

Thesis for the Master's  
degree in chemistry

**Bishnu Prasad Joshi**

**Assessment of phosphorus  
loss risk from soil - a case  
study from Yuqiao reservoir  
local watershed in north China**

60 study points

**DEPARTMENT OF CHEMISTRY**

Faculty of Mathematics and Natural  
Sciences

**UNIVERSITY OF OSLO  
01/2014**



## Acknowledgements

This master thesis has been carried out at the Department of Chemistry, University of Oslo, during 2013. A number of people deserve my thanks and gratitude for their support and kind help. It is therefore my immense pleasure to express my gratitude to them in this acknowledgement.

First of all, I feel honor to convey my heartiest gratitude to my supervisor Professor Rolf David Vogt, who gave me the opportunity to conduct my study for the Sinotropa project and I am very much affectionate for his guide and suggestions. I also want to render my thankful words to research Council of Norway (RCN) for their funding and support for sinotropa project. I express my thanks to my co-supervisors professor Grethe Wibetoe and seniors Alexander Engebretsen (PhD candidate), Christian Wilhelm Mohr (PhD candidate) for their guidance, generous contribution of knowledge and experience.

I express my heart full gratitude to Zhou Bin (PhD candidate) for his help, guidance and ideas. I admire his generous help and teaching to use ArcGIS. I express thanks to Zhou Bin's family for their homely treatment during my stay in China.

I wish to thank Professor Tore Krogstad (at Norwegian University of life sciences) for the discussions made on phosphorus sorption index and laboratory procedures and professor Hailin Zhang from Soil, water and Forage Analytical Laboratory (at Oklahoma State University, USA) for his discussion for Bioavailable phosphorus.

I am also thankful to Marita Clausen, Anne-Marie Skramstad for their help, support and permission to use different laboratory instruments. Thanks to the Sinotropa Project for arranging trip to China and providing platform for soil research. I wish to thank my colleagues and friends at the Department of Chemistry for sharing their ideas and feeling.

At last not the least I would like to express my thankful words to my parents, my life partner, brother and my children and for their support and love. Without their moral support I would not have completed this study.

## Title

Assessment of phosphorus loss risk from soil - a case study from Yuqiao reservoir local watershed in north China

*Olli Varis*

*Streams, lakes, reservoirs and wetlands are used and exploited in a variety of ways. They contain cultural and religious values that are essential. Exploitation of surface waters contributes to the deterioration of water quality and changes in ecology. The natural patterns of seasonality and other variations cause mismatch between supply and demand of water.*

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## **List of Abbreviations**

**AEC**- Anion Exchange Capacity

**BAP**- Bioavailable Phosphorus

**BS**- Base saturation

**CEC**- Cation Exchange Capacity

**CSA's**- Critical Source Area's

**DPS**- Degree of Phosphorus Saturation

**EPA**- Environmental Protection Beauró

**FA**- Fulvic Acid

**IDW**- Inverse Distance Weighted

**LOD**- Loss On Drying

**LOI** -Loss On Ignition

**MBM**- Molybdate Blue Method

**NPS**- Non-Point Source

**OD**- Oven Dried

**OECD**- Organization of Economic co-operation and Development

**PS**- Point Source

**PSD**- Particle Size Distribution

**PSC**- Phosphorus Sorption Capacity

**PSI**- Phosphorus Sorption Index

**PZC**- Point of Zero Charge

**SMS**- Sustainable Map Solution

**STP**- Soil Test Phosphorus

**TAES**- Tianjin Academy of Environmental Science

**TIP-** Total Inorganic Phosphorus

**TOP-** Total Organic Phosphorus

**TP-** Total Phosphorus

**USLE-** Universal Soil Loss Equation

**Note:** For this work BAP has been used instead of STP for the Phosphorus (P) available for plants.



## **Abstract**

Under the significant decrease of industrial point-source pollution globally, non-point source pollution has become the primary cause of the water body degradation. Among the many parameters, phosphorus (P) as the main limiting factor for the algae blooming, is widely considered as the main reason of the eutrophication of fresh water. Thus, P controlling strategies has been more effective and low costing against eutrophication. However, it is still difficult for environmental managers or policy makers to locate the source areas at the scale of watershed. Thus assessing the different levels of P loss risk and identifying critical source areas with relatively high P loss risk at targeted watershed has been considered as more direct path to achieve the object of water quality protection. In this thesis, local watershed of one drinking source reservoir-Yuqiao Reservoir was chosen as a case study.

The Yuqiao reservoir located in Tianjin, north China, is the drinking water source for nearly six million people in Tianjin central city. Over the past decade, water quality of the reservoir has become poor due to increasing eutrophication trend. A case study of Yuqiao reservoir local watershed has been conducted in order to study the spatial distribution and level of risk of P loss. In this case, a simplified indicator tool was used for the assessment of P loss, which was classified into two groups: source and transportation schemes. Degree of phosphorus saturation (%DPS) has been chosen due to its sensitivity with P loss. Meanwhile, the primary carrier of P loss, soil erosion process has been captured using Universal Soil Loss Equation (USLE model) as the transportation scheme. The geographical coupling of the USLE model and the %DPS by means of ArcGIS provides a perspective of the main P sources area (Critical Source Area's, CSA's), which are susceptible for P mobilization and transport process.

A total of 126 soil samples (n) were collected from different land-use type around Yuqiao reservoir local catchment, and analysed for soil pH, organic matter content (LOI%), total and inorganic pool of P, phosphorus sorption index (PSI), bioavailable phosphorus (BAP). Using PSI and BAP the degree of phosphorus saturation (%DPS) has been calculated. 65% of soil samples are alkaline with soil pH above 7.0, reflect the background nature of calcareous soil in the local catchment. The contribution from total inorganic phosphorus (TIP) to total phosphorus (TP) is relatively higher even in natural soil, although the natural soils with high PSI and low BAP content has low susceptibility for P loss. However human influenced land - use types with high TIP content and BAP has higher potent for P loss to Yuqiao reservoir from the local catchment.

As for the final assessment of P loss, it showed that around 4% of local watershed of Yuqiao reservoir area, accounting for 21.6 km<sup>2</sup>, has extremely high risk of P loss and 14% of the area, accounting 76 km<sup>2</sup> has high risk of P loss. In addition, as per the spatial distribution characters, the regions with extremely high or high risk of P loss are located around the shore of Yuqiao reservoir and in the north-east part of the watershed along the Lin River, which was strongly influenced by human activities due to relatively plain terrain conditions , fertile soil and rich water source.

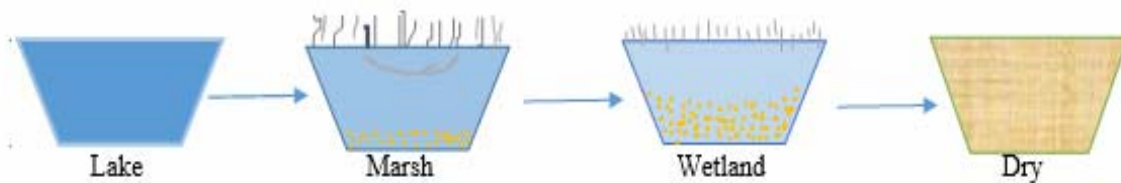
# 1. Introduction

The interferences by human activities on the hydro-biogeochemical cycles have dramatically enhanced the flux of growth-limiting nutrients from the landscape to receiving waters. The main cause of increase in the flux of the nutrients is the intensification of agriculture (Matson et al., 1997). Unfortunately, these increased flux of nutrients can have profound effects upon the water quality of objected water body (Carpenter et al., 1998; Correll 1998).

The combined exponential increase in human population and growth in consumption per capita during last three decades has stressed both aquatic and terrestrial ecosystems service and resources. Mankind have transformed the natural land into agricultural land, forestry, pasture for animal husbandry and urbanization, altering the hydrological and biogeochemical cycles (Vitousek et al., 1997).

## 1.1 Eutrophication

Eutrophication is the process of changing the nutritional status of a given water body by increasing the nutrients load. Water bodies accumulating large amounts of nutrients are called “eutrophic” (from the Greek words “eu” meaning “well” and trope meaning. “Nourishment”). Eutrophication leads to the excessive growth of green algae, referred to as algal bloom. The process of nutrient enrichment represents an aging of the lakes through allochthonous (external) sources, in which the nutrients and organic matter of terrestrial origin accumulate in a lake basin, gradually decreasing the depth of a water body causing the lake character to change to marsh like character and ultimately terrestrial character (Fig. 1). Under natural conditions this aging process take place over geological time. However anthropogenic interferences greatly accelerate the enrichment process and bring down the time lapse for the aging of lakes from millennium to decennials, which is called cultural eutrophication or man-made eutrophication (Rovira and Pardo 2006). Cultural eutrophication is a symptom of human induced imbalances in the biogeochemical cycle of nutrients mainly phosphorus (P), nitrogen (N) and carbon (C). This is caused by nutrients enrichment in the agricultural soils of which the excess is carried down through runoff from agro ecosystems along with sewage waste from human settlements (Khan and Ansari 2005). Thus the process of eutrophication has been characterized as biogeochemical process controlled by the rate of inorganic nutrient input to water body from its surrounding drainage basin (Rast and Thornton 1996).



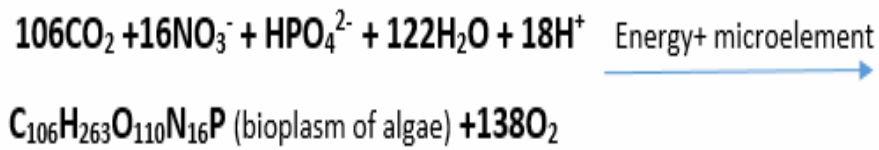
**Fig.1 Eutrophication process, showing the progression from aquatic environment to terrestrial environment (Wetzel 1992)**

Fresh-water eutrophication is one of the major environmental problems around the world. There is a range of known factors that are responsible for water eutrophication, though the mechanisms of transport of nutrients from the sources to the water bodies are not adequately understood (Yang et al., 2008; Tong et al., 2003). This loading of nutrients occurs both from point sources (PS) and non-point sources (NPS). Point sources, such as sewage water and industrial wastewater were historically the most important sources of nutrients to surface waters. With the advancement of sewage treatment technologies the culprit nutrients in the sewage are removed effectively before discharged into the recipient. Now the scientists and policy maker in most developed countries are turning their attention to the remaining NPS, such as agricultural land (Parry 1998).

Cultural eutrophication in developing countries located in the inter-tropical zone is presently receiving increased attention. Social issues, such as rapidly expanding populations with increased urbanization, a growing industrial economy and intensive agriculture to feed the growing population, has intensified the rate of cultural eutrophication of surface waters in these regions.

### **1.1.1 The cause of Eutrophication.**

Anthropogenic inputs of nutrients (mainly P and reactive N) to the biosphere has increased greatly during the last two centuries. The initial step for the eutrophication is as explained above the increased flux of nutrients in particulate and dissolved forms from point- and non-point sources to surface waters. The nutrients loaded water body then produces a great deal of plant biomass by photosynthesis according to the generic reaction presented in Equation 1.



Eqn-- 1

In most surface waters that phosphorus is for the most part of the year the growth limiting nutrient and is as such generally named as the culprit for surface water eutrophication (Manahan 1993). Whole lake experiments have confirmed the fact that addition of phosphorus is essential to create algal bloom (Schindler 1974). Regarding the cultural-eutrophication, most attention has therefore focused on the role of P. The P flux from soils to surface water is generally more limiting than for N and C. Moreover, there is a significant natural exchange of reactive N and C between the atmosphere and a water body, which is further augmented through N<sub>2</sub> fixation by blue green algae. This cause the bioavailability of P to usually be the limiting factor for increased algae growth in freshwaters.

Point sources are localized and are thus more easily monitored and controlled as compared to non-point sources, which are diffuse and much more difficult to trace and regulate. The contribution from these two sources can differ substantially from watershed to watershed, depending upon factor such as, population density, lifestyle of the inhabitants and land-use. Household discharge of gray water and sewage water is the most important source of phosphate in developing countries. Considerable effort has been carried out in developed countries to collect the discharge and remove phosphorus at waste water treatment plants, thereby preventing phosphorus laden effluents from entering the water bodies. But in developing countries this effort has not been implemented fully due to lack of resources and awareness.

In recent year the modern China experiences the impact of drastic climate change. The change to the El Nino and La Nina phenomenon are the most apparent signals of climate change in China. The El Nino is the “warm event” linked with precipitation and flood disaster; and the La Nina is the “cool event” having close relationship with big drought events (Liu et al., 2012). Northern China is experiencing a drier climate though with shorter periods of more intense rain (Wang and Li 1990). The fluctuations in the rate of precipitation can be highly episodic. Increased intensity of precipitation, increases surface runoff and sub-surface lateral flow, causing an increased flushing and erosion of the top-soil. Excessive use of chemical fertilizers and manures over the past 20-30 years has results in an accumulation of P in the top-soil susceptible for erosion. The episodic increased flushing of these P rich top-soils is

therefore causing high seasonal or interannual variation in nutrient loading to the watershed (Schindler 1974). Furthermore, agricultural tillage management generally leads to increased erosion. Increased erosion surges the P flux as it is carried away particulate P (PP) along with eroded top-soil particles. The erosion processes transfer the PP from the terrestrial environment to the aquatic part of the ecosystem where a deposition occurs in the form of sediments (Fig.2). Moreover, inorganic fertilizer and manure applied on the cropland that are in excess of the soils capacity to sorb P usually result in highly elevated losses of dissolved phosphorus in the runoff water. The soil's capacity to sorb P is controlled by either sorption-desorption or precipitation-dissolution reactions depending on the soil composition and the environment (pH,  $P_e$ ) of the soils (Sample, Soper et al. 1980). Moreover, fertilizers which are left unincorporated on the surface of the agricultural soil are especially prone to be flushed out during heavy rain. The high content of easily soluble P thus increase the loading of bioavailable dissolved P to surface waters.

