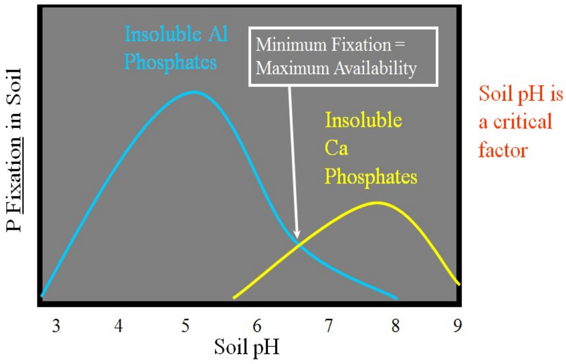
Appendix 1 – Phosphorus in Agriculture

Phosphorus in agriculture

Not all P in soil is bioavailable to plants and therefore, plays a critical role in agriculture. Total content of P in soil is 0.1-0.2%: inorganic P (≈50 %) and organic P (15-80%). The P solubility is very low and corresponds to ≈ 0.03 mg P/kg.

Several soil properties such as abundance of **Ca**, **Al** and **Fe**, **organic matter** content and **pH** influence the solubility and thus, the bioavailability. Among these **pH** is the most **critical factor**.



Reactions that reduce **P availability** occur in all ranges of soil pH but can be very pronounced in **alkaline soils** (pH > 7.3) and in **acid soils** (pH < 5.5) (Figure 1).

Maximum availability of phosphorus generally occurs in a **pH** range from **6.0 to 7.0** (Figure 1).

Figure 1. Behaviour of P at different soil pH values. P is only bioavailable at neutral pH.

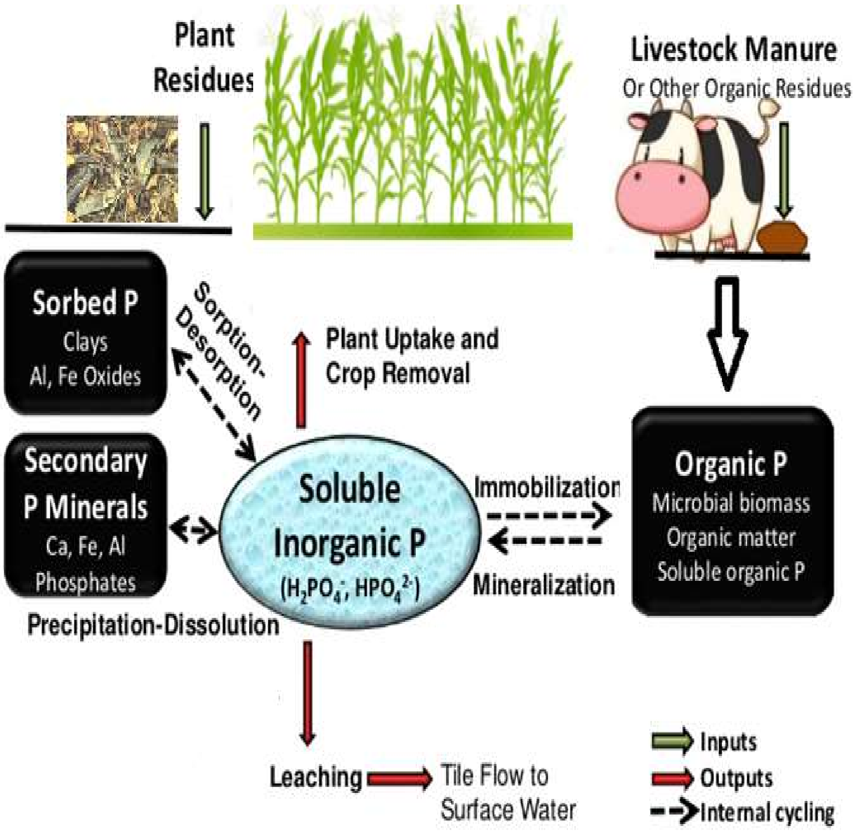


Figure 2. Phosphorus cycle in the agricultural ecosystem. In the soil there are inorganic and organic P forms. Only a limited fraction of P is soluble and thus bioavailable to plants. The remaining part of P forms unsoluble precipitates.

