UiO : Department of Chemistry
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Monitoring of phosphorous fractions

Understanding the hydro-geochemical processes governing mobilization and transfer of phosphorous in an agricultural watershed in north-eastern China

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Water quality in China

- Rapid economic growth in the last 30 years
  - Rising living standards - High consumption
  - Urbanization
  - Population increase
  - Increased agriculture and industries
    - Increased water extraction and **pollution**
- Eutrophication - Most critical problem facing lakes and reservoirs in China
- Over **58%** of the lakes are eutrophic/hypertrophic (*Chai et. al, 2006*)

SinoTropia project

- SinoTropia is a Sino-Norwegian trans-disciplinary project focusing on understanding eutrophication in China.

-Assessing the impact of changes in environmental pressures on **mobilization, transport, fate and impact** of phosphate fractions to the Yuqiao reservoir in Tianjin, China.

- Why Sinotropia?

- Limited knowledge on mobilization,transport and fate of phosphate

-The need for site specific abatement actions

Aim of the study

- Access sources, mobilization and transport of phosphates to the Yuqiao reservoir
  - P fractionation
  - DGTs

Drivers of Eutrophication in China

Animal Husbandry - Manure

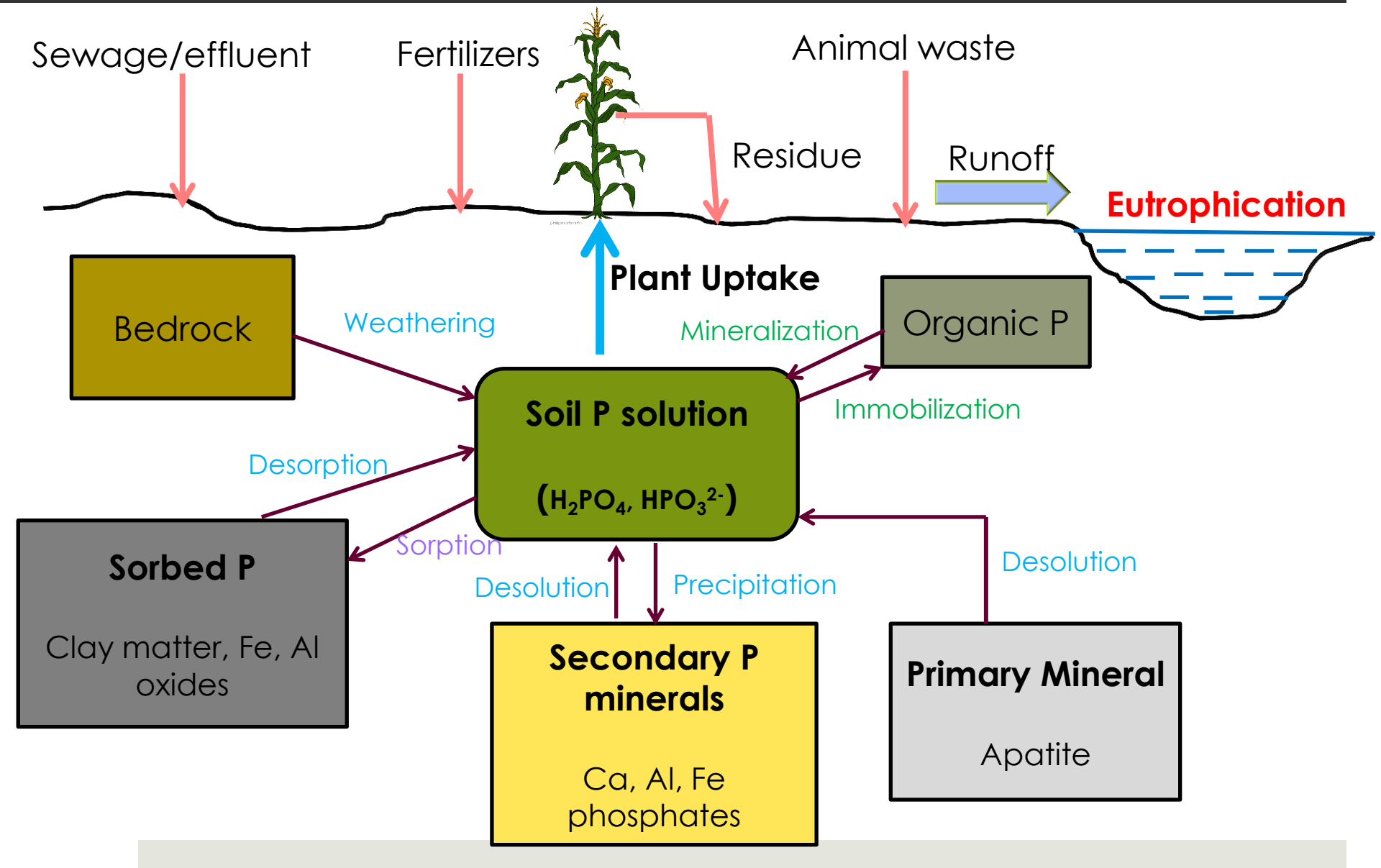
Agriculture - Fertilizers

Sewage/effluent

Soil – Impeable clay

Monsoon climate

Phosphorous



Phosphorous fractionation

Total fraction	**Total P (TP) by digestion**			
Filtration (0.45µm)	**Particulate P (PP) (on filter)**		**Dissolved P (TDP) (filtrate)**	
Fractions	**Particulate Organic P**	**Particulate Inorganic P**	**Dissolved Organic P**	**Dissolved Inorganic P**
Denotation	**POP**	**PIP**	**DOP**	**DIP**
Bioavailability	**Low**	**Low**	**Medium**	**High**