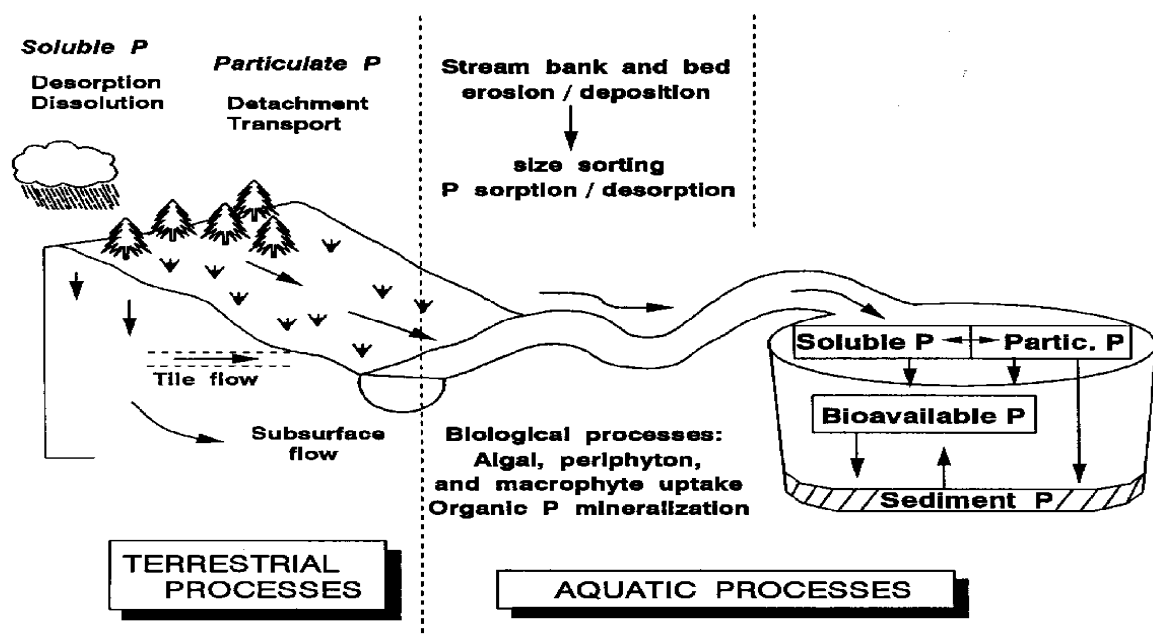


Fig.2 Process in the transfer of P from terrestrial to aquatic ecosystems (McDowell and Sharpley 2001)

### 1.1.2 The damage of Eutrophication.

The organization for Economic Cooperation and Development (OECD, 1982) described the process of eutrophication as 'the nutrient enrichment of waters which results in the enhancement of an array of symptomatic changes. The main problem is the enhanced

growth of algae and macrophytes. The algal bloom has subsequent deteriorating effects on water quality and oxygen level in the aphotic zone. Eutrophication also leads to highly undesirable changes in the structure and function of the ecosystem (Smith 2003) by inducing changes in the composition, size and structure of the phytoplankton community. This shift in community composition favors undesirable blue-green algae which generate foul smell and toxic substances. This is especially a problem with water resources to be used for drinking purpose.

### **1.1.3 Pathways of P loss**

The pathways for P loss follow the hydrological flow-paths depicted in Figure 2. The total P loss is thus defined by the geomorphology and soil chemical and physical properties as well as the land-use and management practices. Organic and inorganic phosphorus compounds are lost to water bodies in soluble forms as well as in association with soil particles and colloids forms (Haygarth and Sharpley 2000). The suspended particulate bound P (PP) consists of P bound to all primary and secondary inorganic mineral and organic compounds. This PP generally constitutes 75-90% of the total P (TP) transported from cultivated land. The susceptibility for erosion and capability of the flowing water to erode are important factors governing the risk for erosion and thereby the nutrients loss from the catchment and thereby an increased flux of P to receiving water body by erosion (Pote et al., 1996). One of the major issues for the scientists studying eutrophication is therefore to identify the Critical Source Area's (CSA's) which are specific and identifiable areas within a confined catchment and that are most susceptible for phosphorus loss through surface and sub-lateral runoff and erosion (Sharpley 1995). The CSA's are dependent on the source factors (P pools in the soils) and hydrological transportation pathways (surface and sub-lateral runoff, channel flow and erosion). A key explanatory factor for the spatial variation in source factors are mainly given by the types of land-use. Land-use types that have high potential to contribute to the phosphorus flux are fields used for intensive farming and vegetable crops (Vanni 2002).

Identifying CSA's has revolutionized the management of P loss from agricultural land. The abatement actions are now targeted on minimizing the loss of P from identified CSA's by reducing the availability of their surface soil P pools and limiting the surface runoff and erosion (Sims et al., 2002; Pote et al., 1996).

## 1.2 Current status of Eutrophication in the fresh water in China

Thirty years of reform and policies for opening up for modern China, have significantly stimulated China's economic growth. An increasing discharge of industrial wastewater and domestic sewage along with diffuse runoff from intensive agriculture, spurred by the population growth and urbanization along with an increase in consumption, has led to severe environmental problems. These problems are becoming an obstacle to sustainable development, which depends heavily on water resources. Since the middle of 20<sup>th</sup> century China has been perplexed by a variety of water issues: - "Too much water (flood and water logging); - too little water (drought and water shortage); - too turbid water (soil erosion); - and too dirty water (water pollution)". These water issues have not only affected the economic development in many sectors but also affected public health and welfare (Liu et al., 2012).

China is a country with a large number of lakes, which occupy 0.95% of the total area of the country's territory. More than 2759 of these lakes each cover an area greater than 1km<sup>2</sup>, though the majority of them are rather shallow. China is thus extremely short of per-capita surface water resources. With its 25.0 x 10<sup>12</sup> m<sup>3</sup> of water (China Water Resource bulletin, 2007), it ranks sixth in the world in terms of total water resources, but due to China's large population it is almost the lowest in terms of per capita water resource availability (Niu and Harris 1996). Moreover, there is a paramount challenge in the uneven distribution of water in this large country, with floods in the south and chronic water stress in parts of Northeast China and in almost all of Northwest China. With the rapid growth of its population and rising standard of living, water consumption is increasing and will continue to increase and China is surely expected to face more severe water shortage problems in the near future. Water scarcity in the country is further exacerbated by anthropogenic pollution of its scarce surface and ground waters resources. In regard to the surface waters resources it is especially eutrophication that is the main problem in China (Jin and Hu 2003). Furthermore, significant changes in climate and atmospheric deposition in recent years have had negative impact on water quality, especially through eutrophication governed by catchment hydro-biogeochemical processes controlling nutrients fluxes to surface water.

In the management of water resources, the western developed countries have achieved significant progress in control of point sources pollution. This is mainly based on end-of-pipe treatment, though efforts are also made to develop a technical system of cleaner production. Today clean production, aiming at reducing the discharge of waste water and pollutants, has become an international action in countries like USA, France, Canada, Japan, Germany, Denmark, Norway and Korea (Liu et al., 2012). With the point-source emissions mainly under control the focus has shifted to prevention and control of non-point source pollution in



western countries. China is still in the process of industrialization and have still not achieved control of their point source emissions.

Lake Eutrophication, is a ubiquitous water quality impairment and a serious environmental problem in China. Lakes which are classified as eutrophic in China have increased dramatically during the past decades (Liu and Qiu 2007). A recent investigation indicated that only 6% of the surveyed lakes are in oligotrophic state, while 44% are eutrophic and 22% are in a hypo-trophic state (Jin and Hu 2003). If control countermeasures are continued as now the waste water-treatment rate will be 60% in 2030, approximately 30 billion tonnes of waste-water would annually be discharge directly into the lakes. Based on these results it was predicted that all urban lakes in China will be in eutrophic or in hyper eutrophic state by 2030. Most of these lakes are used for multiple purposes, including as source of drinking water, irrigation, and flood regulation, aquaculture, tourism, transportation and habitat for indigenous flora and fauna.

The science of eutrophication is truly multidisciplinary as the hydro-biogeochemistry of processes governing mobility, transport and fate of P need to be known, as well as the biological impact of the P flux. Furthermore, social science is needed in order to acquire knowledge regarding anthropogenic activities within the watershed and to understand the barriers and thresholds that exists in society against abatement actions. Abatement strategies to curb eutrophication of lakes need therefore to base on inter-and trans-disciplinary studies. Due to the complexity of the problem sound conceptually based simulation and prediction models are commonly used to assess the impact of abatement actions as well as the effect of environmental drivers and their pressures on the system. The main mechanisms that are found to govern the transport processes are conceptualized and used in these model. However the implementation in China of these simulation and prediction models from developed countries have some challenges. These models need to be adapted with respect to the contest of Chinese socio-environmental conditions before they are implemented as the main processes governing mobility, transport, fate, impact and responses are likely different in China then in the environment in which the model was designed.

Since the 1990s, with the sustained and fast socio-economic development, China has attributed more and more attention to the limited resources and ecosystem service, as well as environmental and ecological issues in general. This is envisioned in a change of philosophy and thinking of water management that has facilitated a cross-century innovation and development of China`s water policy and science and technology in the field of water resources. The Chinese government and the public are becoming increasingly aware of the

severe situation. A range of actions such as “the road to 2050 for China’s science and technology” had been developed. The systematic analysis of the basic characteristics of influencing factors, and trends of change in China’s water issues has been divided into three time horizons; short term (2020), medium term (2030), and long term (2050). Five subfields (water resources, water environment, water ecology, water disaster and water management), have been promoted by the Chinese government to prevent further deterioration of water environments and to recover the aqueous ecosystem as part of a long-term development strategy (Liu et al., 2012).

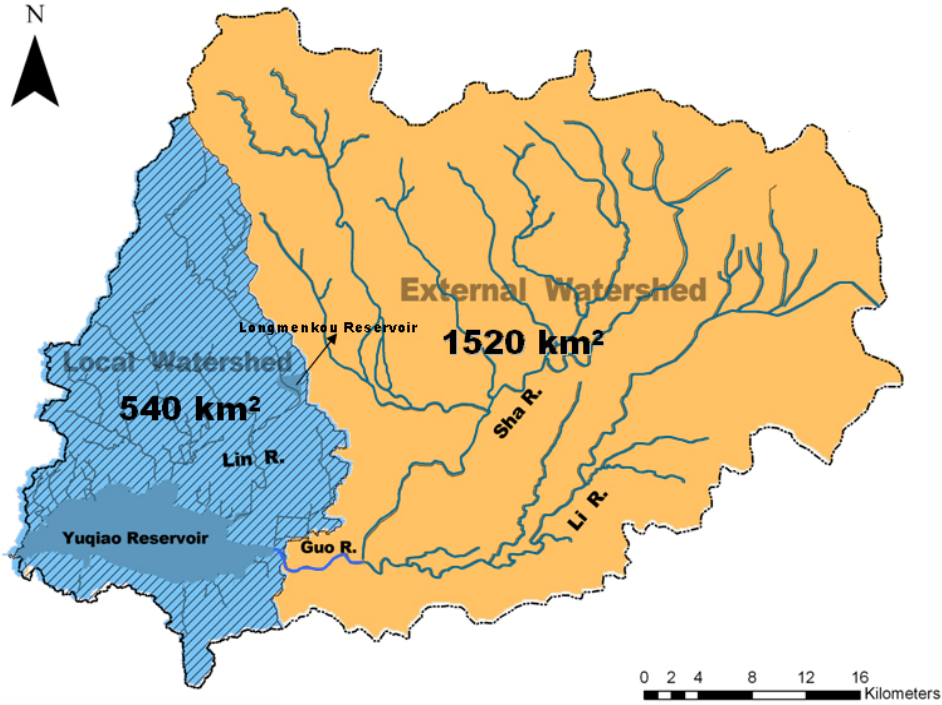
### **1.3 SinoTropia Project**

The SinoTropia project is a research project on eutrophication financed bilaterally by the Research Council of Norway (Project no. 209687/E40) and the Chinese Academy of Sciences. The project was commenced in 2011 and will be completed in 2014. The project is interdisciplinary and focused on policy oriented research. The study site is Yuqiao reservoir and its local watershed. The reservoir and main research field is situated in the agricultural district of Ji county, in the north-east of Tianjin municipality. The project is studying the mechanisms and processes governing eutrophication using the tool of natural science and pressure governing eutrophication using social science. The main motive of the project is to establish better knowledge of the impact of a changing environment and for assessing optimum abatement action for the better water quality in near future. This thesis evolves part of project that focuses on the hydro-geochemical processes that govern the mobilization of nutrients from the diffuse sources (soil) in the local catchment with different land-use, and transport to the Yuqiao reservoir. To evaluate the source factors, phosphorus contents are estimated by measuring different phosphorus (P) pools in the soils (total P, organic P and inorganic P). The geographical coupling of the Universal Soil Loss Equation (USLE model) and the %DPS by means of ArcGIS provides a perspective of the main P sources area (Critical Source Ares’s, CSA’s), which are susceptible for P mobilization and transport process are identified.

### **1.4 Yuqiao Reservoir and watershed**

The study area is the local watershed of the Yuqiao reservoir (Fig. 3) in Jixian County. The site lies at 40°2’18’’N and 117°32’1’’E in the northeast of Tianjin municipality at the foothills of the Yanshan Mountain. The mountains range up to 1200m above the sea level. This reservoir was originally built for flood protection and agricultural irrigation in 1959. The area of its total catchment is 2, 060 km<sup>2</sup> of which 540 km<sup>2</sup> lies in local catchment and rest 1560 km<sup>2</sup> constitute external catchment. The external catchment of the reservoir was included as a

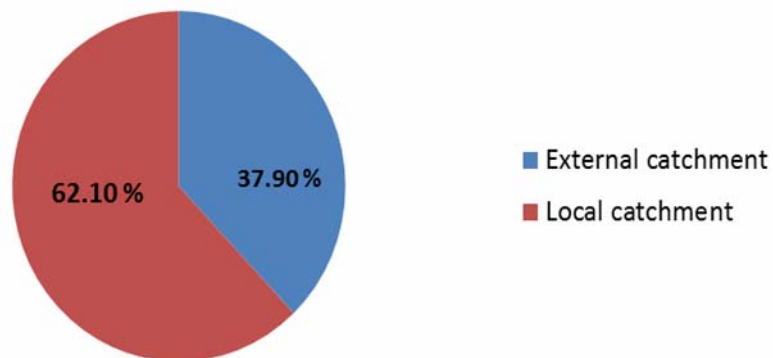
water source by the construction of a channel diverting water from the daheiting reservoir and Panjiakou Reservoir (i.e. Luanhe-Tianjin Water Diversion Project). Contribution of total phosphorus (TP) to the reservoir from the local catchment is much higher compared to external catchment (Fig.4). The local catchment play an important role for P load to the reservoir due to extensive farming and high population density around Yuqiao reservoir (Xueqiang Lu, 2011). Different form of land-use in the local catchment contributes TP in the form of dissolved and particulate P to the water body.



