WATER MONITORING
MEASUREMENT

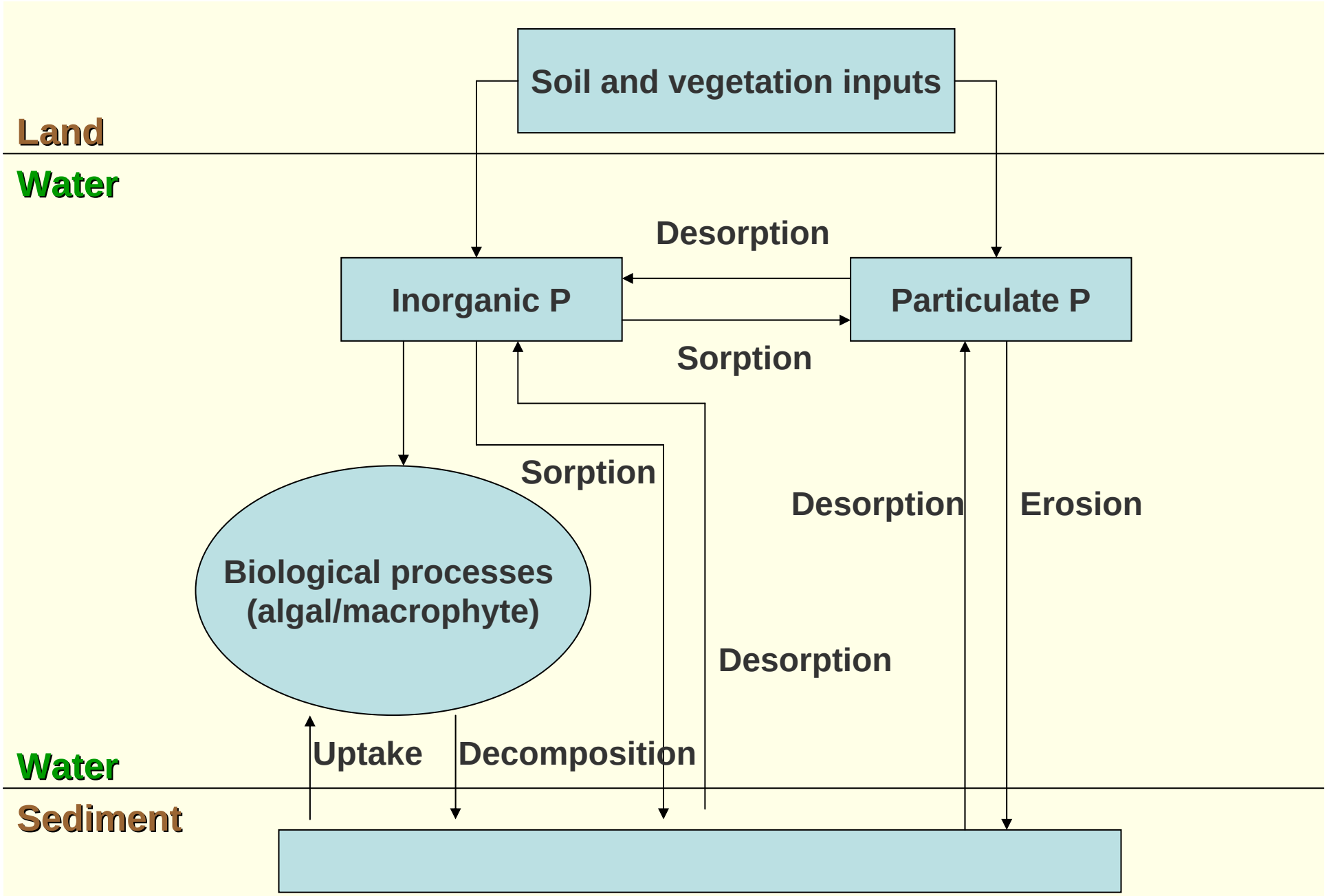
Phosphorus and Phosphate

1. General Considerations

- The phosphate determination has grown rapidly in importance in environmental engineering and science practice because of the many ways in which phosphorus compounds affect environmental phenomena of interest.