Yuqiao reservoir

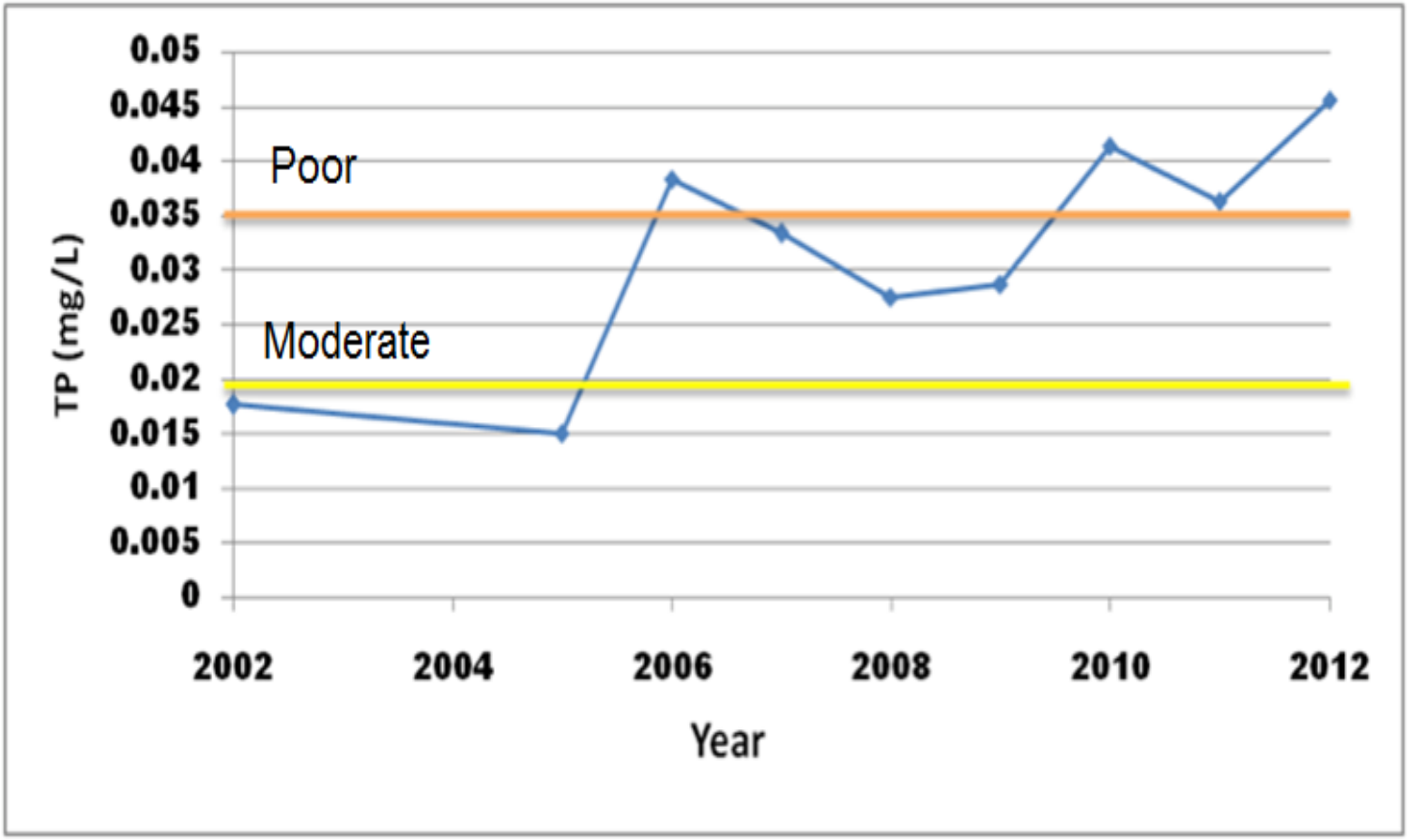
- Source of drinking water

  for over 6 million people

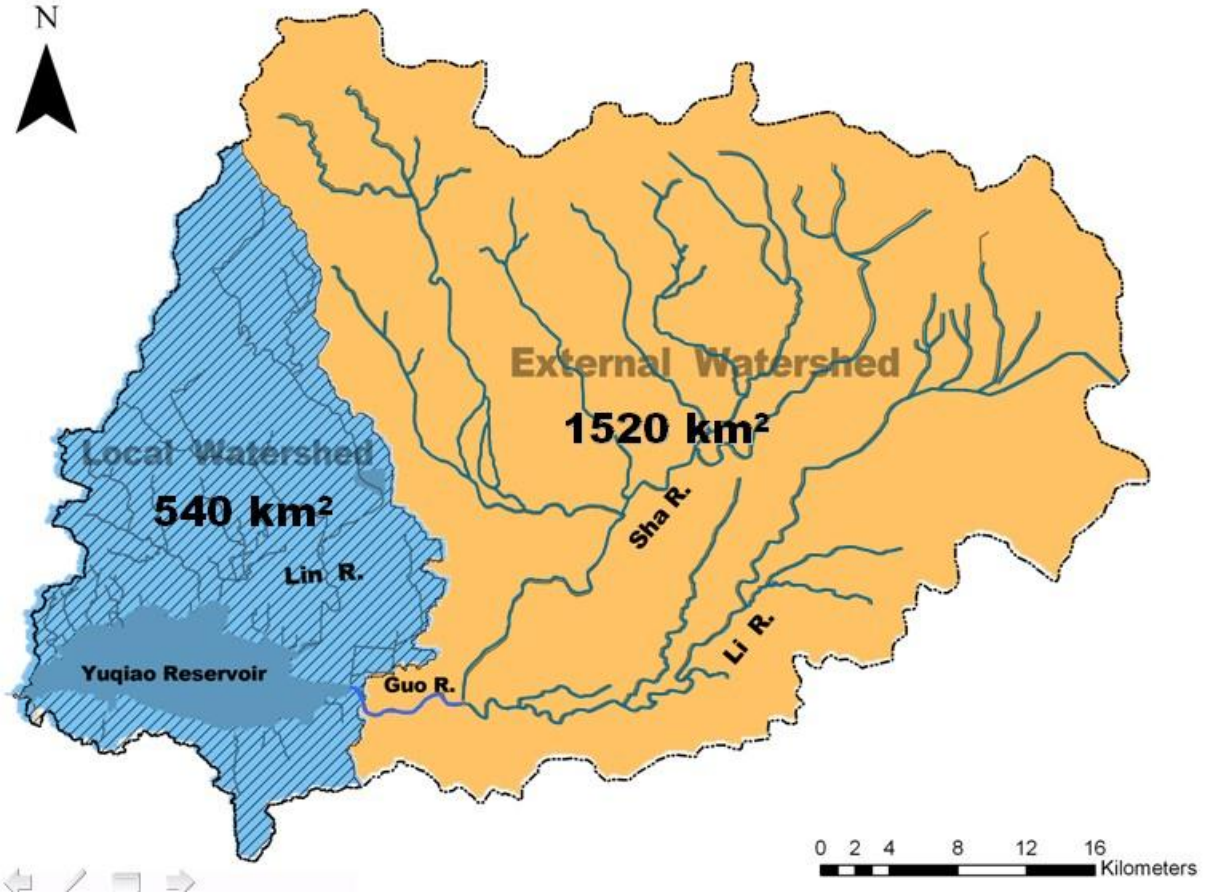
- Facing eutrophication challenges

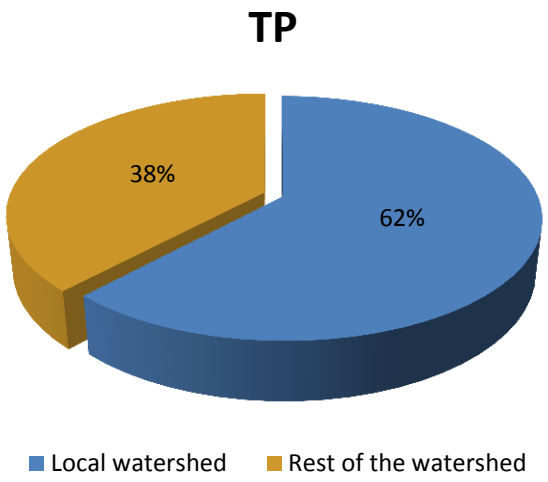
Nutrient level – Yuqiao reservoir

- Reservoir – Experience algae bloom (Summer/Fall)
- Increasing trend of eutrophication