**Fig.3 Map of Yuqiao reservoir watershed with main rivers.**

In 1983, after the Luanhe-Tianjin Water Diversion Project was successfully completed, the Yuqiao Reservoir became the storage reservoir for Tianjin central city and Tianjin Binhai new area. The reservoir has supported the development and daily life of the 6 million people of Tianjin urban center as well as the source of water for industry located downstream from the reservoir. So far, more than 18 billion m<sup>3</sup> of drinking water has been supplied to the urban population of Tianjin.

## Total Phosphorus (%)



**Fig.4 The total phosphorus contribution from local and external catchment (data source: Ji county Environmental Protection Bureau)**

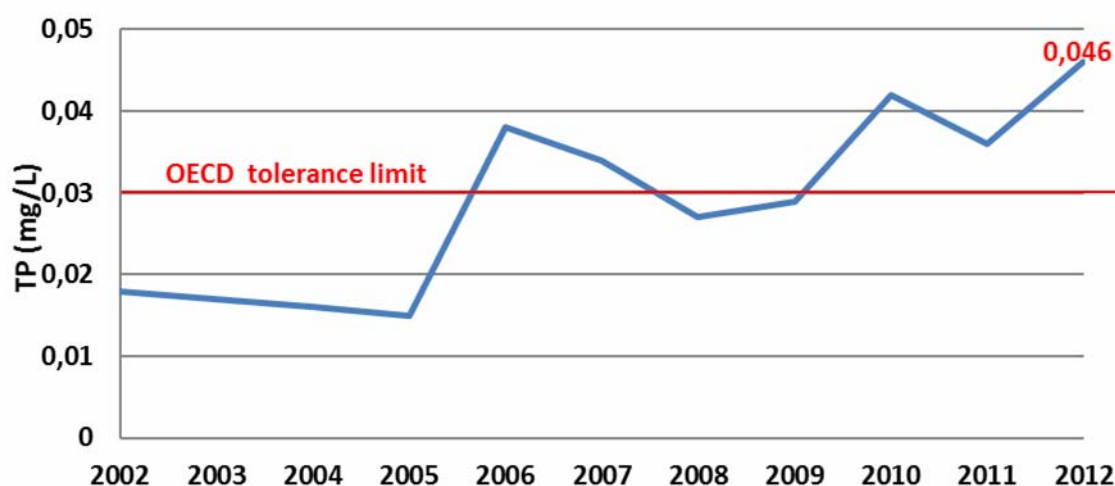
There are two main rivers that flow into the reservoir: Lin River and Guo River. The Lin River which receive water from Baxianshna River and out let of Longmenkou reservoir. The Longmenkou reservoir is small reservoir in Hebei province (Fig.3) plays an important role for sediment retention. The Guo River has two tributary rivers Sha and Li River. The Lin River and Sha River are seasonal river and have high flow only during the rainy season. The main source of inflow of water to the Yuqiao reservoir is through the Luanhe-Tianjin Water Diversion Project, which was implemented in August 1981. This comprehensive water resource exploitation include across-basin diversion, water storage and water delivery. The water diverting channel, which is 234 kilometers in length, runs from its intake under the dam of Daheiting Reservoir and Panjiakou Reservoir in Hebei Province to the destination-Yuqiao reservoir. The Li River which receive diverted flow from Daheiting Reservoir and Panjiakou Reservoir, is the main river and is the main contributor for the constant flow of water in the Yuqiao reservoir (Fig. 3).

The catchment area distribution (Table. 1) shows that major part of catchment lies in Hebei province as compared to the local catchment surrounding the reservoir.

**Table 1; Area distribution of different catchment (Ji County land management, 2010)**

Catchment	Region	Catchment area km <sup>2</sup>	
Li river catchment	Hebei Province	488	
Sha river catchment	Hebei province	887	
Lin river catchment	Hebei province	125	207
		82	
Local catchment	Ji County, Tianjin	540	

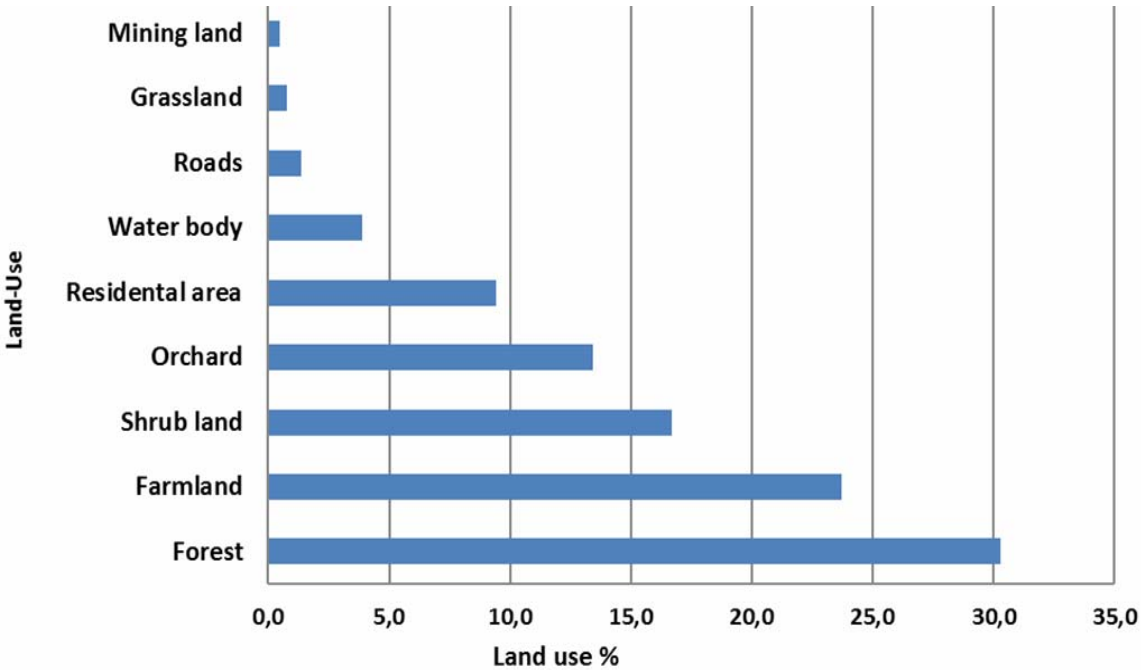
The water quality of Yuqiao reservoir has showed a trend of eutrophication in the recent decade (Xueqiang Lu, 2011). This deterioration of water quality possess a threat to the drinking water supply. Average data for water sample collected in the reservoir each month during the period of 2002 to 2012 by the Ji county Environmental Protection Bureau, shows that the TP in the lake reached an annual value of 0.046 mg P/L in 2012 (Fig.5), which is higher than the OECD tolerance limit of 0.03 mg P/L, above which eutrophication is likely to be triggered (Brady and Weil 2010).



**Fig.5 The mean annual concentration of total dissolved P in the Yuqiao reservoir water from 2002 to 2012 (data source: Ji county Environmental Protection Bureau).**

The local catchment surrounding the reservoir has mixed land-use of agricultural farming (including vegetable fields), orchards, forests, shrubs, fish farms, small scale industries and residential areas. The local people exhibits different types of agricultural practices, i.e. intensive agriculture to livestock production. The total cultivated land including both farmland

and orchard accounts for 37% of total land-use around the Yuqiao reservoir (Ji County land management, 2010). Moreover the peoples are motivating towards the vegetable and orchard farming these days due high market demands and good return. These shifting from regular cereal crops to the cash crops has intensified the use of all mean of different fertilizers for higher crop yield. Compared with the northern part of Yuqiao reservoir, the scale of farmland and orchard is relatively low in the southern part, but due to the proximity to the reservoir the importance of southern shore can not be neglected. Thus the northern as well as southern shore are therefore believed to have significant importance for the nutrients loading to the reservoir.



**Fig.6 The extent of different types of land-use in local catchment of Yuqiao reservoir (Ji County land management, 2010)**

### **1.5 Objective of the work**

The focus of this work is to achieve a better understanding of the hydro-geochemical processes that govern the transport of phosphorus from diffuse sources (soil) with respect to different land use. Physiochemical characteristics and main P pools (total P, organic P and inorganic P) in soils (n= 126), collected from all types of land-use, were analyzed in order to get a better understanding of the effect of the most important land-use and agricultural practice in term of phosphorus load. The geographical coupling of The Universal Soil Loss Equation (USLE model) and the %DPS by means of ArcGIS provides a perspective of the main P sources areas, which are susceptible for P mobilization and transport process. Ultimately the aim is to locate the Critical source Area's (CSA's) with respect to phosphorus load into the reservoir

## 2. Theory

Fresh-water eutrophication is one of the major environmental problems around the world. With increased urbanization and industrialization all over the world, the relative importance of point and non-point source inputs of P progressively increases. The inputs from point sources are easier to identify and control than the more diffuse non-point sources. As a result, non-point sources now account for a larger share of all P inputs to surface waters than a decade ago. This increases the awareness of non-point source pollution of waters from agricultural chemicals in drainage and runoff (Kauppi, Mielikäinen et al. 1992). In areas of intensive farming and livestock production, excessive P applications, as inorganic fertilizer and manure exceeding crop uptake, have increased the pools of soil P (Sharpley 1995). As a result, surface soil accumulations of P have occurred to such an extent that the loss of P in surface runoff has become a priority management concern. The controlling factors of P loss from land to receiving water bodies can be categorized into those that influence the mobilization of P and those that influence its transport. The P loss from the local catchment can exist in either in soluble form or in association with soil particles and collides (Haygarth and Sharpley 2000). Once the P from fertilizers and manures comes in contact with soil particles, its fate in context of potential for subsequent loss from the soil depends largely on the chemical processes governing P concentration in the soil solution-sorption of inorganic P and mineralization of organic matter. The analytical parameter 'Soil test P' is particularly important by representing the soluble P available for transfer to water body. In addition to the availability of the source (soil) the P loss from the catchment depends on the coincidence of transport (runoff, erosion and channel processes) factors (Heathwaite and Dils 2000).

The main task is therefore to understand the dynamic nature of the variables governing the P transfer, this will aid estimation of the amounts of P transferred and importance of managing this transfer to maintain or improve both soil productivity and water quality. Due to the lengthy and labor intensive nature of field studies quantifying P transfers, model simulation has become an important tool for assessing alternative agricultural management practices which can minimize P transfer and its environmental impact.

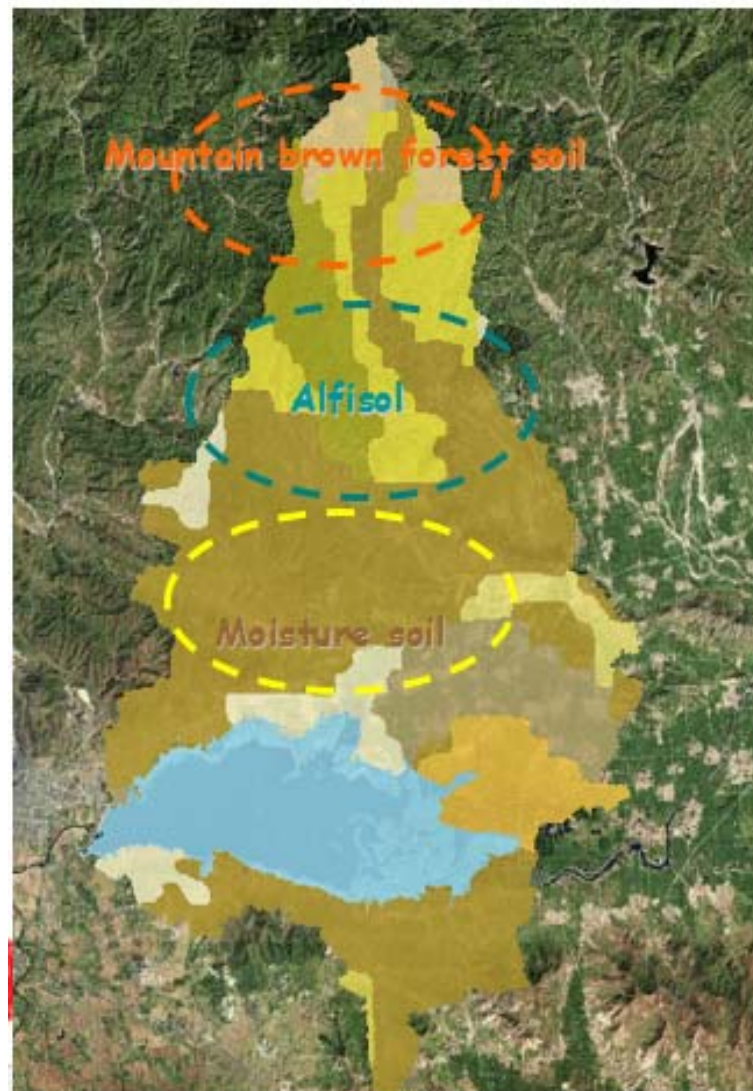
### 2.1 Soil physical Chemistry

Soil by definition is an integrated mixture of the four constituents inorganic, organic matter, water and air (Brady and Weil 2010). The inorganic fraction of soil, often called mineral fraction, consists of sand (2.0 mm to 0.05 mm) and silt (0.05 mm to 0.002 mm), The smallest of the mineral particles are clays, having colloidal properties and can be seen only under electron microscopes (Brady and Weil 1996). Due to their small size the clay particles



possess large surface area per unit of mass. Since the surface of soil colloids (both mineral and organic) exhibits electrostatic charges, they attract positive and negative ions as well as water molecule to its charged surface and take part in ion exchange and / or adsorption reactions (Loon and Duffy 2005).

