrigation Water** - Micronutrients and other trace elements may be added to land in irrigation water.
- **Plant Residues** - Micronutrients and other trace elements contained in unharvested plant residue eventually return to the soil nutrient cycle. Livestock
- **Manures** - Livestock manure contains micronutrients and other trace elements. Manures can be excellent sources of essential nutrients on soils marginal or deficient in these elements. Thus, opportunities to recycle micronutrients in manure should be exploited in areas where soils are deficient in these elements. The concentration of many of the trace elements in manure is generally low. Therefore, the short term risk of excessive accumulations of these micronutrients and trace elements is generally small if manure is applied at recommended rates and frequencies, especially under the new P based manure application regulations. For example, after three to seven consecutive annual applications of solid cattle manure and liquid pig manure at agronomic rates for crop N requirements at various sites in Saskatchewan, accumulations of copper, zinc and cadmium in soil were either not significant or very small (Qian et al. 2003; Lipoth and Schoenau 2007). Over the long term, however, large annual applications of manure may pose some risk (Benke et al. 2008). Manure from livestock that are fed high levels of micronutrients, however, can contain significantly higher concentrations of those micronutrients. For example, very high concentrations for Cu and Zn were measured in manures from nursery piglets that were fed high rates of Cu and Zn (Sheppard and Sanipelli, 2012). Accumulation of these micronutrients in soil from repeated applications of manure high in these micronutrients was also measured (Sheppard and Sanipelli, 2012).

Losses of Micronutrients and Other Trace Elements

- **From Soil Losses of micronutrients and other trace elements from soil include**: volatilization; leaching to groundwater; loss to surface water through runoff and erosion; and direct or incidental loss. Sheppard et al. (2009) derived trace element removal and loss rates for As, Cd, Pb, Se, Cu and Zn for Canadian soils. Leaching and crop removal were the two dominant soil depletion mechanisms for all elements except for Se, where volatilization was the dominant mechanism. Based on the medians for As, Cd and Se, loss by leaching was more than twice that by crop removal whereas the reverse was noted for Cu. Crop removal and loss of trace elements from agricultural soils are generally very small and less than the rates at which many trace elements are deposited or applied (Sheppard et al. 2009). Therefore, most soils used in agriculture will increase in trace metal concentration as a result of agricultural activity and other human activities. In general a doubling of trace metal concentration in Canadian soils is likely during the next 100 years (Sheppard et al. 2009). Therefore, trace metal accumulation is a long term concern that should be considered prior to any deleterious effects to crop yield, quality and/or the environment.

- **Volatilization** - Chemical and biochemical reactions induced by soil microorganisms can volatilize As, Hg and Se in soils. Selected plants are also known to absorb Se from soil and volatilize it. Soil conditions, however, are rarely optimal for substantial amounts of As, Hg or Se to be volatilized.

- **Leaching** - The risk of leaching for most trace elements, except for B, Cl and Se, is low and most of the trace elements added are retained in the top layers of soil because these trace elements are tightly bonded to oxides and/or to organic matter and highly insoluble. As well, the formation of soluble complexes such as chelates may increase the risk of leaching micronutrients and other trace elements, particularly in sandy soils. Despite the retention of most trace elements by soil constituents, downward movement to depths of 120 cm has been noted in fine-textured (clay) soils as a result of preferential flow in soil cracks on soil drying.

- **Runoff**-As with leaching, the formation of soluble complexes such as chelates may increase the risk of micronutrients and other trace elements leaving the field in runoff.

- **Erosion by water** - Erosion of soil rich in trace elements may increase the risk of trace element contamination of surface water. For example, although oxides such as iron oxide strongly retain large amounts of trace elements in an aerobic environment, these oxides can release trace elements when the oxide becomes solubilized in an anaerobic environment such as sediment.

- **Direct loss** - Direct or "incidental" loss is the loss of fertilizer or manure to water before interacting significantly with soil. It can result from over-application, heavy rainfall immediately following application or application directly into a waterway (including ditches). Direct losses of manure can also be substantial if manure is applied onto frozen soils or snow in the winter, where the manure can be directly transported to surface water during snowmelt runoff.