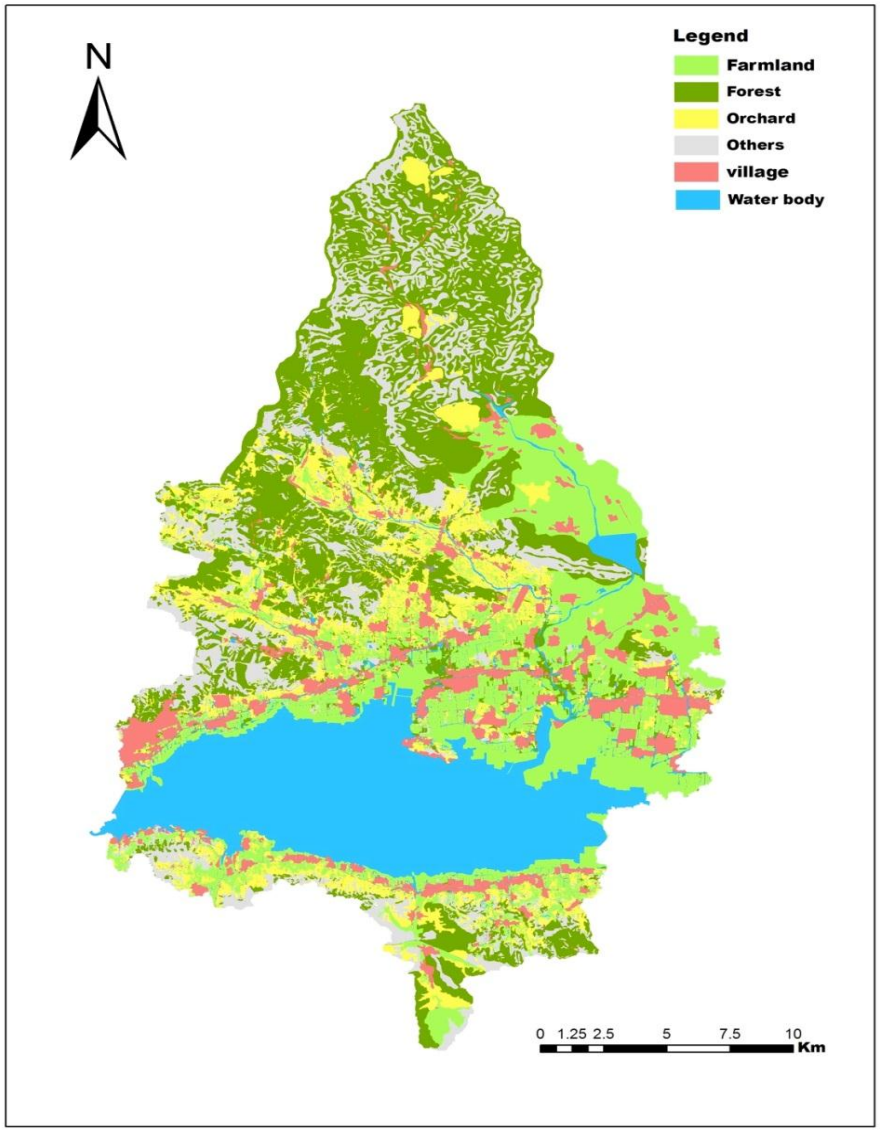


Site description





Land Use



Animal husbandy and aquaculture

Sampling – Two types

Water sampling

- Synoptic and Episodes studies (2012 - 2013)
- Three (3) rivers – 5 points
- 348 samples collected

DGT sampling

- Done during wet months

  (July – September 2014)
- Three (3) rivers – 5 points
- 57 samples collected

Sampling sites - Rivers

- Three (3) river basins
- Five (5) sampling points
- Catchments by **land use**

-proxy for P fraction distribution

- Sampled catchments
  - Forest **(#1)**
  - Farmland **(#2)**
  - Orchard **(#3)**
  - Mixed 2- Mountain **(#4)**
  - Mixed 1– Watershed **(#5)**

Map: Courtesy of Zhou Bin (2014)

Sampling sites - Reservoir and fish ponds

Yuqiao Resevoir

Fish pond

Analysis methods

- **Water analysis**:

- Parameters measured: - pH, Alkalinity, Cations, Anions,TP, PO_4, TSS

- **Particle characterization:**

- Organic and Inorganic phosphates (Loss of Ignition)
- Minerology (XRD)
- Elemental composition: Microwave digestion (68% HNO_3 only)

  ICP-OES (Na, Mg, Al, K, Ca, Mn, Fe, Si and P)

- **DGT analysis**

- DIP and TDP (Molybdate Blue Method and ICP-MS)

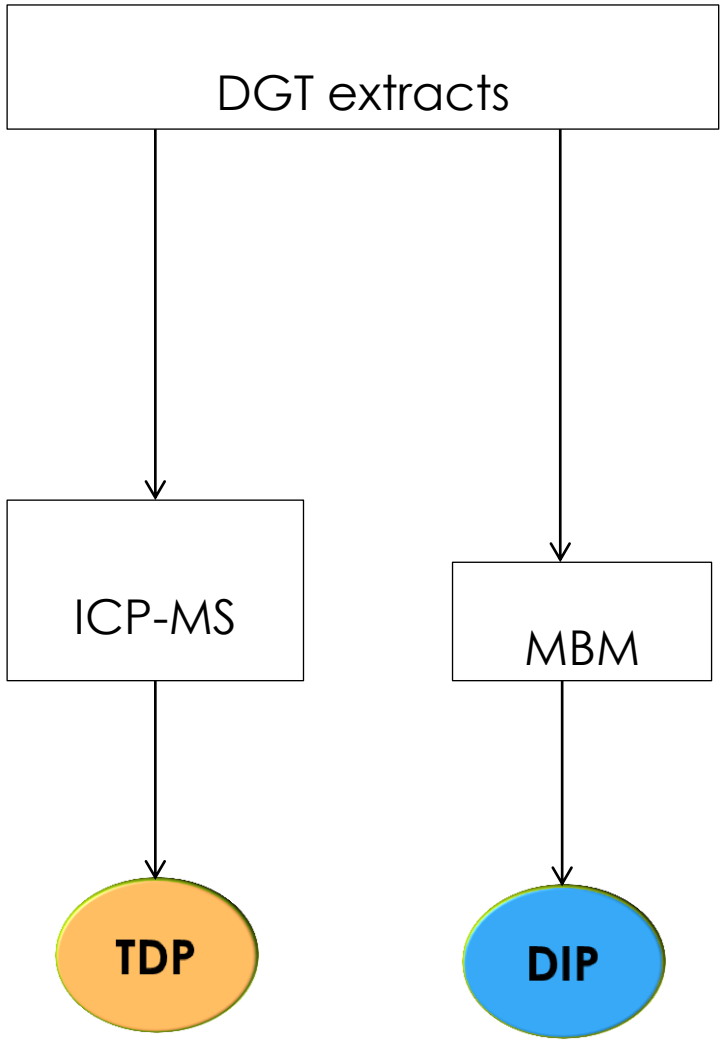
DGT extraction and P analysis

- Disassemble DGT and remove resin gel
- Place resin gel in tube and add H_2SO_4
  - Ferrihydrite dissolves and phosphate is released