- The **inorganic compounds of phosphorus** of significance are the **phosphates** or their molecularly **dehydrated forms**, usually referred to as polyphosphates or condensed phosphates.

- **Organically bound phosphorus** is usually a minor consideration.



The aquatic phosphorus cycle

Source of Phosphorus:

Wastewater Treatment

- **Prior to the development of synthetic detergents, the content of inorganic phosphorus usually ranged from 2 to 3 mg/L and organic forms varied from 0.5 to 1.0 mg/L.**

- **Many heavy-duty synthetic detergent formulations contain from 12 to 13 percent phosphorus or over 50 percent of polyphosphates. The use of these materials has greatly increased the phosphorus content of domestic wastewater.**

Other Phosphorus-containing Wastes

Point sources of phosphorus

- **Sludge** come from aerobic or anaerobic treatment process: may contain about 1 percent phosphorus and has significant fertilizing value.

- **Boiler water**: phosphates are widely used in steam power plants to control scaling in boilers and should be controlled strictly through determination of orthophosphate.

Nonpoint source of phosphorus

- **Runoff** from parks or agriculture fields: may cause phosphorus pollution because of phosphate-containing fertilizers moved into waters with soil particles.

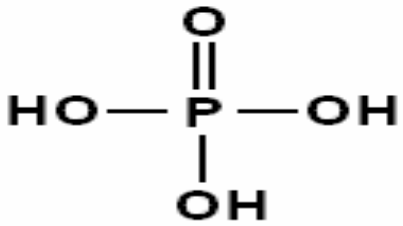
2. Phosphorus containing compounds classification

- **orthophosphates**
- **condensed phosphates: pyro-, meta-, and other polyphosphates**
- **organically bound phosphates**

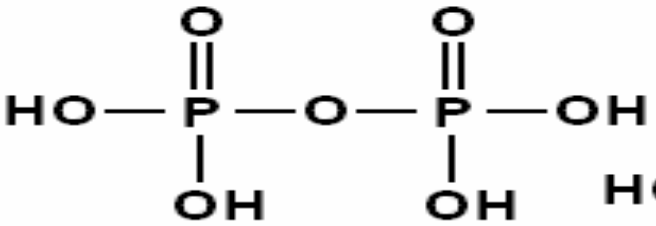
Phosphorus Compounds of Importance

Name	Formula
Orthophosphates	
Trisodium phosphate	Na_3PO_4
Disodium phosphate	Na_2HPO_4
Monosodium phosphate	NaH_2PO_4
Diammonium phosphate	$(NH_4)_2HPO_4$
Polyphosphates	
Sodium hexametaphosphate	$Na_3(PO_3)_6$
Sodium tripolyphosphate (STPP)	**$Na_5P_3O_{10}$**
Tetrasodium pyrophosphate	$Na_4P_2O_7$