Salts and Sodium

Soil salinity is the soluble salt content of soil. The process of increasing the salt content of a soil is called salinization. Salinity develops naturally (from processes such as mineral weathering, groundwater recharge and discharge) and can be modified by human activities on the landscape (such as irrigation and artificial drainage). Groundwater Recharge areas occur where the net movement of water is downward. In these areas infiltration exceeds the storage capacity of the soil and moves downward to the zone of saturation (groundwater). The surface and subsoil are usually non calcareous and non-saline. Groundwater Discharge areas occur where the net movement of water is upward. In these areas, the zone of saturation is at or near the surface and the net movement of water is towards the ground surface. Discharge may be focused in areas such as springs, weeping embankments and baseflow discharge, or it may be diffuse over larger areas of the landscape. These areas may be characterized by soils that are calcareous and often have a build-up of salts. Elevated soil salinity can impede the ability of a growing plant to absorb water from the soil, even in conditions of otherwise adequate soil moisture. Different crops have different tolerances to soil salinity. Therefore, salinization will reduce the types of crops that can be produced on salt-affected land. Soil salinity can be measured in the laboratory and is expressed as electrical conductivity (EC) in units such as deci-siemens per metre (dS/m), milli-siemens per centimetre (mS/cm), or millimhos per centimeter (mmhos/cm), all of which are equivalent. Generally, soils with EC values less than 2 are regarded as non-saline. Soils with EC values greater than 2 create problems for pulses and vegetables. EC values greater than 4 create problems for other crops. Soil sodicity is caused by a high proportion of Na on the soil's cation exchange relative to Ca and Mg. It can adversely affect soil structure by making the soil very susceptible to crusting, impeding water infiltration and hindering root growth. Sodicity is expressed as the soil solution's sodium adsorption ratio (SAR) which is calculated from the measured concentration of Na, Ca and Mg. Soils with SAR values less than 6 are generally regarded as non-sodic and satisfactory for crop production. Soils with SAR values between 6 and 13 are regarded as slightly sodic. Soils with values greater than 13 are regarded as sodic and, therefore, problematic.

Gains of Salts and Sodium

- To Soil Saline groundwater - Long term continuous discharge of saline groundwater results in salinization of soils.

- Application of synthetic fertilizers - A variety of fertilizers are available with salts in varying proportions. For example, potash is potassium chloride, a salt of K and Cl. Municipal biosolids, municipal effluents, industrial waste and other amendments - Municipal and industrial wastes and other amendments contain a variety of salts that contribute to soil salinity when applied to land.

- Livestock manures - Manure contains the salts of NH4, Ca, Mg, K and Na. The salt content of manure is highly variable, depending on the livestock species, diet formulation and salt content of the livestock drinking water. Therefore, when manure is applied to soil, varying quantities of salts are also applied. In areas of adequate precipitation and drainage, application of manure at agronomic rates does not create a problem for crop production over the short term because the salts are leached through the soil profile. For example, after five to eight years of applying liquid pig manure and solid cattle manure at agronomic rates at various sites in Saskatchewan, Schoenau et al. (2005) reported small, but agronomically insignificant increases in soil salinity and sodicity. In areas with borderline saline soils and low annual precipitation, however, manure additions may cause a salt build-up in excess of crop tolerance, even if applied at agronomic rates. In an Alberta study, salinization was measured following 25 years of heavy, annual applications of salt-rich cattle manure (Hao and Chang, 2003). The cattle manure was applied at rates of 0, 30, 60 and 90 T ha-1 yr-1 under non-irrigated and at 0, 60, 120 and 180 T ha-1 yr-1 under irrigated conditions. The total amounts of soluble salts added to soil over the 25 years were substantial. Soil EC, soluble Na and K, and SAR all increased with rate of application. The authors concluded that applying repeated, heavy rates of cattle manure that is high in salt to soil is not sustainable over the long term because it will lead to soil salinization. In Manitoba, Fitzgerald and Racz (2001) calculated loadings of several major water soluble elements including Na from pig manures applied rates that supplied 70 kg available N ha-1. Their calculations showed that salts and Na were applied at rates that exceeded crop removals. Therefore, repeated application of pig manure could increase soil salinity in areas of low precipitation and drainage where the salts are not leached through the soil profile or on borderline saline soils.

Losses of Salts and Sodium

- **From Soil Leaching of salts** - Leaching is the downward movement of water and soluble substances in soil below the root zone. Leaching of salts by rainfall or irrigation prevents salinization of soils that receive repeated applications of manure and other amendments that contain salts. However, leaching of salts is an environmental concern when it occurs at rates high enough to contribute to groundwater contamination.