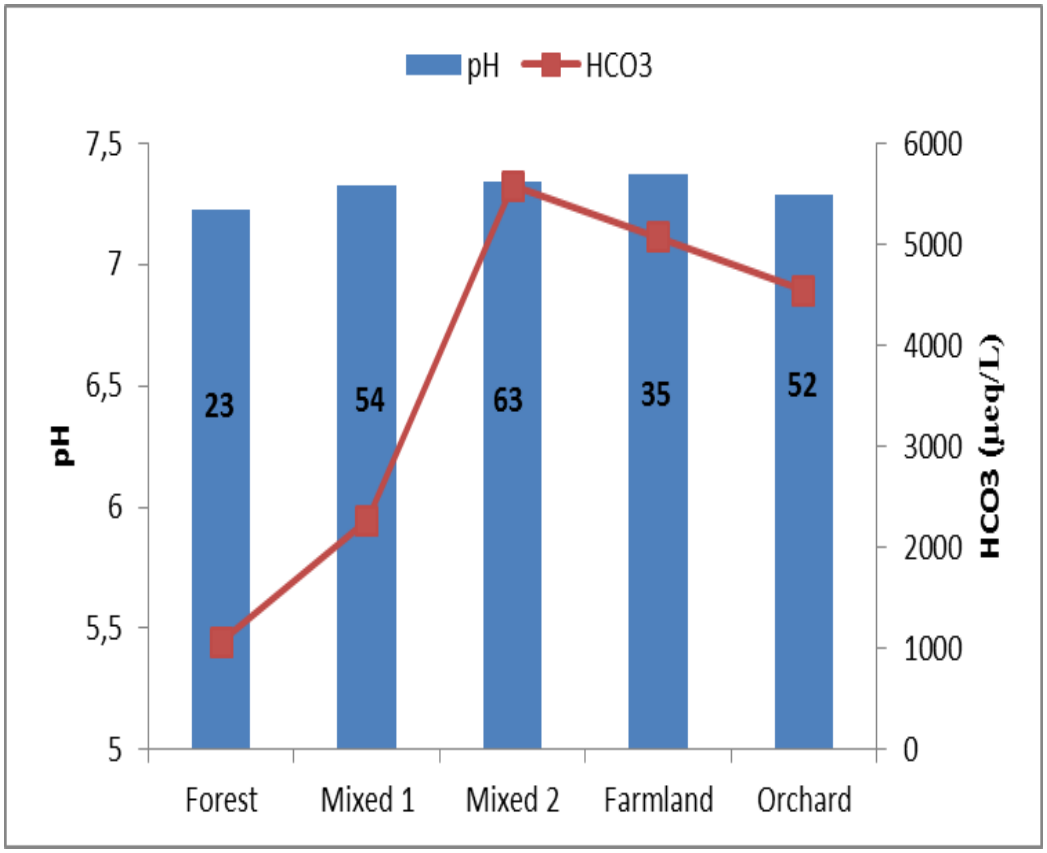
Two P fractions:

- Total Dissolved P (TDP)
- Dissolved Inorganic P (DIP)

Note: Dissolved Organic P (TDP-DIP)

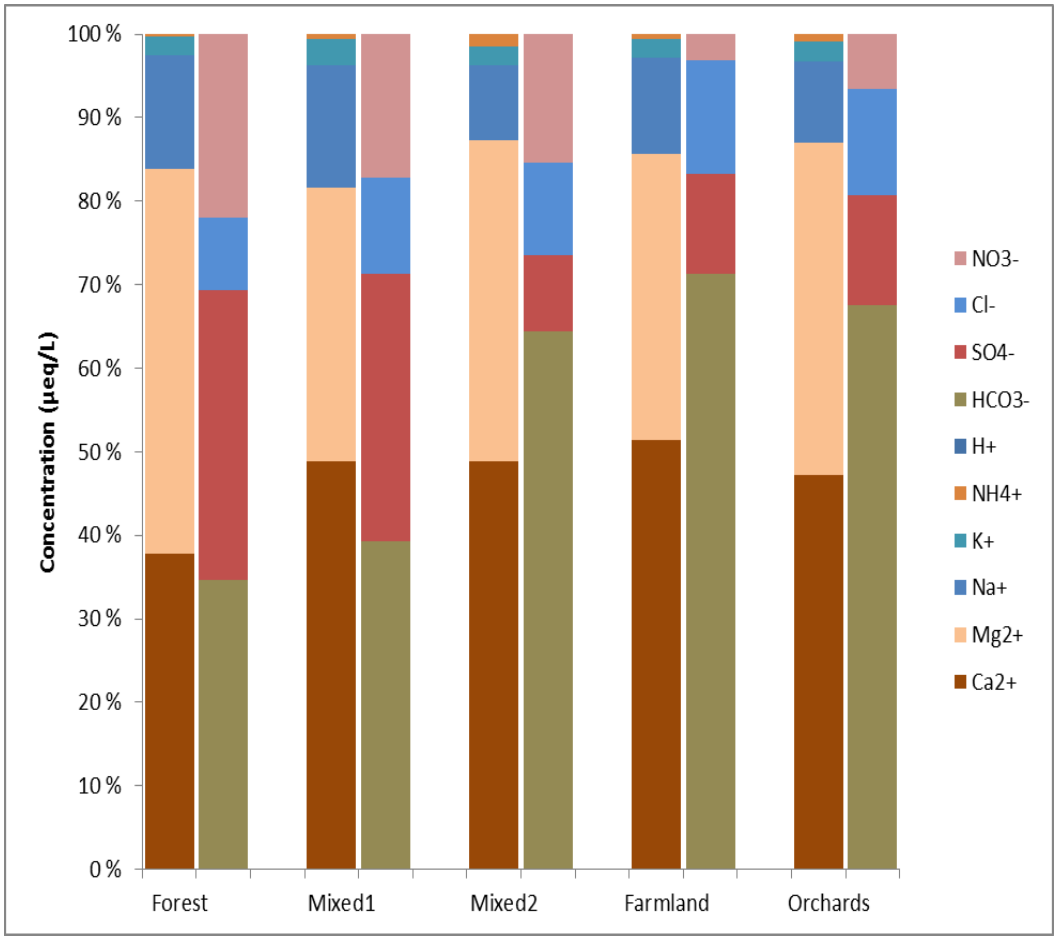


Water - pH and Alkalinity



- pH range **7 – 7.5**
- P governed by Ca precipitation
- Buffering by carbonates rocks, liming and manure
- Difference in amout of bicarbonates
- Large difference in buffering