Chemical structures of orthophosphoric acids and polyphosphoric acids

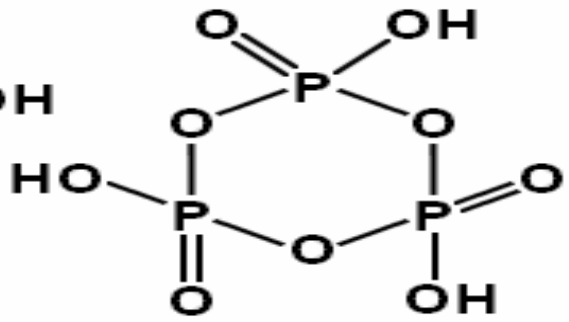


orthophosphoric acid

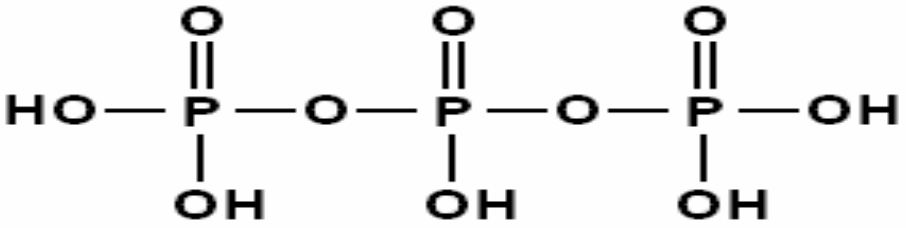


pyrophosphoric acid

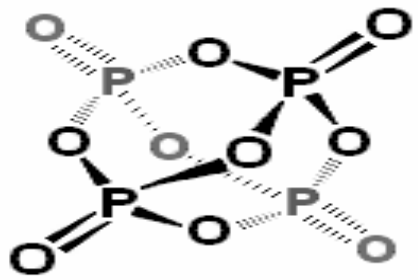
$H_4P_2O_7$



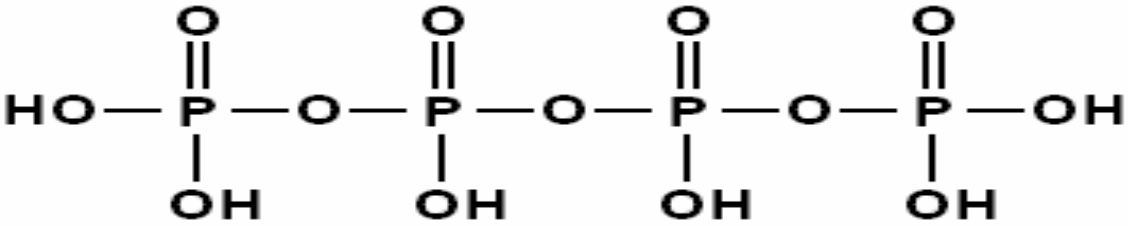
trimetaphosphoric acid



tripolyphosphoric acid



phosphoric anhydride
(P_4O_{10})



tetrapolyphosphoric acid

3. Methods of Determination

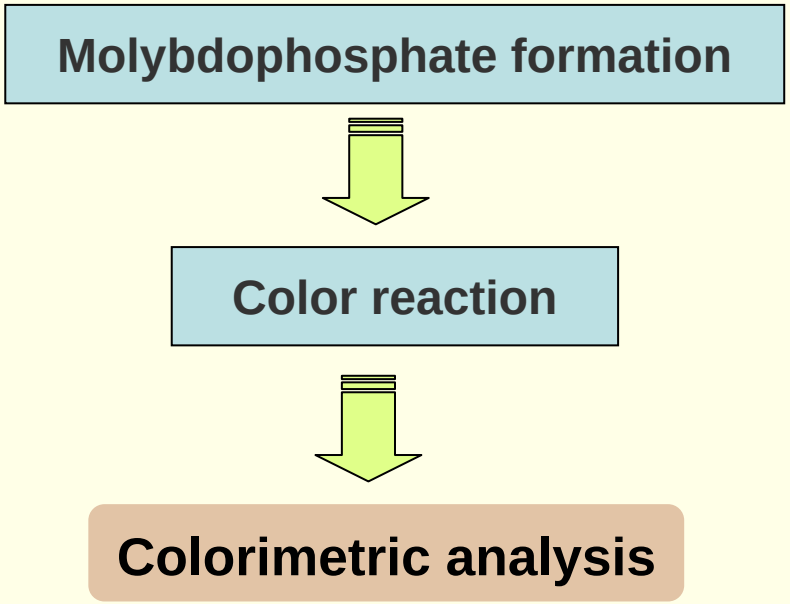
- The amounts of **ortho, poly**, and **organic phosphorous** present are of interest.

- It is possible to measure orthophosphate with very little **interference** from **polyphosphates** because of their **stability** under the conditions of pH, time, and temperature used in the test.