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Organic Phosphorus (inositol phosphates, nucleic acids and phospholipids) from animal and vegetal residues is mineralized by soil microorganisms and transformed into **available forms** (ortho phosphates) (Figure 2).

Microorganisms convert **inorganic P** into **organic phosphate** (immobilization) such as phospholipids, nucleic acids and ATP (Figure 2). The inorganic phosphate compounds during the time became more crystalline and therefore, insoluble . It contributes slowly to soil solution inorganic P.

P dynamics in rhizosphere

Plants have developed various strategies to acquire nutrients from the soil:

1) **Root architecture**

The most common changes regard the root architecture (root morphology, topology, and distribution patterns). The main effect under P deficiency is a considerable modification on root (Figure 1). In particular, plants show an inhibition of primary root growth instead lateral root growth and root hair growth and density increase (Figure 1 B).

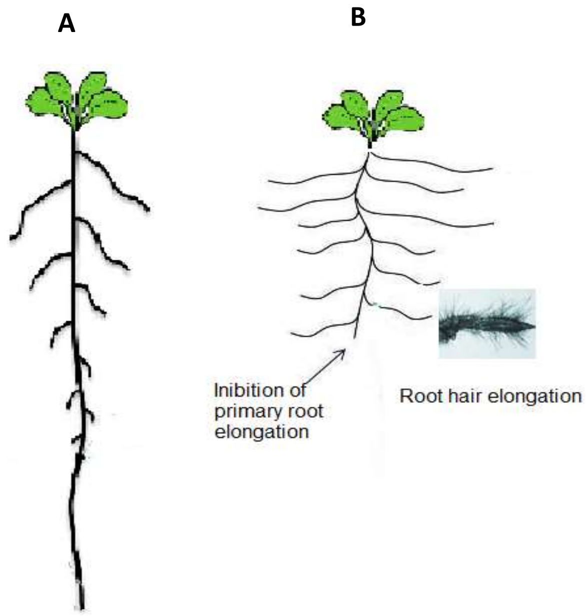

Figure 1. **A)** Plants growth in presence of phosphorus are characterised by normal root development. **B**)Plants grown under P deficiency are characterized by surprising morphological changes of the root; there is mainly a reduction of the primary root length, whilst the length of the lateral roots is increased, as well as the length and density of the radical hairs.

2) **Arbuscular mycorrhizal fungi** (AMF)

Plants can participate in symbiotic associations with fungal organisms. When phosphate is available in soil plants are able to acquire it directly via root phosphate transporters (Figure 2).

Under low phosphate conditions, plants become reliant on interactions with mycorrhizal fungi for phosphorus acquisition. This kind of symbiosis facilitates plant phosphorus uptake from the soil by increasing the root's absorptive surface area.

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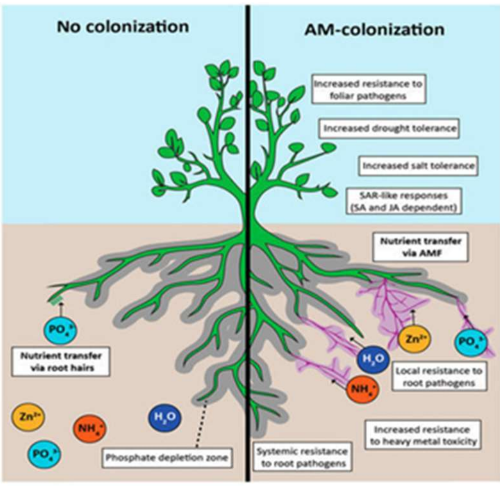

Figure 2. Symbiotic associations with fungal organisms is a strategy to obtain nutrients not readily available from soil.