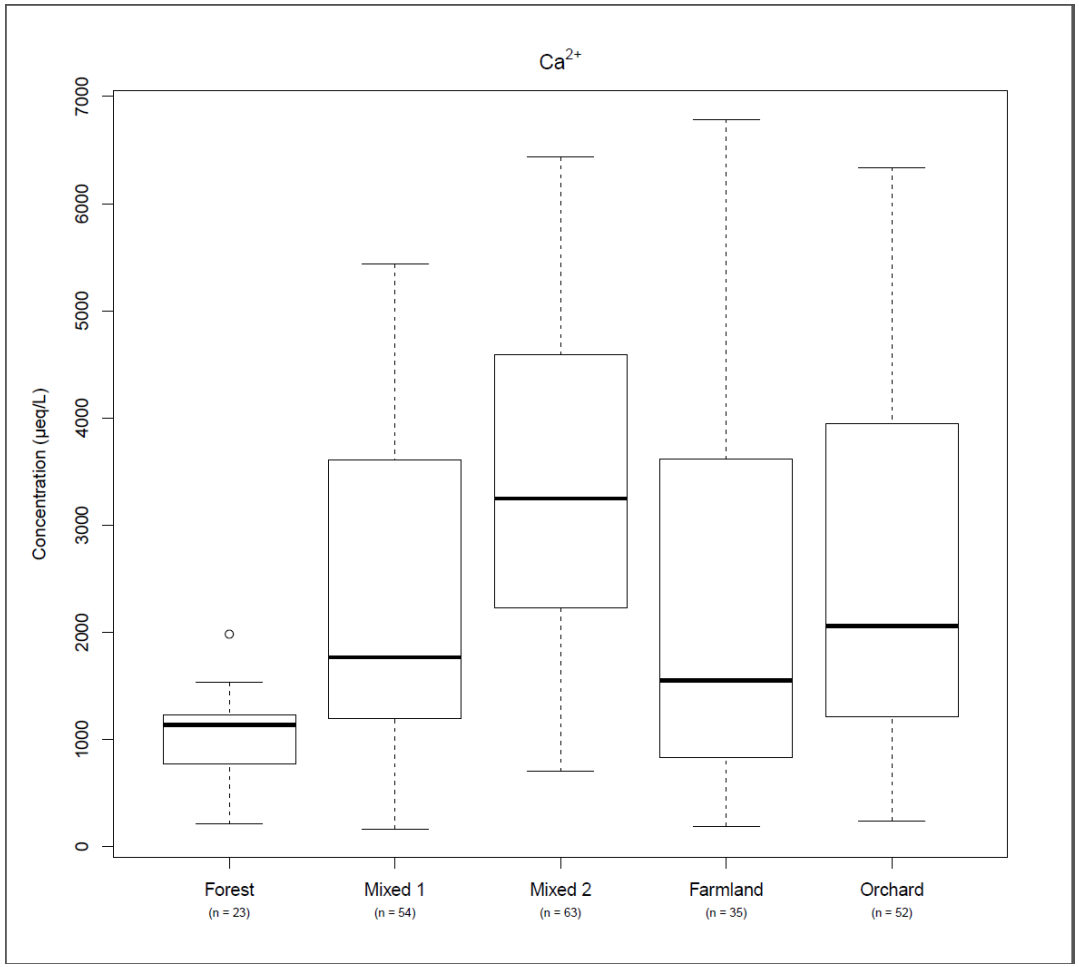
Water - Major cations and anions



- Difference in concentration strength
- Large charge balance descipancy in farmland

- Major cations: **Ca^{2+}** and **Mg^{2+}**
- Major anion: **HCO_3^-** except in the forest with **SO_4^{2-}**
- Suprise low **K^+** and **NO_3^-** in farmlands and Orchards

Water -Cations across land use

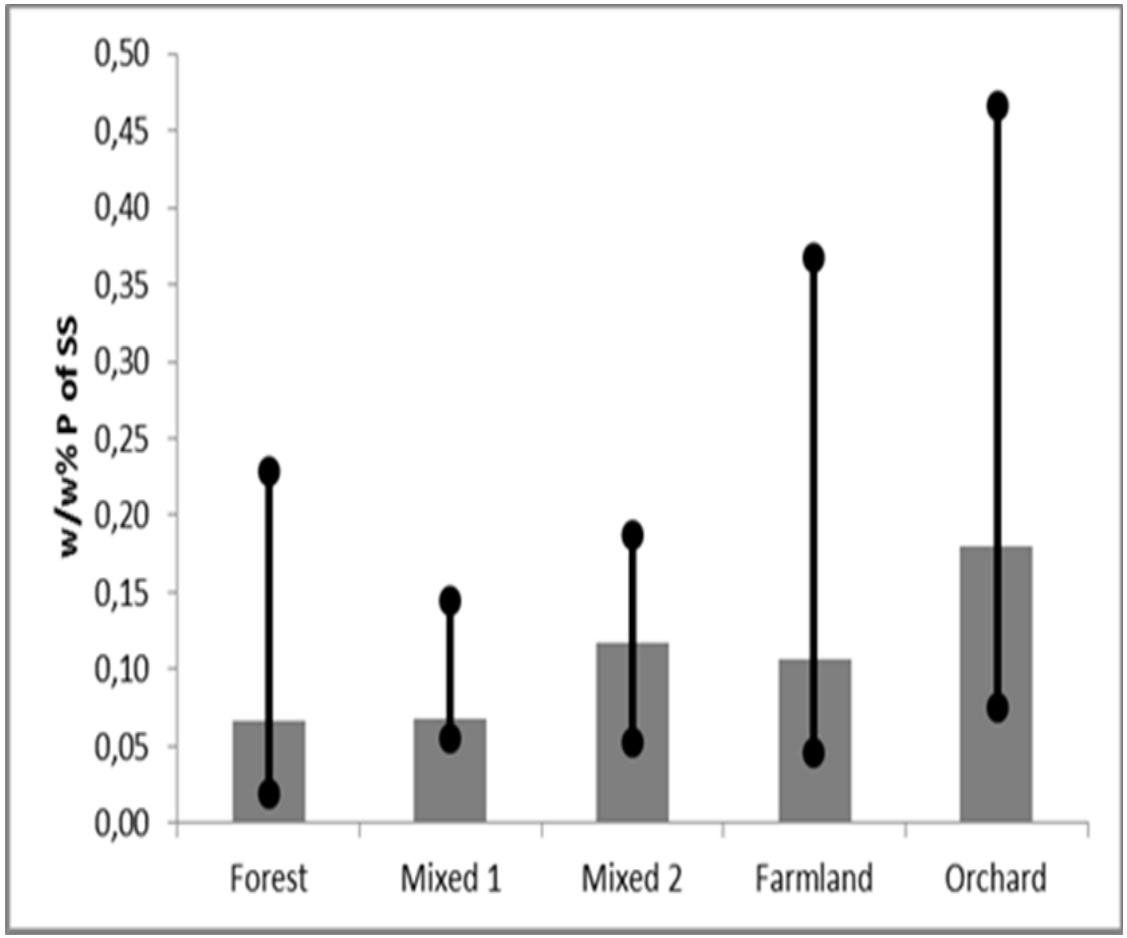


- **K+:** Basically same for landuses
  - Addition as fertilizer does not results in high K^+ concentration in runoffs

  -No surplus in nutrient needs

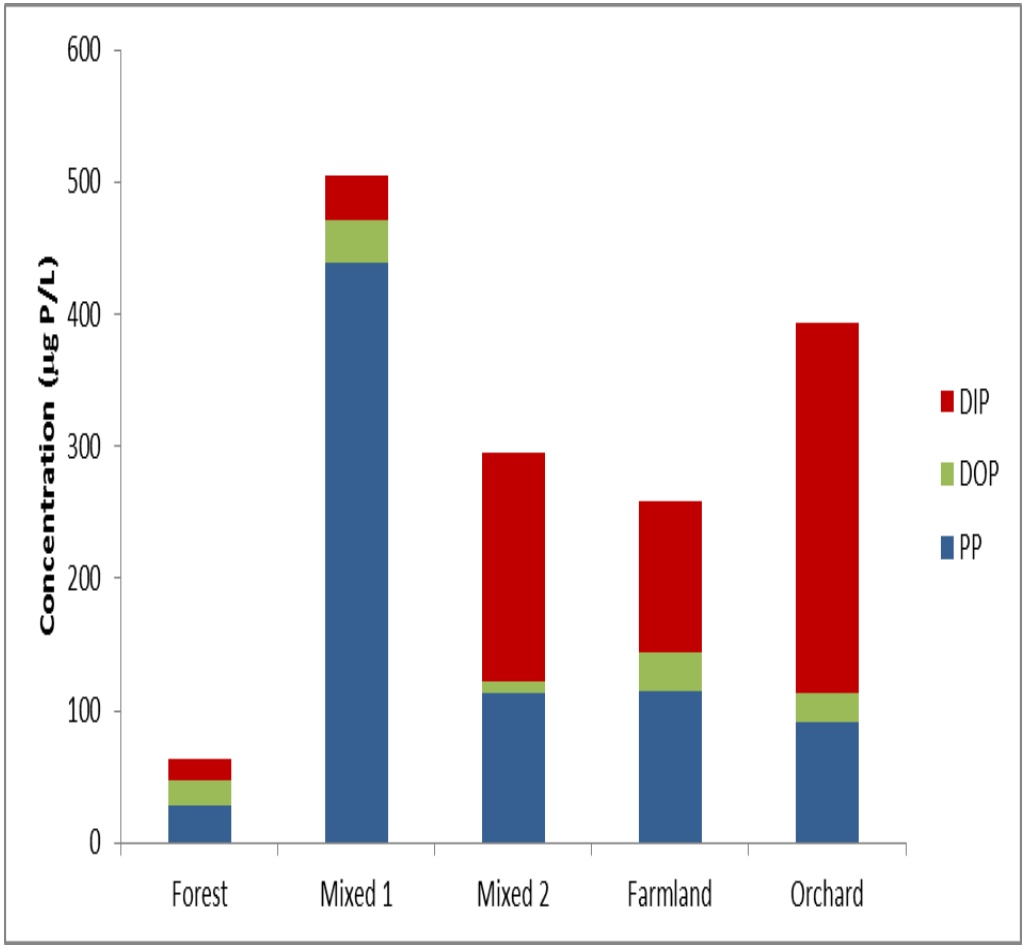
- **$Ca^{2+}$and Mg^{2+}:** Conc. variations
  - Liming
  - Weathering
  - Ion exchange with soil and
  - Management practises