The soil in the study area can be categorized into three parts as shown in soil profile map below (Fig. 7). The mountain brown forest soil in the far northern part of the local catchment consists of silty loam texture with high permeability, the middle part of the catchment with silty clay loam soil represent the alfisol type of soil. This middle part however represent the combination of high and low land in which the high land are converted to orchard or agro forestry after clearing the natural forest. The shore around the YuQiao reservoir both in north and south part is represented by moisture soil with silty clay loam with low permeability.



**Fig.7 Soil distribution map for local catchment.**

## 2.2 Phosphorus in soil

Phosphorus is the eleventh most abundant element in the earth crust. Its average concentration in the geosphere has been estimated to 0.1 % W/W. It occurs in the geosphere almost exclusively as phosphate or more specifically as orthophosphate, with an ionic form of  $\text{PO}_4^{3-}$ . The global phosphorus cycle shows that P is found in the atmosphere in association with dust particles (Loon and Duffy 2005). Terrestrial phosphorus is composed of a number of specific minerals including apatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ ] and vivianite [ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ]. A great part of the phosphorus in soil is sorbed to soil particles or incorporated into soil organic matter. The organic part consists of undecomposed biotic residues, microbes, and humic matter in the soil, whereas inorganic forms are usually associated with Al, Fe, Ca and Mg compounds of differing solubility. The binding and release of P is controlled by either sorption-desorption or precipitation-dissolution reactions, depending on the environment in the soil or sediment (Guzman et al., 1994).

The distribution of the different species of orthophosphate in soil water is pH dependent (Fig 8). The solubility of phosphorus is controlled by the availability of iron and aluminium under acidic conditions and of calcium under alkaline conditions; each of these metal ions forms insoluble phosphate salt. Phosphorus has therefore its maximum solubility under slightly acidic conditions. At this pH the pre-dominant aqueous phosphate species is  $\text{H}_2\text{PO}_4^-$ . At different pH, the shifts in orthophosphate ions species result from the protolyzation of the first, second, and third hydrogen ions of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) to give  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ , respectively. P is frequently supplied as fertilizer and manures to replenish P lost to the crops in agricultural soil (Loon and Duffy 2005).

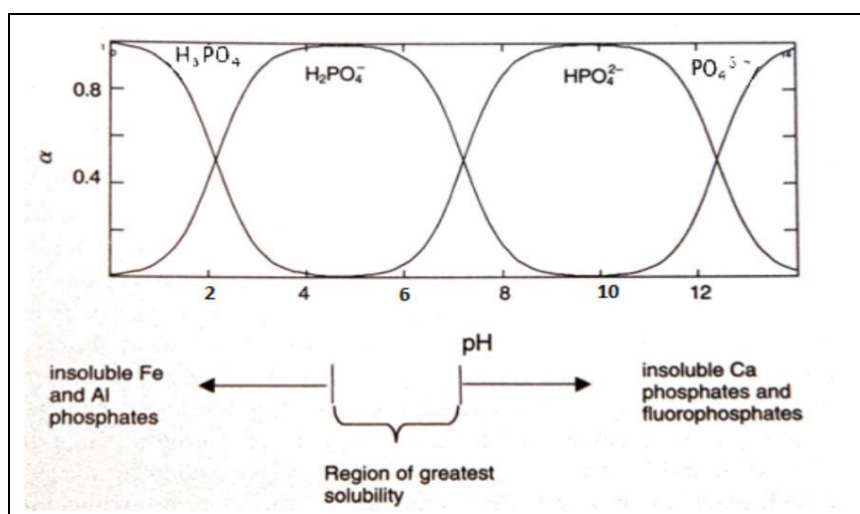


Fig.8 Phosphorus aqueous species and factors controlling solubility in water at different pH ranges (Van Loon and Duffy, 2005).

Especially the process of sorptive binding of P by iron (Fe) and aluminium (Al) oxide and oxyhydroxide phase is of great importance in terrestrial ecosystems (Walbridge and Struthers 1993). These oxides are also referred to as hydrous oxides. Surfaces of Fe and Al oxides in the presence of water are usually covered with hydroxyl groups (Stumm and Morgan 1996). These hydroxyl groups can be exchanged for phosphate groups (Goldberg and Sposito 1984). The crystalline as well as amorphous forms of these oxides, the most common being goethite (FeOOH) and gibbsite (Al(OH)<sub>3</sub>), bear variable charge surfaces. The charge on the surface of the minerals are either pH independent or pH dependent. The pH independent charge is due to isomorphic substitution of cations in the crystal lattice with cations in the crystal lattice with less charge (e.g. Si<sup>4+</sup> with Al<sup>3+</sup> or Al<sup>3+</sup> with Ca<sup>2+</sup>). The pH dependent charge is due to protonation or deprotonation of the weak acid functional groups (e.g. -OH). Thus, oxide surfaces have positive charge, negative charge, or no net charge depending upon the pH of the solution. The net total particle charge of the minerals surface is zero at the pH where the surface positive charge equals to surface positive charge. This point of zero charge (PZC) (McBride 1994) is one of the most important parameters used to describe variable-charge surface in regards to sorption processes (Morais et al., 1976). Most soil materials have a net negative surface charge at pH commonly encountered in the environment. Trivalent cations, such as Fe<sup>3+</sup> and Al<sup>3+</sup>, sorb strongly to the net cation exchanger. These ions may act as a charge bridge allowing the ortho-phosphate anion to be sorbed to the soil through binding to the trivalent cations.

### **2.2.1 Bioavailable Phosphorus (BAP)**

Bioavailable P expressed in mg P kg<sup>-1</sup> is defined as the sum of immediately available P and the P that can be transformed slowly into labile form by naturally occurring physical (e.g. desorption), chemical (e.g. dissolution) and biological (e.g. enzymatic degradation) processes (Anderson and Arlidge 1962). P is a macronutrient and represents as a significant challenge for soil fertility management due to that it can be rapidly fixed in relatively insoluble form in soils and therefore rendered unavailable to plant. Soil with high clay content have high affinity for P and relatively low desorption. In contrast many organic soils have low binding capacity for P and P is easily released (Singh et al., 1999). The P in soil exists in organic and inorganic pools. Inorganic P associated with Al, Fe, Mg and Ca has varying solubility and availability to plants. Phosphorus has to be added in the form of fertilizer or manure to the soil for optimum crop growth and yields. However the availability of phosphorus in the soil is determined by the continuum of forms from very insoluble (fixed) to soluble (labile) pools (Fig.9). Generally the availability of P in the soil is low because the rate of conversion of stable form of soil P (organic and inorganic pools) to labile or available form

of soil P usually occurs too slowly to meet crop requirement. The phosphorus cycle in agricultural soil in Figure 9 shows that P in the form of fertilizer and manure added in the soil are available to plants in either solution P or soil test P. A part of manure P contributes to solution P directly whereas fertilizer P first fixed as inorganic P and then convert to soil test P which are uptake by crops in the form of solution P. According to the figure the process of fixing labile organic P from manure to stable organic P in the soil is reversible (as shown by arrows), whereas it is not completely reversible (fixing is more dominant than labile shown by arrows) in case of inorganic P from fertilizer P. That indicates P rapidly fixed and unavailable to plant, which is the major challenges for soil fertility.

The soil test value for bioavailable P in the soil represents the concentration of P in the soil extracted using the specific soil test method. In alkaline soil (usually calcareous soils) the labile pool of the soil P is mainly adsorbed on the active surface of  $\text{CaCO}_3$  (Ca-P). The lowest solubility of these calcium phosphate minerals is at about pH 8. In acid soils the labile soil P is mainly adsorbed on the active surface of amorphous forms of  $\text{Al}(\text{OH})_3$  (Al-P) and  $\text{Fe}(\text{OH})_3$  (Fe-P). The slow conversion from phosphate adsorbed to the oxyhydroxides to iron and aluminium phosphate minerals result in the reduced solubility of P in strongly acidic soils. Solubility of P is therefore the greatest in neither alkaline nor acid soils (Fig. 8), i.e. in neutral soils.

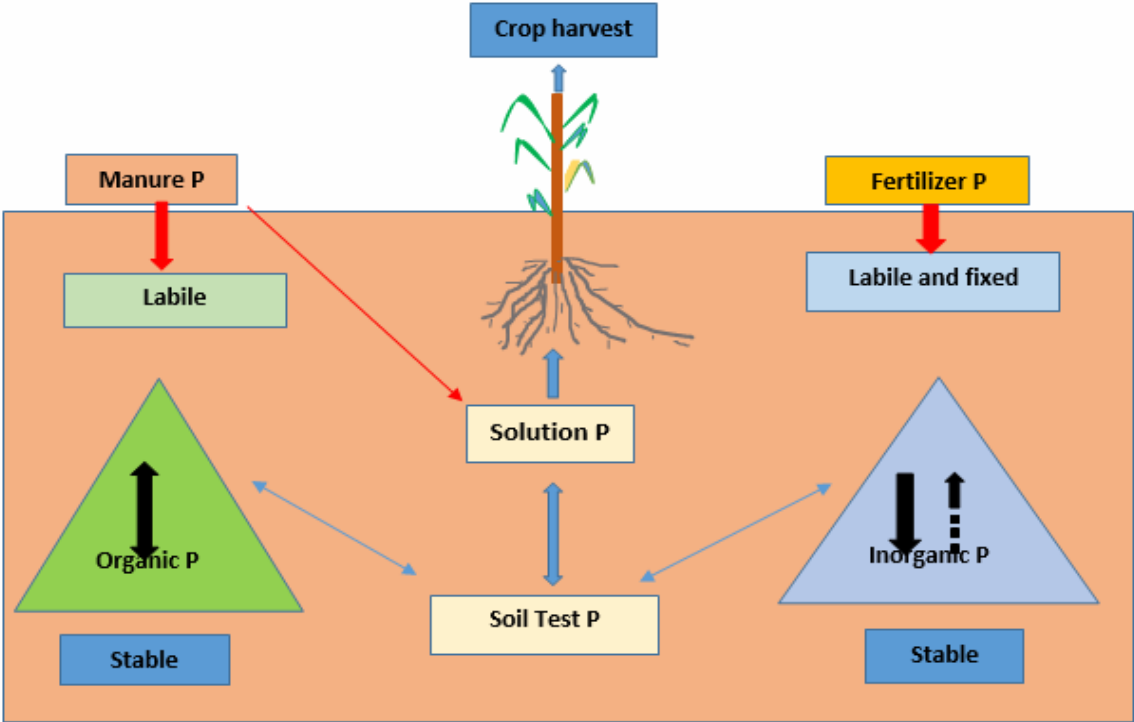


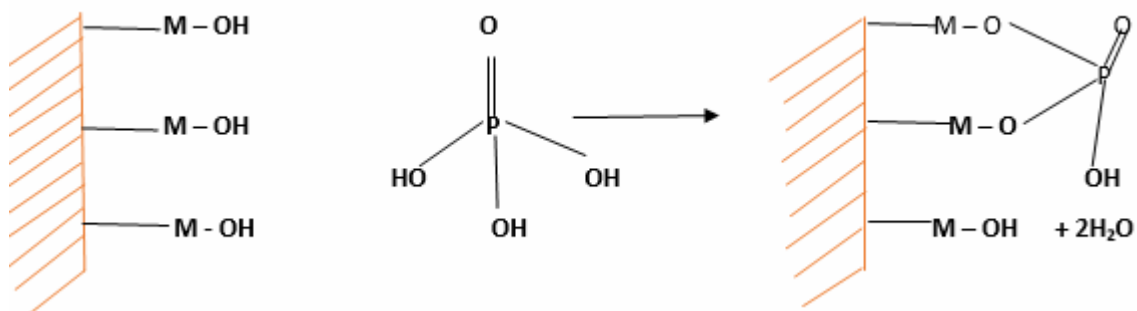
Fig.9 The phosphorus cycle in agricultural soils (USDA, 2003)

## 2.2.2 Phosphorus Sorption Index (PSI)

The mobility of labile inorganic phosphate is mainly by sorption and desorption processes taking place in the soil. The soil phosphorus sorption index (PSI) was developed to estimate the phosphorus sorption capacity of the soil and is expressed in  $\text{mg P kg}^{-1}$  of soil (Bache and Williams 1971). Studies by (Mozaffari and Sims 1994; Eghball et al., 1996) have found that the PSI is highly correlated with P adsorption capacity, and thus can be used as a simple proxy for the estimation of P sorption capacity of the soil.

The sorption capacity of P to the soil surface depends on various factors such as the pH of the soil, soil texture and organic matter content. If the pH of the soil is above PZC the soil surface will have a net negative charge and exhibit the ability to exchange cations, while the soil will mainly retain anions if its pH is below its PZC (Appel et al., 2003). Sorption of organic compounds on the mineral surfaces affects soil-P capacity as the organic functional groups bind trivalent cations, which in turn bind phosphate. The negatively charged organic substance readily form complex with trivalent cations, such as Fe and Al which in turn bind phosphate. On the other hand organic ligands may form a sphere of organic complexes surrounding the positively charged oxyhydroxy mineral compounds and thereby competing with  $\text{PO}_4^{3-}$  for binding sites (Tipping 1981).

The most important sites for phosphate anion ( $\text{PO}_4^{3-}$ ) sorption are surface coatings of oxides and oxyhydroxides of metal cations, typically  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$  (Lopez et al., 1996). The basis for sorption of  $\text{PO}_4^{3-}$  is the ligand exchange with surface hydroxyl group attached to these metal ions. The P in the  $\text{PO}_4^{3-}$  form thereby an inner-sphere complex through covalent bond with the metal ion of mineral surface hydroxyl groups. (Fig. 10)



**Fig.10 Ligand exchange at the mineral surface, forming an inner sphere complex between the surface metal and a phosphate group (Stumm and Morgan 1996).**

### 2.2.3 Degree of soil P saturation (DPS)

Degree of P saturation (DPS) is a commonly used index for environmental risk assessment of P leaching (Beauchemin and Simard, 1999). Soil DPS(%) is defined as the degree of P sorbed in the soil relative to the P sorption index (PSI) of the soil, and is determined from the ratio of bioavailable phosphorus (BAP) to the sum of PSI and BAP using Equation 2, adapted from (Pautler and Sims 2000; Indiaty and Sequi 2004).

$$DPS(\%) = \frac{BAP}{BAP + PSI} \times 100 \quad \text{Equation 2}$$

where, BAP is Bio-available Phosphorus (mg/kg), and PSI is Phosphorus Sorption Index (mg/kg).