- Both **poly** and **organic forms** of phosphorus must be **converted to orthophosphate** for measurement.

Orthophosphate Measurement

The standard procedures for water and wastewater use **colorimetric methods**. The whole procedure includes three steps as follows:



Orthophosphate Measurement

The initial reaction is: Phosphate ion combines with ammonium molybdate under acid conditions to form a molybdophosphate complex：

$$PO_4^{3-} + 12(NH_4)_2MoO_4 + 24H^+ \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^+ + 12H_2O$$

Three colorimetric methods are used for measuring orthophosphate. They are essentially the same in principle but differ in the nature of the agent added for final color development.

- **Vanadium (钒)** is added and forms a **vanado-molybdophosphoric acid complex（钒磷钼酸）** that yields a much more intense yellow color, permitting analysis for phosphorus down to the mg/L or lower range.

- Either **ascorbic acid（抗坏血酸）** or **stannous chloride（氯化亚锡）** may be added to reduce ammonium phosphomolybdate into **molybdenum blue(钼蓝)**:

$$(NH_4)_3PO_4 \cdot 12MoO_3 + Sn^{2+} \rightarrow \text{(molybdenum blue)} + Sn^{4+}$$

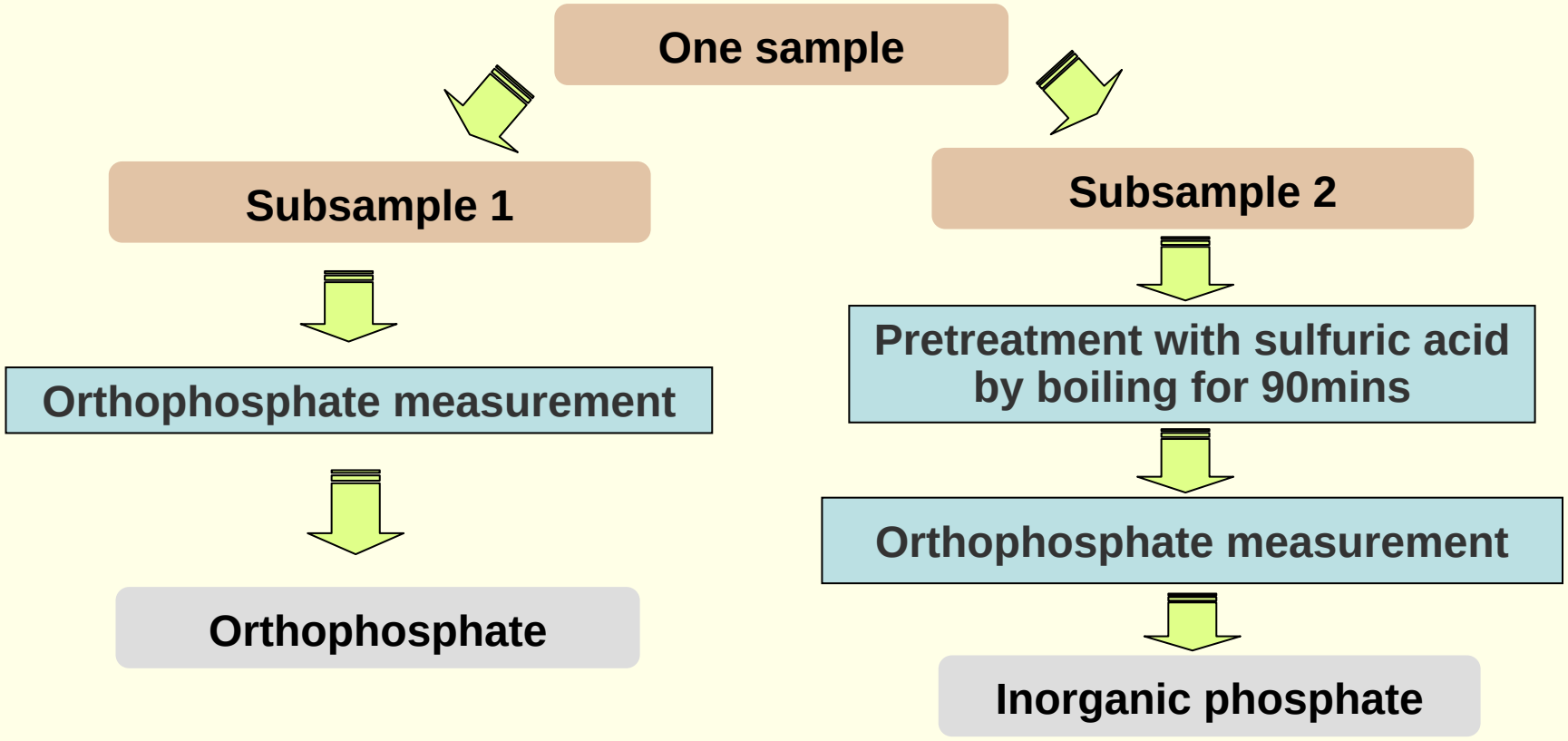
Polyphosphates Measurement

- **Conversion from polyphosphates to orthophosphates:**

Polyphosphates may be converted to orthophosphate by boiling samples that have been acidified with sulfuric acid for at least 90 min. The hydrolysis may be hastened by heating in an autoclave at 20 psi. The excess acid added to speed the hydrolysis must first be neutralized before proceeding with the addition of the ammonium molybdate solution.

Polyphosphates Measurement

Divide one sample into two subsamples, and measure orthophosphate and polyphosphate respectively.



Total inorganic phosphate – orthophosphate = polyphosphate

Organic Phosphorus Measurement

- **Presence:** The amount of organic phosphorus present in industrial wastes or in sludges is sometimes of interest.

- **Pretreatment:** This analysis requires that the organic matter be destroyed by digestion so that the phosphorus is released as phosphate ion.

Organic Phosphorus Measurement

- **Sample Preparation – wet oxidation**
  - Perchloric acid digestion
  - Sulfuric acid-nitric digestion
  - Persulfate digestion method

The whole digestion process should be carried out in an autoclave very carefully to avoid unnecessary dangers. The right order of acids adding should also be noticed.