Soil pH

Soil pH is a measure of soil acidity (pH7). Acidic (low pH) soils have a high concentration of hydrogen ions (H+) in soil solution while alkaline or basic (high pH) soils have a low concentration of H+ in soil solution. Since hydrogen ions affect the charge on soil surfaces and the forms of nutrients in solution, pH plays an important role in determining the amount and strength of adsorption of nutrients to soil surfaces. Hydrogen ions also participate in many precipitation and dissolution reactions; therefore, pH also plays an important role in the solubility of nutrients in soil. Very low soil pH (acidic soil) results in high concentrations of aluminum and/or manganese in soil solution which can reduce plant growth and soil microbial processes. Very high soil pH can result in major and minor element deficiencies due to the extreme insolubility of some components in soil. Soil pHs that are slightly acidic to neutral (pH 6.0-7.5) are often the best for overall availability of nutrients (Figure 4), plant growth and microbial processes.

- **Effects of manure on soil** pH - The ability of manure to influence soil pH depends on the amounts of various constituents in the manure. When manure is applied to soil, nitrification and decomposition produce various acids. Nitrification is the conversion of NH4 to NO3 by soil microorganisms. It releases H+ into soil solution. Organic acids and carbonic acid are produced during the decomposition of the organic fraction of the manure (Chang et al. 1991). Liquid and poultry manures have relatively high concentrations of NH4-N and low concentrations of organic matter; therefore, as is the case with NH4-forming synthetic fertilizers, liquid and poultry manures may lower soil pH. Solid manures contain significantly more organic matter than liquid manures. The organic matter added with manure acts as a pH buffer, releasing H+ (acidity) in response to the addition of alkaline materials and accepting H+ in response to the addition of acidic materials. Some solid manures also contain significant concentrations of Ca, Mg and lime (CaCO3). The organic matter and lime-like materials in solid manure tend to offset the acidity produced when the NH4 in the manure is converted to NO3. Application of solid cattle manure moves soil pH towards neutrality in acidic (Benke et al. 2009) and alkaline soils (Chang et al. 1990; Hao and Chang 2002), thus improving nutrient availability especially for P and micronutrients (Figure 4). This move towards neutrality is also favourable for plant growth and a variety of beneficial microbial processes. Therefore, solid manure should be regarded not only as a source of nutrients, but also as a beneficial soil conditioner (Schoenau and Davis 2006). The overall effect of manures on the pH of calcareous prairie soils, however, is probably small due to high concentrations of Ca, Mg and Ca/Mg carbonate in these soils.

Soil Organic Matter and Microbial Activity

Soil Organic Matter Soil organic matter encompasses the vast array of C compounds in soil and includes plant and animal residues at various stages of decomposition, cells and tissues of soil organisms and substances synthesized by the soil population. These compounds play a variety of roles in soil nutrient, water and biological cycles. Soil organic matter improves the following soil properties:

- **Structure, tilth and aeration** - Improving soil structure makes the soil more friable, less compacted, easier to till and improves aeration.
- **Water infiltration rate** - Increasing water infiltration rate reduces runoff and increases the amount of water available to crops. Reducing runoff also

decreases sediment and soluble nutrient transfer from soils to surface waters. Walters et al. (2002) showed that applications of composted beef cattle manure to soils decreased runoff and that sediment loss was directly proportional to runoff volume. Increased water infiltration rate and reduced runoff volume may translate to less nutrient loss from fields that receive manure than equivalent applications of N and P as commercial fertilizer due to the addition of organic matter with the manure.

- **Water holding capacity** - Increased water holding capacity is of particular importance in sandy soils and in areas of low precipitation. The organic fraction in very sandy soil is responsible for much of its total water holding as well as available water capacity.

- **Cation exchange capacity (CEC)** - Soil organic matter has a cation exchange capacity of about 200 to 250 cmolec/kg, or about 2 to 3 times that of the highest cation exchange capacity for clay minerals. Coarse sandy soils, low in organic matter, have cation exchange capacities of 2 to 5 cmolec/kg. Thus, the concentration of organic matter in soil greatly influences cation exchange capacity, particularly for sandy soils.

- **Buffering pH**-Soil organic matter acts as a pH buffer or stabilizer, releasing $H+$ in response to the addition of alkaline materials and adsorbing $H+$ in response to the addition of acidic materials.