### 2.3 Geographical information system (GIS)

Recent enhancements in geographic information systems (GIS) closely follows advancements in computers capacity which make it possible to model complex spatial information. Arc GIS (version 9.1) is a commercial software package used for the interpretation of spatially distributed data (Yilmaz, Yildirim et al. 2008). In this work the two sub-programs of ArcGIS; Arc Map and ArcCatalog are used. Arc Map is the primary application where the data are analysed and processed. ArcCatalog is used for creating and editing the spatial data files. The two spatial data types used are vector and raster files. Vector data contains features defined by a point, line, or polygon and ArcGIS implements vector data as shape files. Raster data are composed of a rectangular matrix of cells. Each cell has a width and height and is a part of the entire area represented by the raster. The cell size dimensions can be as large or as small as necessary to represent the area accurately. All raster layers used for this thesis had a grid resolution of 30 m<sup>2</sup>.

### 2.4 Soil Erosion.

Soil erosion is defined as the process by which the soil particles are detached and transported by the physical actions of primarily water and wind. The erosive energy of water is governed by the runoff intensity and amount, which is governed by intensity and the duration of rainfall. Soil erosion by water may be classified as sheet erosion, channel erosion and stream bank erosion (Fig. 2). The rate at which sheet erosion occurs depends on the erosive energy of the rainfall, soil texture and the soil's erodibility factor, which is given by the site's slope, slope length, the degree of soil cover, the presence of conservation practices such as contour farming, ridge-planting, no-till cultivations, crop rotations and strip cropping

which interrupt the downward flow of runoff water (Carter 1994). The main factors which determine the channel and the stream bank erosion are erosive energy and particle size of the soils.

The Universal Soil Loss Equation (USLE) relates these factors and is expressed in Equation 3 (Wischmeier and Smith 1965).

$$T = R \times K \times LS \times C \times P \quad \text{Equation 3}$$

where T is the soil loss from sheet, channel and stream erosion in  $\text{tons.ha}^{-2}.\text{year}^{-1}$ , R is the rainfall erosivity factor expressed in  $\text{Mj.mm.ha}^{-2}\text{h}^{-1}\text{year}^{-1}$ , K is the soil erodibility factor in  $\text{tons.ha.Mj}^{-1}.\text{mm}^{-1}$ , L is the slope length factor in meter (m), S is the slope gradient factor, C is the crop management factor, and P is the conservation practices factor.

The spatial variation in USLE can be determined by sandwiching the grid or raster data for the different factors in the USLE equation and finding the product of them for each grid within an ArcGIS platform. This can then be used to identify the critical areas for high soil erosion and to calculate the estimated average annual soil loss (T) that is occurring within the local catchment of Yuqiao reservoir. The evaluation and quantification of each of these factors are discussed in section 3.5.3.

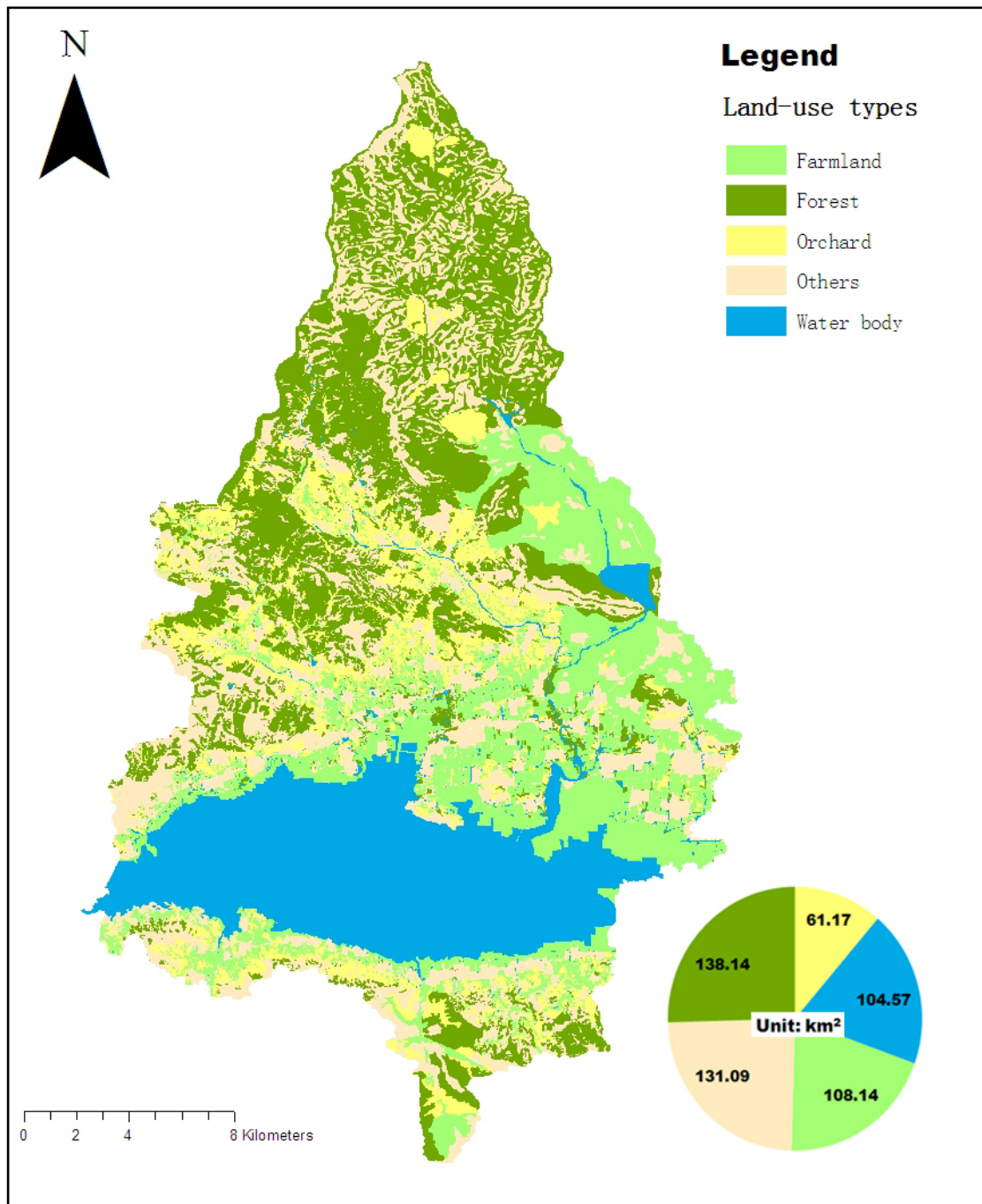
### **3. Materials and Methods**

The land within the local watershed of the Yuqiao reservoir is used for a set of different land-use, as described in chapter in 1.4. To determine the source and loss of P from the different land-use one need to understand the process governing these processes. This we may assess by studying the empirical relationships between pools of phosphorus in the soils and their key explanatory physiochemical characteristics. A comprehensive set of soil samples were therefore collected from farmland, orchard, forest and vegetable field and analysed for different pools of P, as well as main physiochemical characteristics. The obtained soil chemical data were analysed using a Geographical Information System (GIS) computer tool.

#### **3.1 Distribution of different land-use**

The local catchment surrounding the reservoir has a mix land-uses type, mainly comprised of- forest, farming, fishing, shrub, orchard and residential area (Fig.11). The farmlands are mainly located close to the reservoir and in the north-east part of the local catchment. A dense natural forest exists in the far north while a few commercially grown forest are situated in the low-land area. The land used for orchard farms are for the purpose of this study divided into orchard in low land area and in hilly area, whereof 80% of orchard field lie in the hilly area. The population in the catchment is around 137 000 people. The residents rely heavily on farming, but after the expansion of the reservoir in 1956 the farmland was limited leaving only 260 m<sup>2</sup> of farmland for each family of four members (Ji county statistical report 2012). The farmland is intensively managed to produce mainly winter wheat and summer maize. Some villagers are also practicing cash crops farming of vegetables and fruit orchard (mainly apple and Chinese nut). Vegetable grown in household gardens are commonly used for their own consumption. Interviews of local people revealed that they use little chemical fertilizers in their household garden, instead they apply organic manure to grow seasonal vegetable for their own kitchen. When they were asked the reason behind these they simply answered “chemical in fertilizers are not good for our health.” The farmers seem well aware of adverse effect on soil quality after using excess chemical fertilizers in their field, but they have little knowledge about the transfer of nutrients from their field to water body through surface runoff and sub-lateral runoff.





**Fig.11 YuQiao reservoir local watershed with different land use**

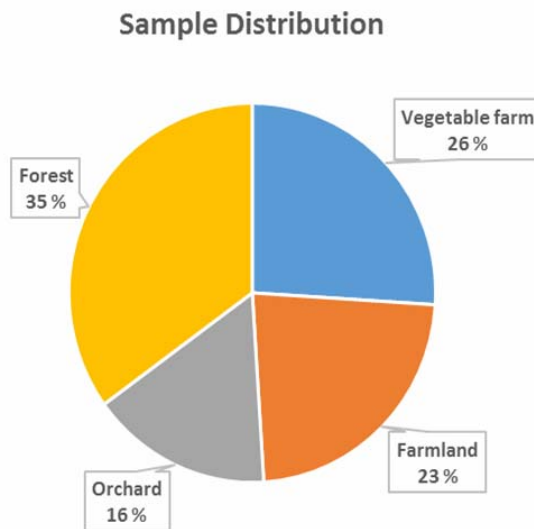
The implementation of guidelines for the application of chemical fertilizers based on the measurements of P pools in the soil is not practical due to the small patches of agricultural plots. The farmer therefore apply the chemical fertilizers, along with available human sewage and animal manure without any regulatory guidelines, though adhering to tacid indigenous knowledge (Orderud and Vogt 2013). The total number of livestock in the local catchment is reported to be 98 000 pigs, 17 000 buffaloes, 2 000 horses, 22 000 sheeps, 585

000 chickens, 174 000 ducks, and 24 000 geeses (Ji county statistical data 2010). The above livestock produced 372.0 tons manure each year which is equivalent to 9.3 tons of phosphorus per year (China EPA, 2004). Livestock's manure produce by their husbandry are spread on the fields at an average of 10.0 kg of phosphorus per mu (1mu = 660m<sup>2</sup>) amounting to about 15.0 g P m<sup>-2</sup>. In addition they apply about 22.0 kg inorganic fertilizer to each mu, amounting to about 30.0 g P m<sup>-2</sup> (Ji county statistical report 2012). This is an order of magnitude greater compared to only 2.3 g P m<sup>-2</sup> used on grain crops and 5.0 g P m<sup>-2</sup> on vegetables crop in Norway (Bechmann et al., 2013).

The local farmers apply the chemical fertilizers twice during the crop raise; once during tilling and next in the course of crop development. However for the maize farm they apply only manure during the seedling and chemical fertilizers during the crop development. They use mixture of chemical fertilizer, manure and sewage for wheat and vegetable crops. The proportion of manure used for vegetable crops is higher than in any other cultivated land due to higher demand of nutrients for vegetable crops and use of organic manure in the soil increases the aeration and infiltration quality of the soil. According to local farmer simple reason for using excess organic debris is easy access to vegetable farms, because vegetable farmlands are located near the road and residential areas.

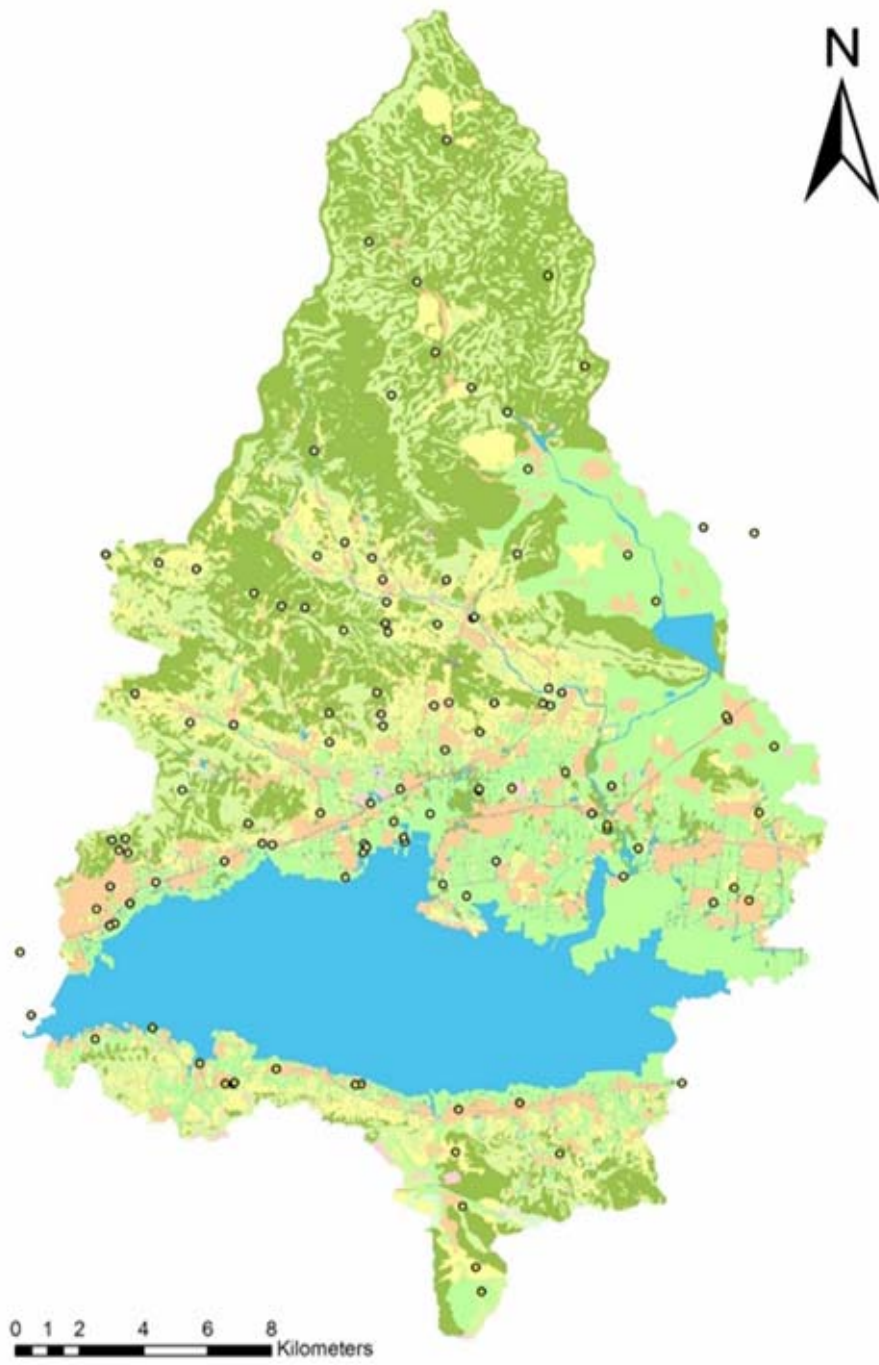
### **3.2 Sampling**

The total 126 soil samples (n=126) collected in the local catchment during two phase of sampling are shown by yellow dots in Figure 13. The first phase of sampling during April 2012 and second phase during August 2012. The sampling stargey was based on the fact that the local catchment located in the north part of YuQiao reservoir is believed to be responsible for the main flux of the phosphorus to the reservoir, however due to proximity to the water body, the south shore cannot be neglected. Thus for an overall view of the phosphorus transport 16 samples were also collected from the south part and rest of the samples were from the north part of the local catchment.