Suspended matter



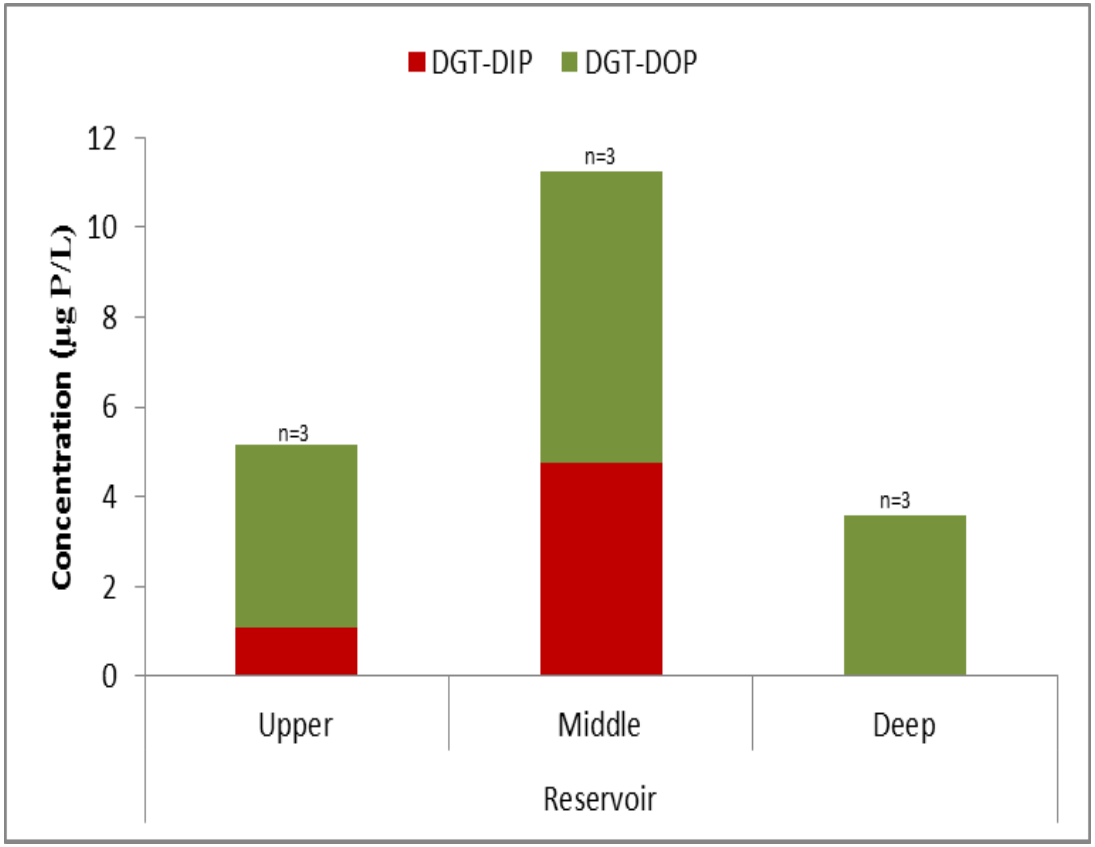
- Loading variations
  - Land Use
  - River velocity
  - Soil
  - Topography
- High loading in **Farmland** and **Orchards**
  - Tilling
  - Soil erosion
  - Management practises

Phosphorous fractions



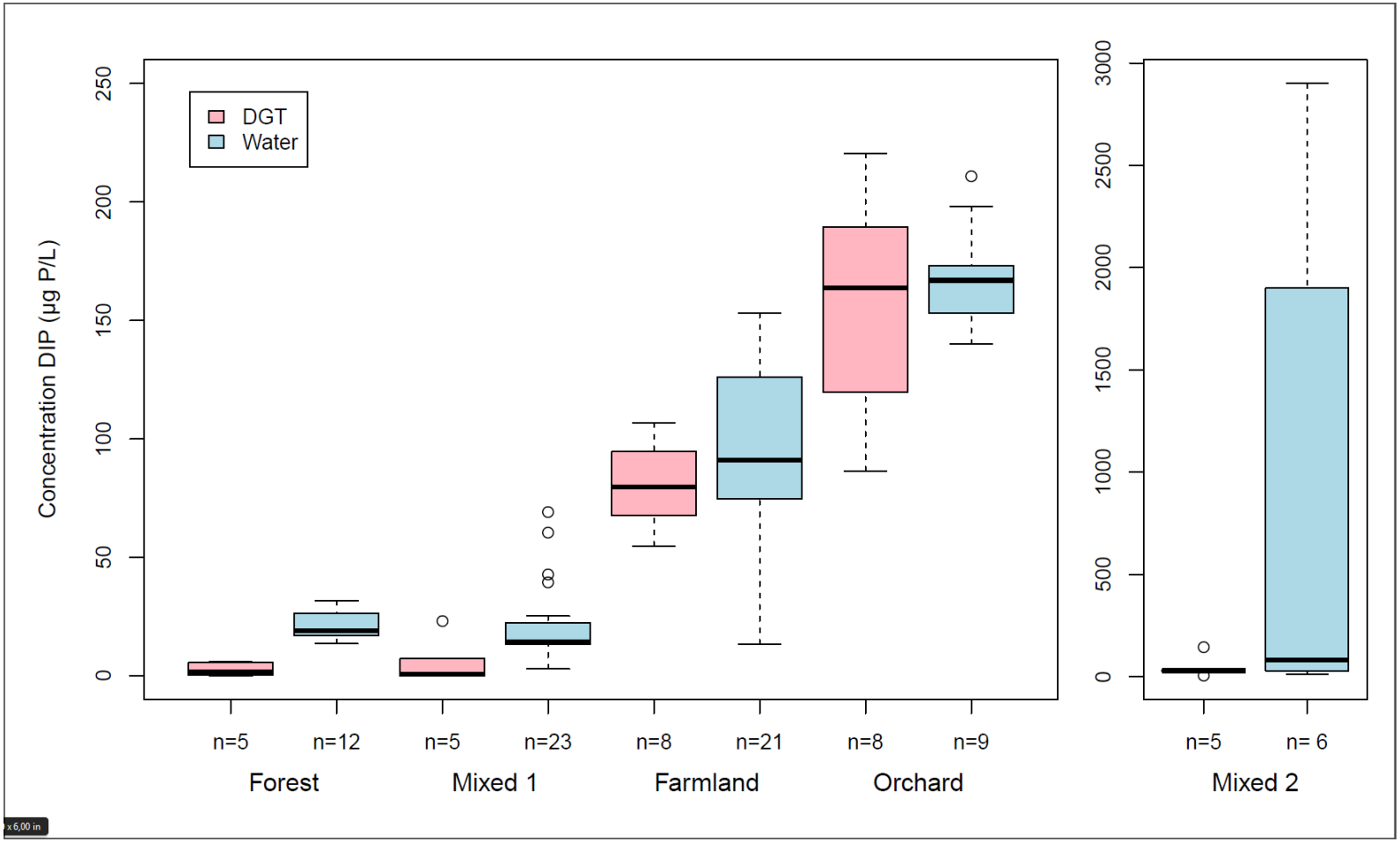
- **TP**: - Forest<Farmland<Mixed 2< Orchard<Mixed1
  - Same sequence in **soil**
    - Pettersen (2014) and
    - Joshi (2014)
- **PP**: - Related to loading of suspended solids
- **DOP**: -Relatively high in forest
  -DOM
- **DIP**:-Relatively high in orchard
  -Agricultural practises