- **Chelation of micronutrients and trace elements** - Some micronutrients and trace elements bond with soluble organic compounds to form chelates and other soluble organic complexes helping to dissolve and mobilize micronutrients and trace metals. Chelation increases the solubility of nutrients, preventing the formation of insoluble precipitates and decreases the toxicity of some micronutrients. Although chelated nutrients may not be immediately available, they are mobile and can quickly convert to plant available forms near the root surface. Because organic matter contributes to improved soil properties, increasing soil organic matter generally results in increased soil productivity. But on many soils, suitable soil properties occur at relatively low levels of organic matter (2-4 per cent). The largest source of organic matter added to soil is the residue remaining following crop production. Fertilization indirectly increases soil organic matter levels by boosting crop yields and, consequently, the amount of residues returned to the soil. Soil organic matter cannot be increased quickly, however, because only a small fraction of the crop residues added to soil remain as soil organic matter following decomposition.

Effects of manure on soil organic matter - Manure is an excellent source of nutrients as well as organic matter. Manure indirectly increases soil organic matter because it increases crop yields and the amount of residues returned to the soil. Organic matter is also added directly to the soil with manure application, particularly solid manure.

The organic matter content of manure is highly variable. Solid and semi-solid manures have higher organic matter contents than liquid manure because of added bedding. Long term applications of solid manure can result in very large increases in soil organic matter (Sommerfeldt et al. 1988; Hao et al. 2003). Although liquid manure adds less organic matter to soil than solid manure, these additions are still greater than with synthetic fertilizers. King (2002) found that three annual applications of liquid pig manure to forage increased the light fraction of organic matter in soil, even though total organic C content in soil was not significantly affected over this relatively short period.

Soil Microbial Activity

Soil microbial activity is important because microbial processes are responsible for decomposition of crop residues and mineralization of organic nutrients to inorganic forms for plant uptake. It is generally accepted that the larger the soil microbial community and the greater the diversity, the greater the potential for nutrient mineralization. Application of manure to soil affects microbial communities. Manure additions to soil have beneficial effects on nutrient cycling, soil microbial biomass, soil microbial activity and enzymatic processes, provided that the manures do not contain high concentrations of undesirable constituents (ex: potentially toxic trace metals). An enzyme is a protein that speeds up a biochemical reaction.

The enzymes involved in mineralization exist both inside and outside of microbial cells.

- **Microbial biomass** - Addition of manure increases soil microbial biomass as the organic materials provides an energy source for microbial growth. For example, in Quebec soils, Lalande et al. (2000) showed that microbial biomass carbon was greater in surface soils after 17 applications of hog manure than in untreated soils. In Manitoba soils, Czurak-Dainard (2005) found that fields with longer histories of pig and cattle manure application generally contained higher concentrations of microbial biomass carbon than soils with no manure. Manure amended soils also exhibited higher concentrations of microbial biomass N than soils without manure. Cattle and hog manure had similar effects on soil microbial biomass carbon and N.

- **Microbial activity** - In her study with Manitoba soils, Czurak-Dainard (2005) found highly variable rates of soil respiration in manured and unmanured soils, with no significant differences between these two groups of soils. However, she found that manured soils had significantly greater concentrations of dehydrogenase enzyme, another measure of microbial activity, than unmanured soils. Fields treated with cattle manure had greater concentrations of dehydrogenase than fields treated with hog manure.

- **Enzyme activity** - In addition to increasing dehydrogenase activity, addition of manure to soil increases the activity of a variety of other soil enzymes (Lalande et al., 2000). For example, the activity of urease, the enzyme that converts urea in manure or synthetic fertilizer to ammonium N, increases with application of manure (Czurak-Dainard 2005). Amounts of phosphatase in soils, enzymes that mineralize organic P is often greater in manure-amended than non-amended soils (Lalande et al. 2000). However, in Manitoba soils, Czurak-Dainard (2005) found no significant differences in phosphatase activity between manured and unmanured fields and treatments. In this Manitoba study the effects of manure on the activity of glutaminase, a N mineralizing soil enzyme, were not consistent across sampling periods and varied by type of crop. However, for late summer sampling dates, the average for manure-amended soils was greater than for nonamended soils and for early and late summer sampling dates, soils amended with cattle manure had more glutaminase activity than soils treated with hog manure.