**Fig.12 Sampling distribution from different land use**

The main rationale for selection of sampling sites were to collect a similar number of samples from the four main land-use types Vegetable farm, Farmland, Orchard and Forest. While taking the soil samples from the farmland different types of cropping practice were marked e.g. farmland with maize and farmland with other crops. During the field work it was seen that farmers apply nutrients (mixture of organic debris and chemical fertilizers) for orchard tree in a ditch near the tree. Thus the sampling from the orchard farm was marked with sample near the tree as orchard tree zone (orchard TZ) and away from the orchard tree (orchard) to see the difference in nutrients pool. The samples from two horizons plough layer ( $A_p$ ) 0-20 cm and B-horizon 20-30 cm were collected from 31 sites including lysimeter sites ( $n=22$ ) to see the distribution of nutrients through the soil horizons. Also the topographic gradients were taken into the consideration in an effort to cover all types of land forms, including mountains and lowland near the Yuqiao reservoir. The coordinates and elevations of each sampling sites in Figure 13 was recorded using GPS (GARMIN) instrument, to locate the exact sampling sites. The information regarding the local practice of farming and mode of applying fertilizers are discussed with local farmers and local leaders with the translation from Zhou Bin.



**Fig.13** Location of sampling sites around the Yuqiao reservoir

Tools shown in the Figure 14 were used for soil sampling.



**Fig 14 Multifunctional hand shovel and soil auger.**

Pre-treatment of soil samples including air drying and sieving (2mm) was carried out in the soil laboratory of the Tianjin Academy of Environmental Sciences (TAES). The soils were subsequently divided into two parts. One part of the samples were kept at TAES for the analysis of bulk density, CEC, Base saturation, and Particle Size Distribution (PSD) and the second part were brought to Department of Chemistry, UiO, Oslo, and analysed for pH, water content, organic matter content and P pools. The air dry and sieved samples were given the code SSXXX (where SS stand for Sinotropa Soil and XXX denotes the serial number) and stored in paper boxes at room temperature at the Department of Chemistry, UiO.

### **3.3 Soil Analysis**

Soil samples were analysed for pH measured in Water and KCl suspension, water content by loss on drying (LOD), organic matter content by loss on ignition (LOI), P-pools, Bioavailable P (Olsen for alkaline soil and Bray-1 for acidic soil), Phosphorus Sorption Index (PSI) and Degree of Phosphorus Sorption (DPS) was calculated using PSI and BAP. The basic principle for each method, are described below.

Laboratory equipment used during the extraction and analysis of the samples were cleaned by first soaking the equipment in 5 % (v/v) of concentrated HNO<sub>3</sub> (65%, v/v) followed by rinsing with Type-II and Type-I (appendix-A) water prior to use. Sample bottles and volumetric flasks were also cleaned with 2M HCl and soaked with 4M NaOH overnight. The

analytical balance Sartorius LC320ID, with an accuracy of  $\pm 0.0001$  gm., was used for weighing.

### 3.3.1. pH

pH of the soil suspension was measured both in water (v: v, 1:5) and in 1M KCl (v: v, 1:5) solution on air dried soil samples according to ISO 10390 (1998). The main purpose of using a salt extract for measuring the soil pH is to minimise the effect of differences in solute concentrations due to climatic variations. The pH measurement was carried out using Orion Research Expandable Ion Analyser EA920 with a Ross Electrode.

### 3.3.2. Water content

Loss on Drying (LOD) or water content ( $W_{dm}$ ) of the air dried soil samples was estimated using the standard method as described in ISO11465 (1995). The mass difference ( $m_3 - m_1$ ), measured using the balance (Sartorius LC320ID) before and after drying at  $105 \pm 5^\circ\text{C}$  was used to calculate amount of water in the air dried soils using the Equation (4).

$$W_{dm(\%)} = 100 - 100 \times \left( \frac{m_3 - m_1}{m_2} \right) \quad \text{Equation 4}$$

where,

$m_1$  denote the mass of the drying tray in gram (g.).

$m_2$  denote the mass of soil sample in gram (g.) before drying

And  $m_3$  denote the mass of soil sample in gram (g.) after drying

The factor  $W_{dm}$  was used as a correction factor for the weight of soil used in quantitative analysis.

### 3.3.3. Loss on Ignition (LOI)

The soil organic content consists mainly of carbon, oxygen, hydrogen, nitrogen, sulphur, and phosphorus; all these constituents, except phosphorus, are derived from the atmosphere. The Organic matter content of each soil samples were determined based on weight loss upon ignition (LOI) following the procedure described in (Krogstad 1992), and calculated using Equation (5).

$$LOI(\%) = 100 - 100 \times \left( \frac{m_3 - m_1}{m_2} \right) - W_{dm} \quad \text{Equation 5}$$

where,

$m_1$  denote mass of empty weight tray in gram (g.)

$m_2$  denote mass of air dried soil samples in gram (g.)

$m_3$  denote mass of samples with tray after 4hrs of ignition at  $550 \pm 25^\circ\text{C}$  in gram (g.)

$W_{dm}$  denote loss on drying factor from section 3.3.2

### 3.4 Determination of phosphorus by molybdenum blue method

The molybdate blue method (MBM) used to determine the  $\text{PO}_4^{3-}$  concentration in the soil extracts was developed by Murphy and Riley (1962) and ISO 6878:2004. When a solution of  $\text{H}_2\text{SO}_4$ , ammonium heptamolybdate and potassium antimony tartrate is mixed with a solution containing phosphate, antimony molybdophosphate complex is formed. The phosphate complex is reduced to the blue coloured phosphomolybdenum complex in the presence of ascorbic acid (reducing agent) and potassium antimony tartrate (catalyst). The intensity of colour developed is proportional to the concentration of orthophosphate ions present in the solution. The intensity of the colour was determined spectrophotometrically at the wavelength ( $\lambda$ ) of 880 nm using UV-VIS spectrophotometer (UV-1800, SHIMADZU). The glassware used for P-analysis in contact with the molybdate reagent were cleaned according to the Norwegian Standard NS4724 and rinsed twice with Type-II water once with Type-I water (Appendix A). For the determination of the molybdenum blue method, the calibration curve for phosphorus standard solution of known concentration was obtained see Appendix B-3.

#### 3.4.1 Extraction of inorganic and organic phosphorus pools in the soil

The method used for extraction of inorganic and organic phosphorus pools in the soils (Møberg and Petersen 1982) is based on the fact that inorganic P (Ino-P) is bound to metal oxides, hydrous oxides or oxyhydroxides and clay minerals that are soluble in medium to strong acids, whereas part of P captured in organic matter as organic P (Org-P) is not released. The phosphorus bound to Fulvic acid (FA) is soluble in aqueous conditions, but will not be measured by the Molybdate-Blue Method (MBM, section 3.4), it will exist as  $\text{FA-PO}_4$ , not as free  $\text{PO}_4^{3-}$  (Loon and Duffy 2005). This principle is used to extract and distinguish inorganic-P in the soil samples using 6M  $\text{H}_2\text{SO}_4$ .

Total P (TP) is determined applying the same extraction method after igniting the soil samples at  $550 \pm 25^\circ\text{C}$ . The ignition of the samples convert organic P to inorganic P. The

extracted samples will then contain the TP in inorganic form.

The organic phosphorus pool in the soil samples (TOP) was calculated as the difference between the value of TP and TIP, according to Equation (6)

$$TOP = TP - TIP$$

Equation 6

Where,

TP represent the total phosphorus in mg.kg<sup>-1</sup> of soil samples.

TIP represent the total inorganic phosphorus in mg.kg<sup>-1</sup> of soil samples.

TOP represent the total organic phosphorus in mg.kg<sup>-1</sup> of soils samples.

### 3.4.2 Bioavailable Phosphorus (BAP)

Of the total 126 soil samples collected in the study area, 84 samples has pH above 7.2 and rest of the samples (42) has pH less than equal to 7.2 in water. To estimate the bioavailable phosphorus in these alkaline and acidic soil two methods I,e. Olsen P (Olsen et al., 1954) and Bray and Kurtz P-1 (Bray and Kurtz 1945) were used, respectively.

**Table 2 Soil properties affecting selection of the appropriate phosphorus test and recommended methods (Source <http://soils.usda.gov/technical/methods>)**

Soil	pH	Minerals	Methods
Acidic, slightly acid to slightly alkaline	≤ 7.2	Al-P, Fe-P, Mn-P and Mg-P	Bray and Kurtz P-1
Alkaline, calcareous	> 7.2	Ca-P and Mg-P	Olsen P

Based on different pH range, different soil P tests Bray-1 and Olsen, for acid soil and for alkaline soil respectively were developed to determine the amount of plant-available P in soil and from this how much P as fertilizer or manure should be added to meet desired crop yield goals

#### a. Olsen P

The “Olsen P” extraction (Olsen et al., 1954), or sodium bicarbonate soil test phosphorus (P) extraction was conducted according to the method described in Pierzynski (2000). This method is used to determine extractable P in alkaline or calcareous soils. The extracting



solution is 0.5M NaHCO<sub>3</sub> at pH 8.5. The carbonate in the extractant decrease the solution concentrations of soluble Ca<sup>2+</sup> due to the precipitation of CaCO<sub>3</sub>, which in turn increases the solubility of phosphate. To occur the secondary precipitation reaction with dilute acid and co-adsorption of phosphate must have sufficient H<sup>+</sup> activity to overcome the common ion effect of Ca<sup>2+</sup> (Olsen et al., 1954). These two affects has been eliminated during sodium bicarbonate extractions at pH 8.5.

#### **b. Bray and Kurtz P-1**

The Bray and Kurtz P-1 soil test P (Bray and Kurtz, 1945) was conducted according to the protocol given in Pierzynski (2000). This method is commonly used for extracting bioavailable phosphorus from acidic or neutral soil. In acid soils, the fluoride in the Bray and Kurtz extractant (0.025M HCl in 0.03M NH<sub>4</sub>F pH 2.6 ± 0.05) released the P bound to aluminium by decreasing Al activity in solution through the formation of strong Al-F complexes. The fluoride is also effective in suppressing the readsorptions of solubilized P by soil collides (Hiemstra and Van Riemsdijk 2000). The acidic nature of the extractant contributes to dissolution of P adsorbed to Al and Fe oxy-hydroxides.

#### **3.4.3 Phosphorus Sorption Index (PSI).**

Phosphorus sorption capacity of soils is generally determined by measuring sorption isotherms following the procedures outlined in Pierzynski (2000). But this method is too time-consuming, complicated and expensive for the routine data needed for agronomic and environmental characterization of the P sorption capacity of soils. Bache and Williams (1971) solved this problem by developing a “Phosphorus Sorption Index” (PSI), which is fast and can be used as a proxy for the soil P sorption capacity.

The main principle behind the Phosphorus Sorption Index (PSI) is to measure the extent of phosphorus with known concentrations that is adsorbed on the surface of soil particles. The extent to which this occurs is an important property reflecting both the availability of phosphate to plants and loss of phosphate via soil erosion. This property (PSI) of soil is commonly measured by shaking soil samples with sorption solution of 75 mg P kg<sup>-1</sup> of soil (Note: this provides a ratio of 1.5 g P kg<sup>-1</sup> soil) in the ratio of 2:20 (w/v) and adding two drops of toluene to inhibit microbial activity (Pierzynski 2000). The change in phosphate concentration was measured using MBM after 18hrs of end to end shaking at room temperature.

#### **3.4.4 Degree of Phosphorus Saturation (%DPS)**

DPS for soil samples representing different types of land use was calculated using the

relation given in Equation 2 (page no.24). The result for DPS% calculated as the ratio of STP to sum of STP and PSI has been evaluated in terms of its effectiveness for identifying the potential of soil P losses (Pautler and Sims 2000).