Organic Phosphorus Measurement

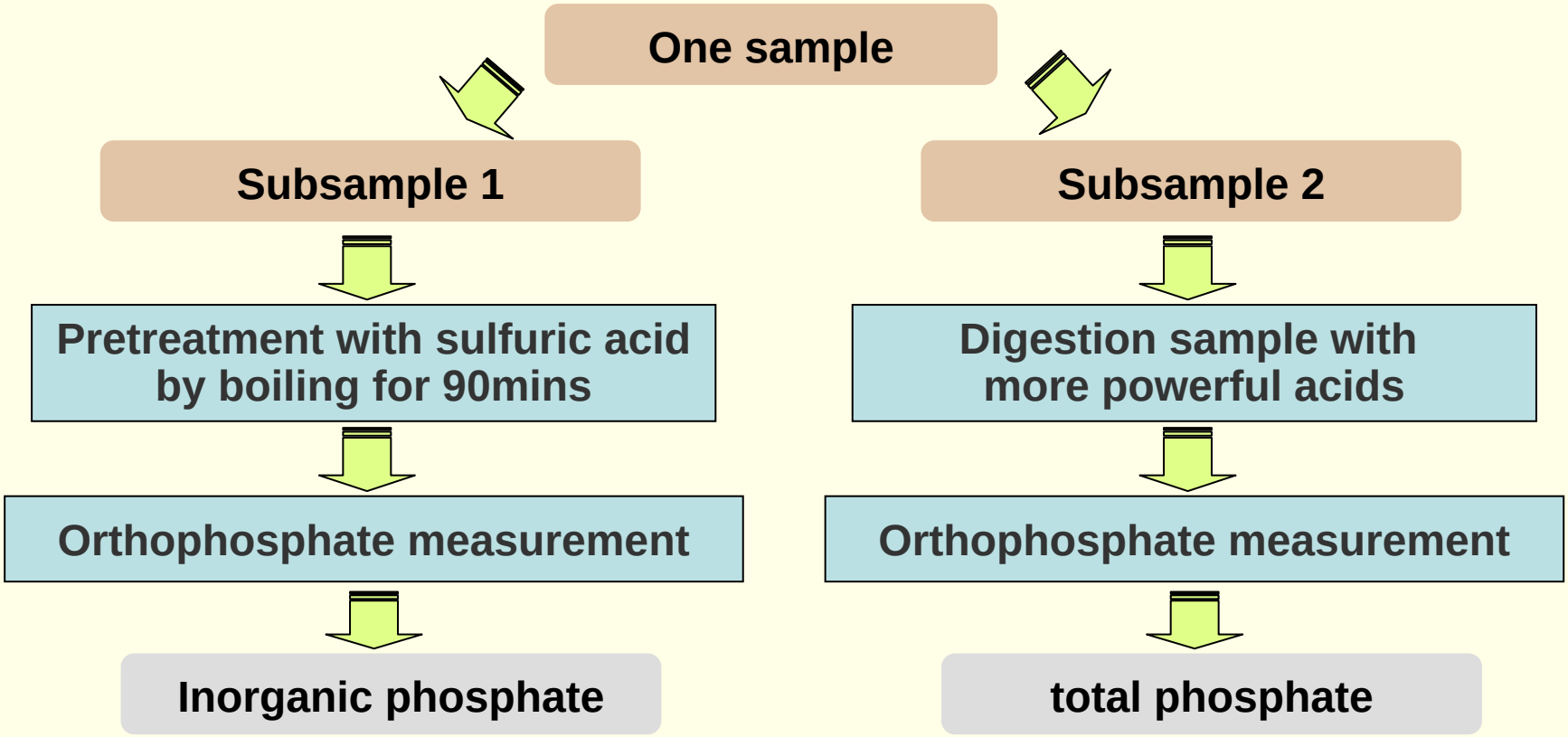
Measurement: Once digestion has been accomplished, measurement of the phosphorus released can be made by any of the methods applied to orthophosphate.

- **Calculation:** All forms of phosphorus (total) are measured in an organic phosphorus determination.

Total phosphorus – inorganic phosphorus = org-P

Organic Phosphorus Measurement

Divide one sample into two subsamples, and measure orthophosphate and polyphosphate respectively.