DGT P fractions



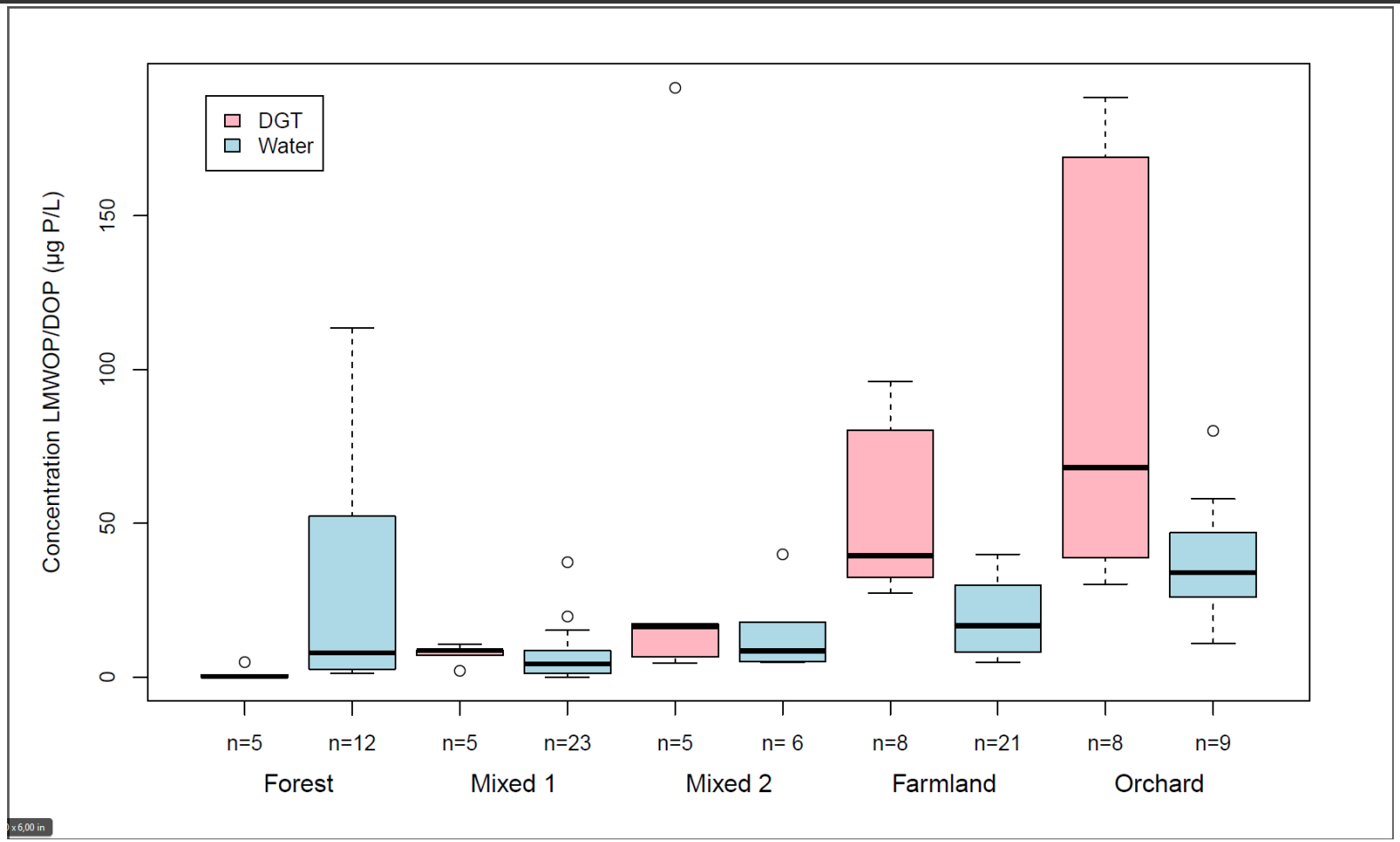
- **Rivers**: Similar P trend
  - Same as in water and soil
- **Fish ponds**: Difference in amount of TP
- **DIP:** Constitutes more than 50% of TDP in the rivers and fish ponds
- **Reservoir**: Suprise high concentration in middle depth

Water Vs DGT fraction – DIP fraction



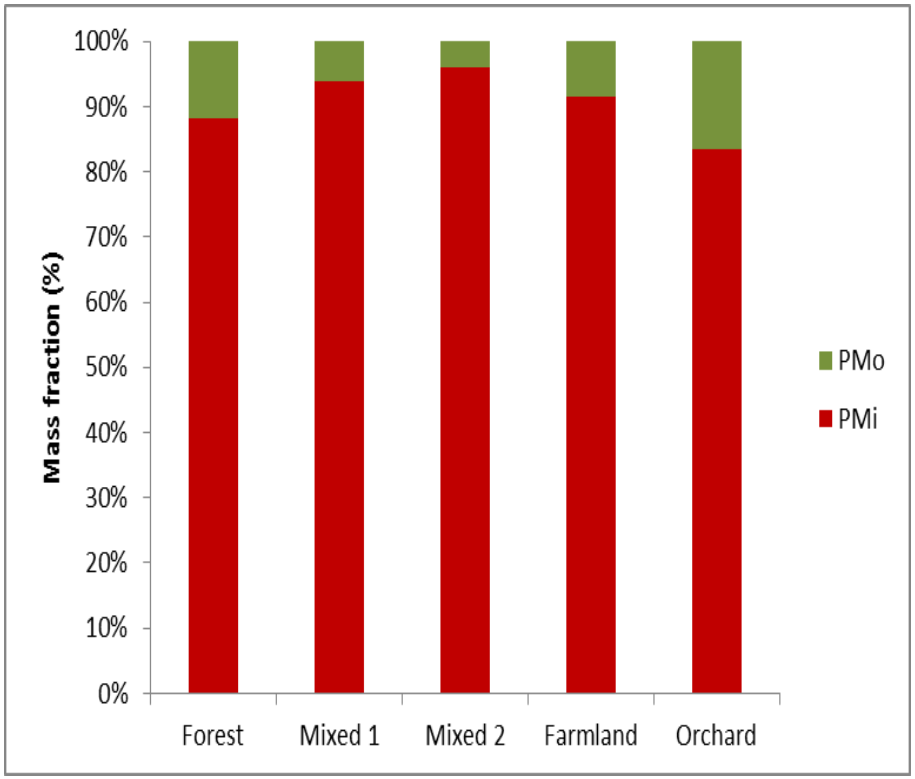
- **Results**: The two methods produce comparable results
- **Difference**: Methods(grab Vs Average) and hydrological fluctuations