### **3.5 Geographical information system (GIS)**

In this study, Arc Map has been used for spatial data analysing and processing. Spatial distribution maps for P pools are based on data from the chemical analysis of soil samples, and different erosion risk factors were calculated using the data obtain from local weather station (R factor), remote sensing picture using Normalized difference vegetation index (NDVI) for C factor, Digital Elevation Model (DEM) (L&S factor), land-use data from Ji county land management department (P factor) and Soil Database from 1982 (K factor). These factors were sandwiched to produce soil erosion profile using Geographical Information System (GIS) (ArcGIS software version 9.3.1). The product of soil erosion profile map and the spatial distribution of %DPS were used to localized Critical Source Area's (CSA's) within the local catchment.

#### **3.5.1. Inverse Distance Weighted (IDW) Interpolation.**

One of the most commonly used techniques for interpolation of spatially scatter points is inverse distance weighted (IDW) interpolation. Inverse distance weighted methods are based on the assumption that the interpolating surface should be more influenced by nearby points rather than distant points. The interpolating surface is a weighted average of the scatter points and the weight assigned to each scatter point decreases as the distance from the interpolation point to the scatter point increases. Several options are available for inverse distance weighted interpolation. The GIS software from Sustainable map Solutions (SMS) uses Shepard's Method (Shepard 1987) for IDW. Shepard's method has been used extensively for inverse distance weighted interpolation because of its simplicity.

The weight function (Appendix F) is a function of Euclidean distance and is radially symmetric about each scatter point. As a result, the interpolating surface is somewhat symmetric around each point and tends toward the mean value of the scatter points between the scatter points.

#### **3.5.2 Straight Line Distance Function.**

A straight line distance surface (Appendix F) is used to find the shortest distance, a straight line, from each cell to the closest source. Similar to using a ruler to measure the distance between two points on a piece of paper, the Straight Line Distance function measures the

distance between cells from the centre of each cell on the surface to the centre of a source cell.

In this case of a straight line distance surface there is only one source location. Each cell value indicates the distance to the source. The distance (x) from cell A to the source is measured along a straight line. A straight line distance surface makes it easy to find the nearest location of interest. While there can be more than one source, each cell value is the straight line distance to only one source, the closest one. If there is more than one source in a straight line distance surface, cell values indicate the distance to the closest source. In this case, cell A is closest to Source 1, so its value is the distance between them.

### **3.5.3 Soil erosion model (USLE).**

The Universal soil loss equation (USLE model) calculates long-term average annual soil loss by multiplying six factors which describe the watershed characteristic regarding erosion. These are rainfall erosivity factor (R), soil erodibility factor (K), slope length (L), slope steepness (S), cover management practices (C) and support conservation practices (P) (Renard, Foster et al. 1997). These six different factors are calculated using the relation describe in appendix E.

The USLE equation is summarized as (Wischmeier and Smith 1965):

$$T = R \times K \times LS \times C \times P \quad \text{Equation 7}$$

In GIS is the USLE factors are structured as individual digital layers and multiplied together to create the soil erosion potential map. This provides a map showing the soil erosion potential of the watershed using existing data sources.

The erosive power of rainfall is represented by the rain Erosivity Factor (R), which is calculated as the product of the kinetic energy of the rain storm and the maximum 30-minute intensity of rainfall.

Because none of the weather stations in the study area record rainfall intensity for 30 minutes, the modified model (Yu 1998) given in the Equation 12 (appendix E) was adopted to calculate the monthly rainfall intensity based on the 24hrs rainfall intensity data. These data are compiled from the four weather stations located within the local catchment of the YuQiao reservoir. Based on the monthly data the value for 12 months of each year were summed.

The soil erodibility factor (K), is the average soil loss in tons.ha.Mj<sup>-1</sup>.mm<sup>-1</sup> per unit area for a particular soil type in cultivated, continuous fallow land with an arbitrarily selected slope

length of 72.6 ft. and slope steepness of 9%. K is a measure of the susceptibility of soil particles to detachment and transport by runoff. Texture (Ji county Soil database, 1982) is the principal factor governing K, but soil structure, organic matter content and permeability also play an important role.

The topographic factor is the combined function of L and S, describing the slope length-gradient. The LS factor represents a ratio of soil loss under given conditions to that of a site with the "standard" slope steepness of 9% and slope length of 72.6 feet. The steeper and longer the slope, the higher is the risk for erosion (Stone, Ontario. Ministry of Agriculture et al. 2000).

The crop/vegetation and management factor (C), is used to determine the relative effectiveness of soil and crop management systems in terms of preventing soil loss. The C factor is a ratio comparing the soil loss from the land under a specific crop and management system to the corresponding loss from continuously fallow and tilled land. The C Factor is determined by the crop type and tillage method. The equation developed by Cai (2000), is used for determining C factor in this study (Cai et al., 2000). In this equation the C factor is empirically related to the NDVI index. The Normalized Difference Vegetation Index (NDVI) is a simple graphical indicator that can be used to analyse remote sensing measurements, and assess whether the target being observed from space contains live green vegetation or not. Its value is always between -1 and +1

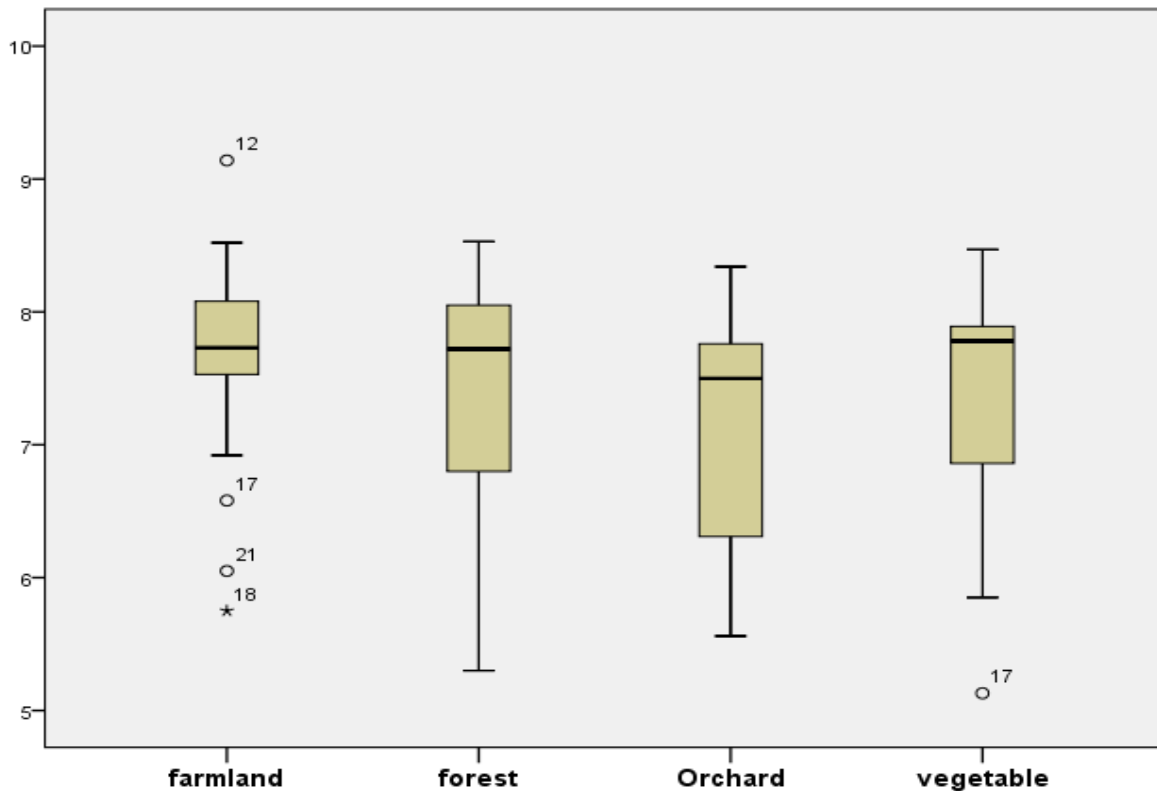
The support practice factor (P), reflects the effects of practices that will reduce the amount and rate of the water runoff and thus reduce the amount of erosion. The P factor represents the ratio of soil loss by a support practice to that of row farming straight up through the slope. The most commonly used cropland practices to avoid erosion are cross slope cultivation, contour farming and strip-cropping. According to degrees of soil erosion from different management measures, some quantitative relationships between land-use type and P factor were put forward in previous studies by (Sivertun and Prange 2003).

## 4. Results and Discussion

The result and discussion part consists of two parts, where the first part (source part) deals with the data from physiochemical analysis of soil samples and their interpretation and the second part (transportation factor) include USLE model couple with ArcGIS to identify critical source area's with respect to phosphorus flux into the YuQiao reservoir from the different land use practice in the local catchment.

### 4.1 Soil pH

Result obtained from pH measurement of soil samples from top layer measured in water ( $\text{pH}_{\text{H}_2\text{O}}$ ) and in potassium chloride ( $\text{pH}_{\text{KCl}}$ ) suspension are shown in figure 15. The pH measured in  $\text{CaCl}_2$  was found one unit lower than the pH measured in water, because of ion exchange process. The calcium chloride can furnish  $\text{Ca}^{2+}$  ion in the solution to replace some of  $\text{H}^+$  ions on the soil surface, increasing the concentration of  $\text{H}^+$  ions on the soil solution. The majority of soil samples from A-horizon lie in the  $\text{pH}_{\text{H}_2\text{O}}$  range from 5.5 to 8.5. However most of the samples (65%) have alkaline pH ( $\text{pH} \geq 7.0$ ). The soil in the watershed thus span from slightly acidic to alkaline, though with a majority in the alkaline  $\text{pH}_{\text{H}_2\text{O}}$  range. This implies high base saturation due to carbonate weathering in natural soil and liming in agricultural soil. Around 80% of sampling sites lies in the pH range from 6.0 to 8.0. This is the pH range in which phosphate is considered most mobile as it is not precipitated out by either labile Al or Fe, at low pH (acidic pH), and  $\text{Ca}^{2+}$ , at higher pH (at alkaline pH). The pH range found in the soil samples are therefore optimal for the mobility of orthophosphate ions. Figure 15 shows that the pH in farmland is higher and more buffered than other land-use. This is likely due to that the most fertile soils which are used for agricultural practice have high CEC and BS and therefore have good buffering capacity. The orchard and forest land-use with lowest average pH indicates the poor soil with low CEC and BS, since these soils are likely not limed. The reason for the large span in pH in forest is likely due to large variation in factors governing pH like climate. However the decrease in pH is not significant since the forest in our study area located in semi-aired zone with comparable low LOI% with respect to cold and humic region (Oades 1988). Since the vegetation growing on a soil has marked influence on soil acidity because differences in base content of their litter. Soils supporting conifers in cold and humic climate tend to be more acid than those hard wood species in semi-aired zone, partly because conifer leaves and their litter have a lower base content.



**Fig.15 Soil pH<sub>H2O</sub> from A-horizons for different land-use**

In the case of soil in vegetable farm, the range of higher pH indicates use of excess manure, remains of plant and microbial decomposition of these organic debris account for the acidic pH as compare to other form of land use.

## 4.2 Phosphorus

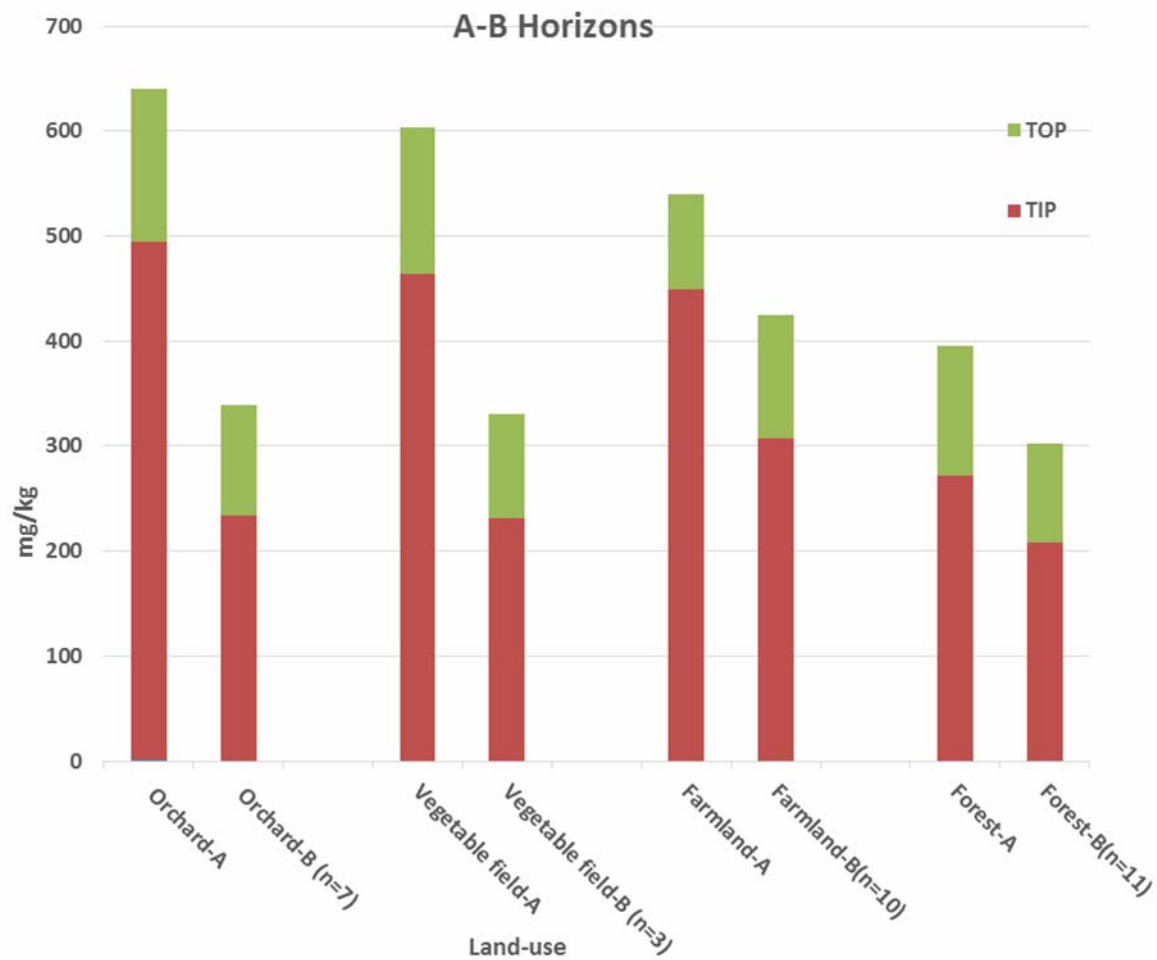
The size and distribution of different pools of P depends mainly on soil properties, land-use types and agricultural management practices. The majority (65%) of the sampling sites at Yuqiao are from human influenced land-use, such as vegetable farmland, farmland (cereals crops) and orchard. On these soils the amount of P added annually is an order of magnitude greater than the pool of P in the soils, suggesting that there is a large surplus of P that is added to the soils.