3) **Chemical and biological processes of rhizosphere**

Plant roots can greatly modify the rhizosphere environment through the exudation of organic compounds such as citrate, malate, and oxalate (Figure 3).

Root-induced acidification can decrease rhizosphere pH by 2 to 3 units relative to the bulk soil, resulting in substantial dissolution of sparingly available soil P.

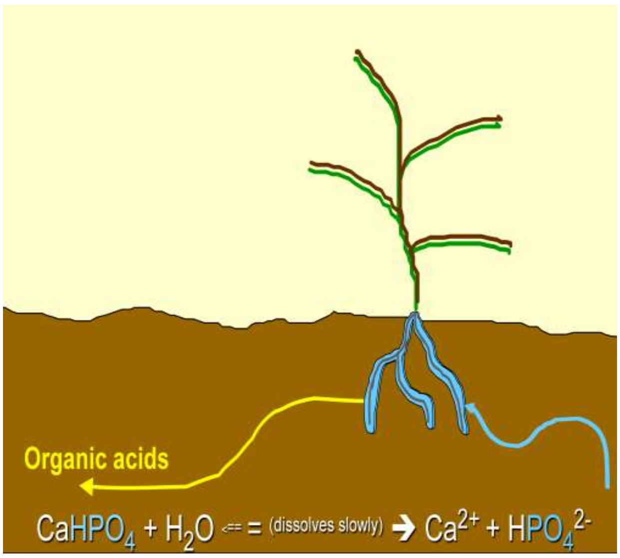

Figure 3. Plant roots modify the rhizosphere pH through the exudation of organic compounds.

Appendix 1 – Phosphorus in Agriculture

Source of phosphorus for crops

Nowadays, **phosphorus** is mostly derived from **phosphate rock mining**. The **phosphate rock** were formed in continental **shelf marine** environments or in **igneous deposits** mostly in shield areas and rift zones.

Phosphate rock is converted to phosphoric acid. The majority of P fertilizer is produced by reaction of phosphate rock with acid (H_2SO_4, HNO_3) (Figure 6).

Main source of fertilizer P are:

-Apatite, ($Ca_{10}(PO_4)_6(OH)_2$), is also a component of teeth and bones, is dissolved in acid to make soluble fertilizer P:

$$\textbf{Apatite} + H_3PO_4 \rightarrow Ca(H_2PO_4)\bullet H_2O$$

-**Ammonium phosphate** is produced by reacting 1 mole ammonia with 1 mole of phosphoric acid:

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4;$$

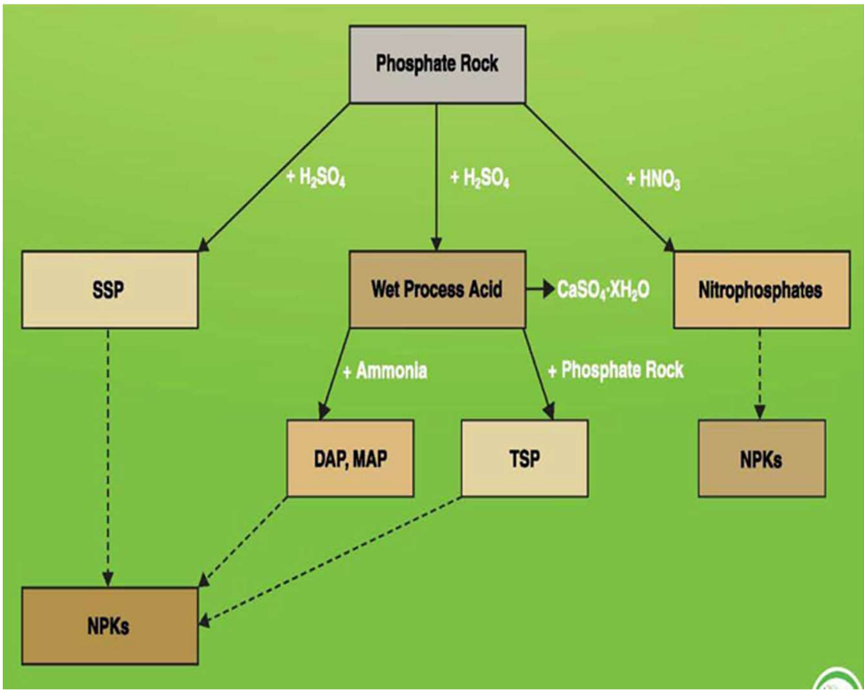

Figure 4. Main pathway of phosphatic fertilizers production originated from phosphate rock extraction

-Diammonium phosphate (DAP) is produced by reacting 2 moles ammonia with 1 mole of phosphoric acid:

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2H_2PO_4$$

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However, phosphorus from **phosphate rock mining** is limited and **non-renewable resource**. Due to this, phosphate fertilizers are going to be limited in future.

Are there other phosphorus source?

Wastewater treatment plants and **animal husbandry facilities** are the two most important sources of phosphorus.

Phosphorus can be recovered from wastewater in crystal form of **magnesium ammonium phosphate** (MAP), also known as **struvite.**

Struvite ($MgNH_4PO_4 \bullet 6H_2O$) is a mineral obtained through a basic precipitation reaction of **ammonium**, **phosphate** and **magnesium** in a white powder (Figure 5).

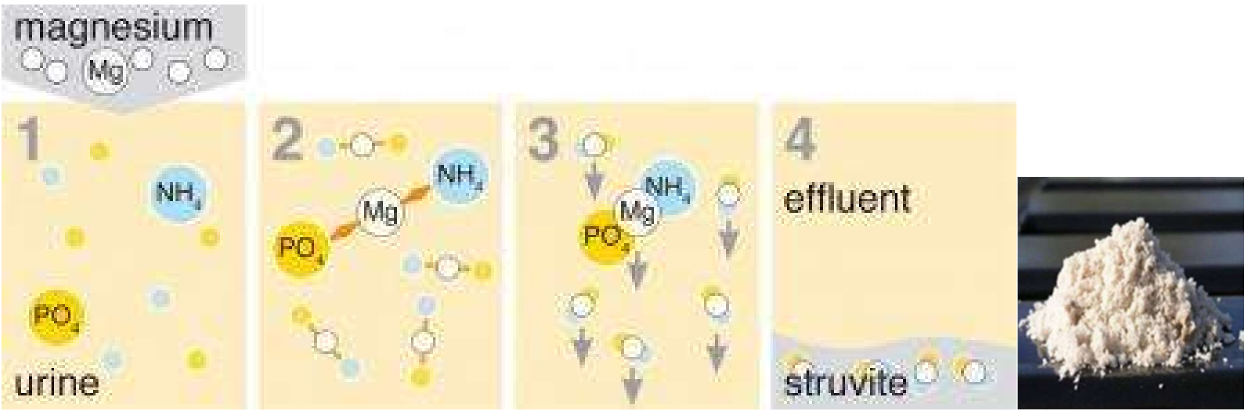

Figure 5. Production of struvite from urban wastewaters

In this activity, students are encouraged to build *struvite reactor* using recycled materials and to produce struvite from **synthetic wastewater solution** (SWW) considering the effect of pH, and concentration of reagents

Reactions

$$\mathbf{Mg^{2+}\,(aq) + NH_4^+\,(aq) + PO_4^{3-}\,(aq) + 6\,H_2O\,(l) \rightarrow NH_4MgPO_4\,.\,6\,H_2O\,(s) + 2\,H^+}$$

pH adjusted to 8.0

Struvite is formed when $\mathbf{Mg^{2+}, NH_4^+, PO_4^{3-}}$ are present in **equimolar quantities** (1:1:1).