Water Vs DGT fraction – DOP fraction



- **Results**: DGT-DOP higher than water-DOP (except in forest)
- **Discrepancy**: Errors due to value of difusion coeffiect used and LOD
- **Farmland/Orchard**: Difference due to large temporal variations (episodes)

Particulate characterization

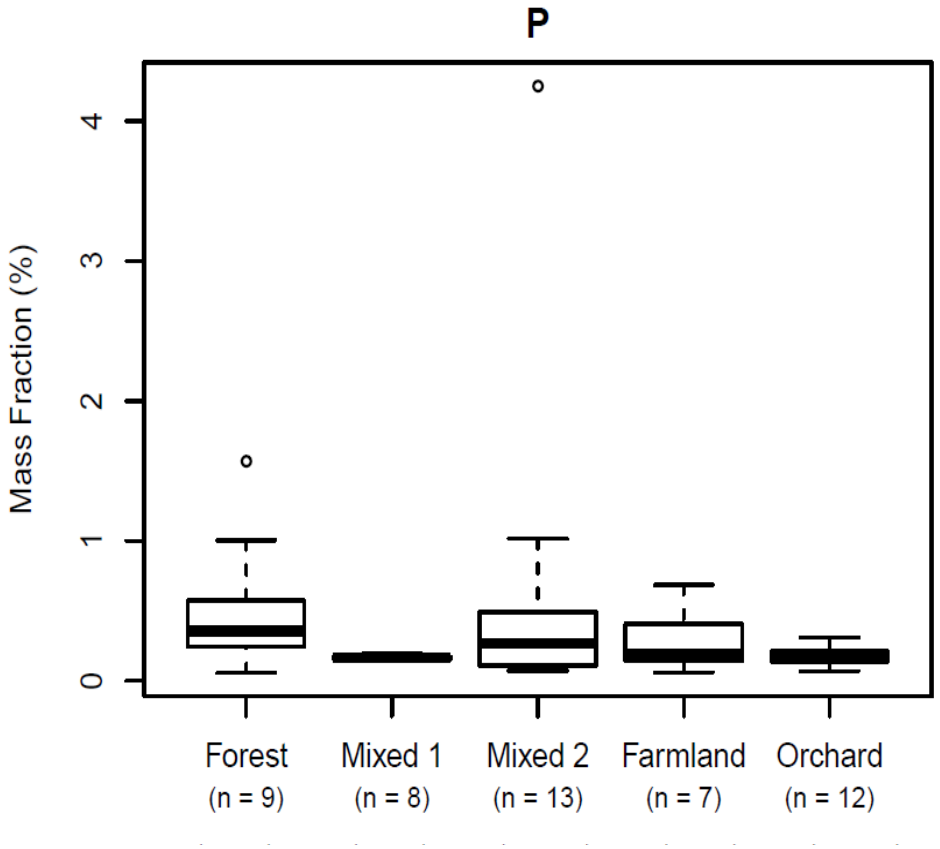


- Role of particles
  - Absorb or desorb P
- Different flow regimes
  - High flow
  - Low flow
  - Episodes

(July - September 2014)

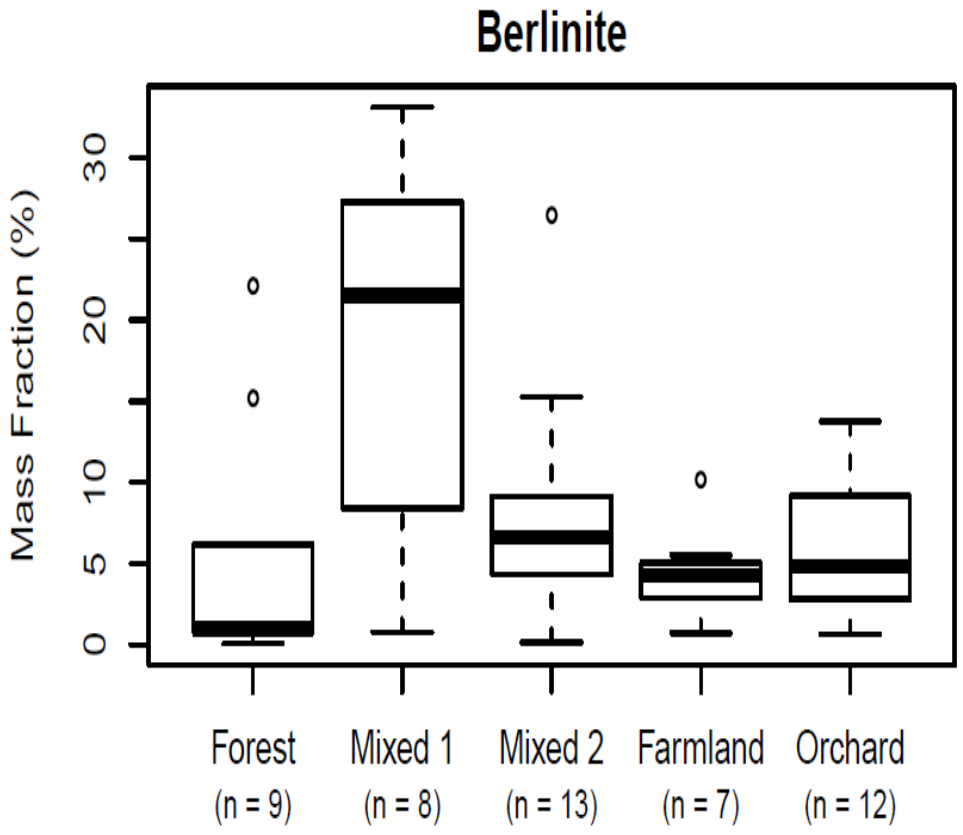
- Over **85%** content is inorganic

Particles – Elemental composition



- Main cations: - **Al** and **Ca**
- **Ca:** Lowest in the forest and orchards and highest in mixed water sheds
  - They have lower base saturation than farming land (Joshi, 2014)
- **P**: Different from river samples
  - Probably due to method used (MBM Vs ICP-OES)
  - Highest in forest and low in orchard – Difference in sorption index (PSI) which is highest in forest (Joshi, 2014)

Partcles - Mineral composition



- No apatite and Vivianite
  - P likely from **anthropogenic** sources
- No clear mineral variation with land use and flow regimes
- Main mineral:-**1:1 clay,** in soil its quartz (Pettersen, 2014)
  - Easy of erosion
  - Clay – P mobility and transport
- Berlinite(AlPO4)
  - Crystalline form
  - Industrial source

Conclusion

- Water chemistry is governed by Ca^{2+}, Mg^{2+} and HCO_3^-
- P precipitation is governed by Ca^{2+}
- Dominant P fraction in agricultural land is DIP
- DGT and grab water sampling are comparable (DIP)
- Al and Ca are the main elements in the eroded particles
- Eroded particles content is mainly clay(1:1) mineral
- Presence of Berlinite should be investigated further

Thank You!