Total phosphorus – inorganic phosphorus = org-P

A: total reactive phosphorus

B: total acid-hydrolyzable

C: total phophorus

D: total organic phosphates

E: dissolved reactive posphorus

F: dissolved acid-hydrolyzable phosphorus

G: total dissolved phosphorus

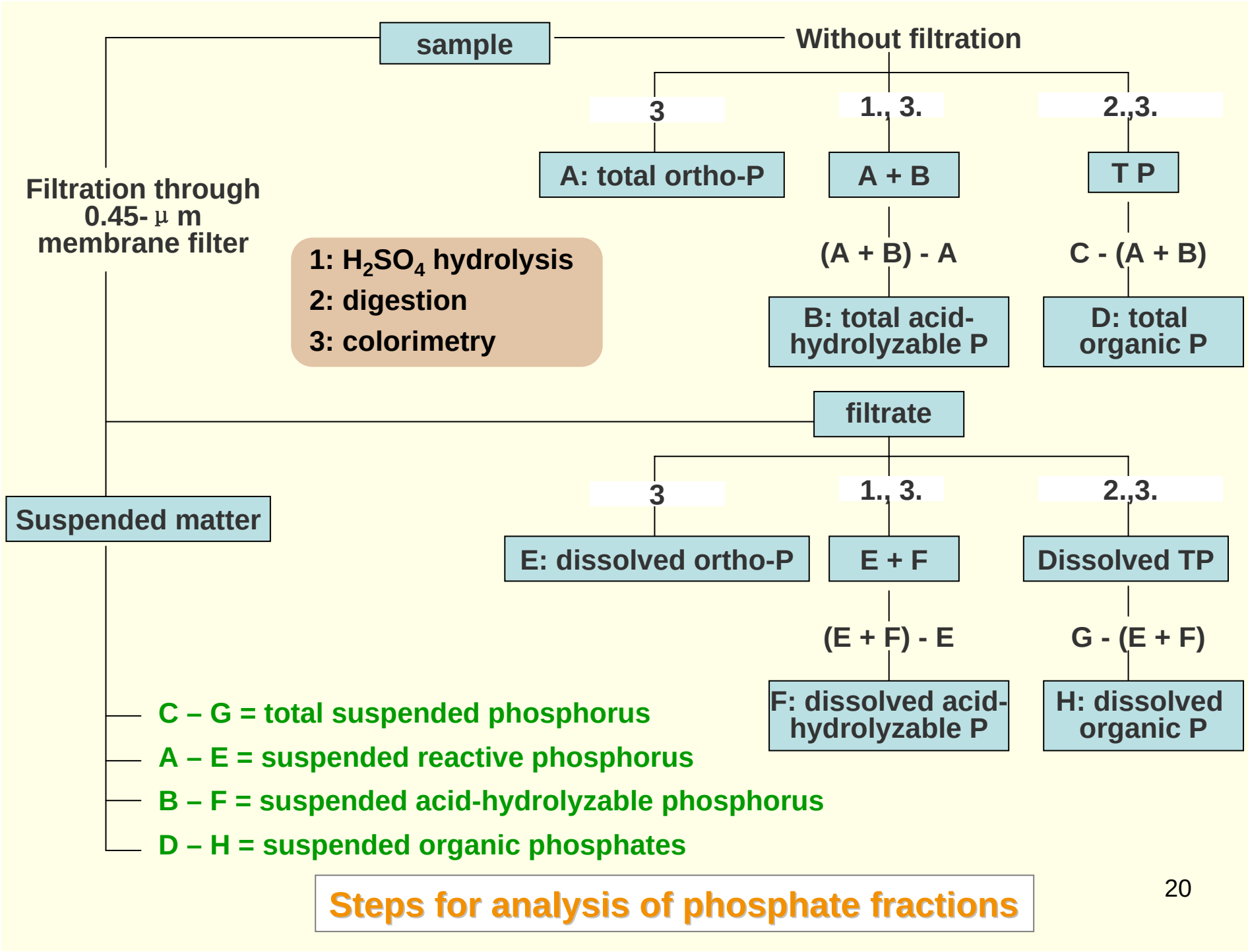
H: dissolved organic phosphorus

C – G = total suspended phosphorus

A – E = suspended reactive phosphorus

B – F = suspended acid-hydrolyzable phosphorus

D – H = suspended organic phosphates



Steps for analysis of phosphate fractions

4. Applications of Phosphorus Data

- **In the past, the data have been used to control phosphate dosages in water systems for corrosion prevention and in boilers for scale control.**

- **The data are also important in assessing the potential biological productivity of surface waters.**

- **Phosphorus is an important nutrient in biological methods of wastewater treatment, its determination is essential with many industrial wastes and in the operation of waste treatment plants.**

Problems

- What practical uses are made of polyphosphates?
- Why are limits sometimes placed on the discharge of phosphates to receiving waters?
- Why is phosphate sometimes added in the biological treatment of industrial wastewaters?
- What analytical procedures are available for the analysis of orthophosphate?
- What is the difference between orthophosphate, polyphophates, and organic P? In which form must the P be for colorimetry?
- How is the analysis for phosphorus conducted to differentiate between the three forms of phosphorus?
- Would you expect the analytical results for orthophosphate to be higher than, lower than, or the same as the original value in a sample of domestic wastewater that had been acidified to prevent bacterial action and stored for several days prior to analysis?