The total phosphorus (TP) pool in the general soils typically range from 0.2 to 5 g P kg<sup>-1</sup> with a global average of 0.6 g P kg<sup>-1</sup> (Liu et al., 2007). The TP pools in the vegetable farmland, farmland, orchard and forest soils from the study area ranged from 0.15 to 3.5 g P kg<sup>-1</sup>, with an average of 0.7 g P kg<sup>-1</sup>. The phosphorus content in these soils are therefore not especially high. The values of TP were found comparable with the TP value for agricultural soil in Norway. According to Krogstad & Løvstad (1987) the TP content in the upper 0-20 cm

of Norwegian soils is close to  $1 \text{ g P kg}^{-1}$ ; however, for heavily fertilized agricultural soils these values reach up to  $2 \text{ g P kg}^{-1}$ . The P pools in the heavily fertilized soils are limited by the soils capacity to bind P. The differences in the high range of TP are therefore likely due to different capacity of the soils to hold P. On the other hand, one would expect that the wet and humic rich Norwegian soil would have larger P binding capacity compared to dry and organic poor soils in Ji County. The likely main cause for this apparent contradiction is the considerable stronger over-fertilization of P in the soils at Yuqiao. The soil capacity to hold P is also determined by the soils pH and the content of Ca, Fe and Al, as well as clay minerals. The difference in the  $\text{pH}_{\text{H}_2\text{O}}$  content for different land-use is not significant, since 80% of samples lies in the pH range of 6.0 to 8.0 in which P is most mobile. Thus the clay content and concentration of  $\text{Ca}^{2+}$  play an important role in capturing the P.

The soils in China are considerably older than the adolescent Norwegian unconsolidated deposits, which were deposited less than 12 000 years ago. The weathering of the soils by incongruent dissolution leads to clay formation in acid soils and oxide formation in neutral soils. The soils in China are therefore predominantly of secondary oxy-hydroxide and clay minerals, while the soils in Norway are still composed of primary minerals of crushed igneous granite and gneiss. The Point of Zero charge (PZC) of the oxy-hydroxides of Al and Fe are very high (pH 8.2-8.5) compared to primary minerals Feldspar, Smectite and Quartz (pH 2.2 – 2.9). The soil pH at Yuqiao is mainly between 6 and 8. The soil pH close to the PZC of the oxy-hydroxides implies that the soils have a more predominant positive surface charge, making them into significant anion exchangers. This will enhance their capacity to bind the ortho-phosphate anion.

On the other hand, the clays in Norway are still 1:2 type swelling clays, while the mature Chinese clay is renowned of its 1:1 clay Kaolinite type. The PZC of Kaolinite is relatively low (pH 4.6), while Illite, commonly found in Norway, has a PZC of 8.8. This implies that the Chinese clay is mainly a cation exchanger while the Norwegian clay is more of an anion exchanger. The main feature of the 1:1 Kaolinite clay type is that it is a non-swelling clay. This means that it does not crack when dried which leads to that the permeability of this very compact material is extremely low. The Kaolinite clay is therefore found as a compact clay layer under the  $A_p$  layer in the lowland region. There is therefore very little water that passes through this compact layer rendering it impermeable and inert. The presence of thick deposits of this clay is apparent by several brick factories in the region mining clay from an open pit.



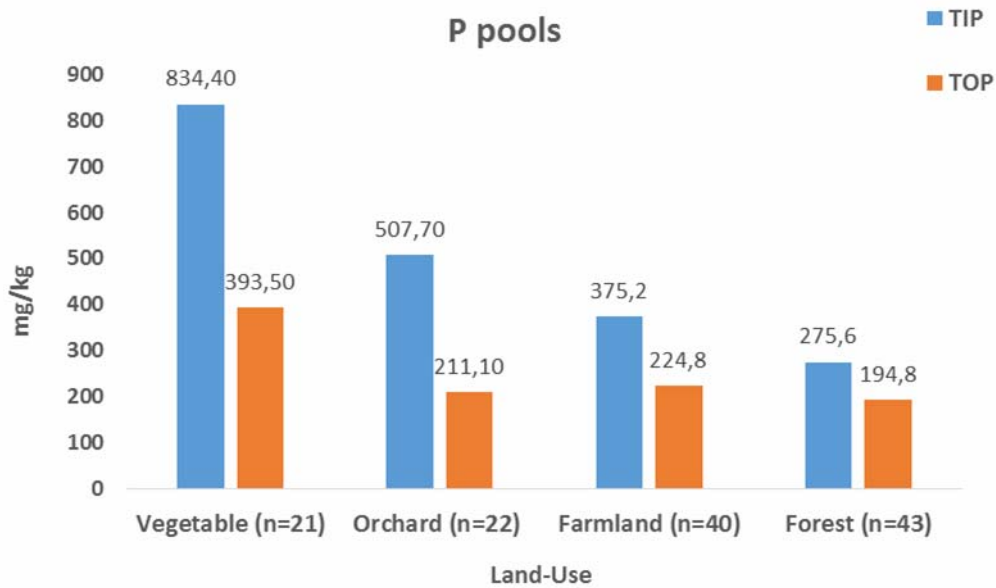
**Fig. 16 Phosphorus pools of the soil horizons (A-B) for different land-use**

The amount of TOP and TIP in the soil samples from the A and B horizons from 31 plots with different land-use are shown in Figure 16. The A and B-horizons for Orchard and Vegetable fields have large variations in TIP and TOP pools whereas the variations is not significant for farmland and forest. The TIP concentration in all type of land-use is higher in the A-horizon than in B-horizon. This is likely due to the 1) application of fertilizer and manure to the A<sub>P</sub> layer, higher capacity to bind P of the A layer then the B layer (due to higher organic content) and due to rather impermeable clay found in many of the B horizons. A compact impermeable clay layer was commonly found in the lowland areas. The cause for the large difference in P pools for A and B-horizons in the Orchard and Vegetable fields is likely due to that these fields are mainly situated in the lowland region where the rather permeable A<sub>P</sub> layer is lying on top of an impermeable clay layer restricting the leaching of soluble P into the B layer.



In general the contribution of TOP to the TP content in the surface soil layer varies between 50 to 70% in mineral soil and up to 90% in organic soil (Zhang, Werner et al. 1994). The TOP in the natural soil of Vansjø forested catchment, in cold and humid SE Norway climate, contributes 85% of total phosphorus (Mohr 2010). On average the TOP constituted 70% of the TP. The average TOP pool in the top soils at Yuqiao is small ( $0.3 \text{ g P kg}^{-1}$ ) and contributes on average only 20-30% to the TP (Fig. 17). Usually the TOP pool is found to be slightly smaller in the B horizon than in the A horizon. This is further discussed in Chapter 4.3. The exceptions are for farmland and forest in the highlands. The TOP pool is usually governed by the organic content of the soils. The differences between the land-use practices and between the soil horizons are therefore likely mainly linked to differences in the content of organic matter. In the highland forests the dry and coarse skeleton soils with high organic matter have high infiltration rate allowing the nutrients to be easily leached and pass to the B horizon.

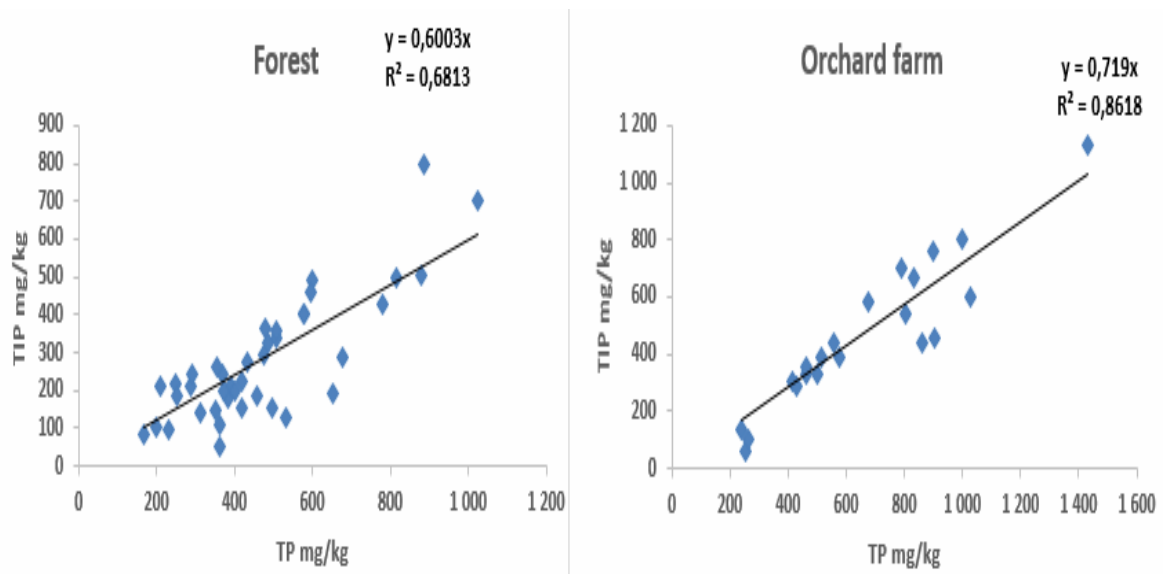
P losses in soluble form from soils are generally very low because of the strong P sorption capacity of soil. However, dissolved and particle bound P losses through surface runoff are relatively high for human influenced land-use. The loss of particle bound P is high due to that the soils are more susceptible for erosion. This is especially the case after tilling. Loss of dissolved P is mainly due to the use of inorganic fertilizers and manure. The use of manure may actually enhance the loss of dissolved phosphate. Several mechanisms are responsible for the release of labile P into the solution upon addition of organic manure. Firstly, large humic molecules stain the surface of clays and metal hydrous oxide surface, masking their positively charged P fixation site and thereby preventing these surfaces from interacting with  $\text{HPO}_4^{2-}$  ions in solution (Brady and Weil 2010). Secondly, organic acid and other small organic ionic compounds added with the manure can compete with phosphate ions for positively charged sites on the surface of soil particles and hydrous oxides through anion exchange reactions. Thirdly, humic acids chelate reactive metal like Al and Fe in stable organic complexes (Brady and Weil 2010). Both Al and Fe are important for the soil's capacity to bind phosphate. Thus addition of organic manure may attribute both to a P accumulation in surface soils as well as to an increased mobility of labile P from the soil (Sims et al., 2002). The high level of surface soil P in vegetable farms eventually leads to increased loss of P to water bodies through surface runoff.



**Fig. 17 Phosphorus pools for A-horizons from different land-use**

#### **4.2.1 Phosphorous pools in forest soils**

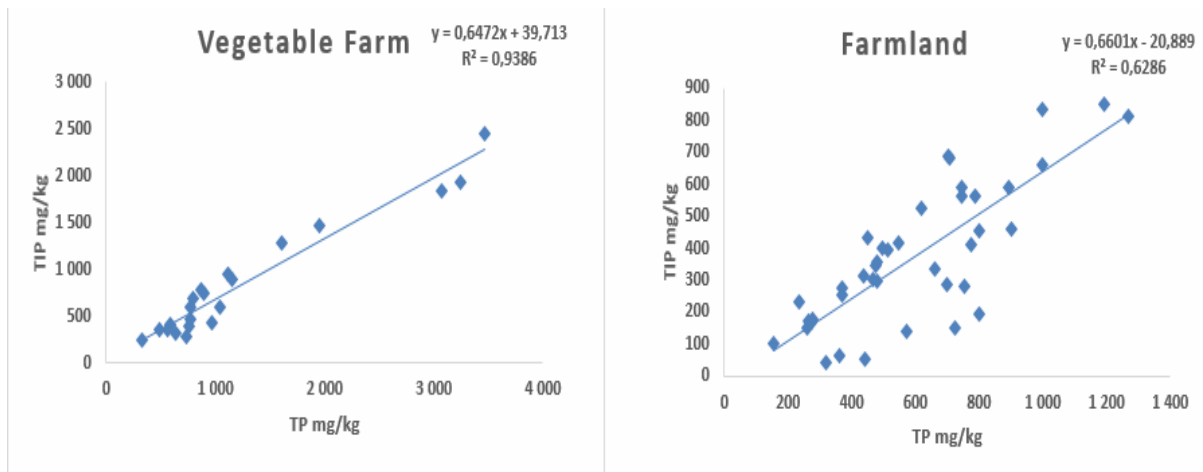
The Forest soils in this study area have TP in the range of 0.017 to 1.0 g P kg<sup>-1</sup>, of which about 60% is as TIP. The main reason for the relatively high content of TIP in the forest soil, compared to the levels in the local agricultural soils, may be that in few soil samples from timber forest grown for commercial purpose the farmers takes all the measure like fertilization, adding manure and removing unwanted plants. Furthermore, top layer soils (SS006, SS012, SS027, SS042, SS052, SS068, SS067) from the forest areas that are located in the outskirts of farmland or orchard in low land have high contribution of TIP (>80%) to the TP (Fig. 18). These forests can retain phosphorous dust particulate. Furthermore, the forests that are planted in the lowland are often established as buffer zones between the agricultural land and the reservoir and thereby accumulate dissolved and particulate phosphorus from surface runoff from the upslope agricultural soil. Commonly, the TIP is found to constitute 50 to 70% of TP in mineral soils (Pierzynski 2000), implying that the distribution of TIP and TOP is as commonly found.



**Fig. 18 TIP relation to TP in Forest and Orchard farm**

#### **4.2.2 Phosphorous pools in soils from vegetable fields**

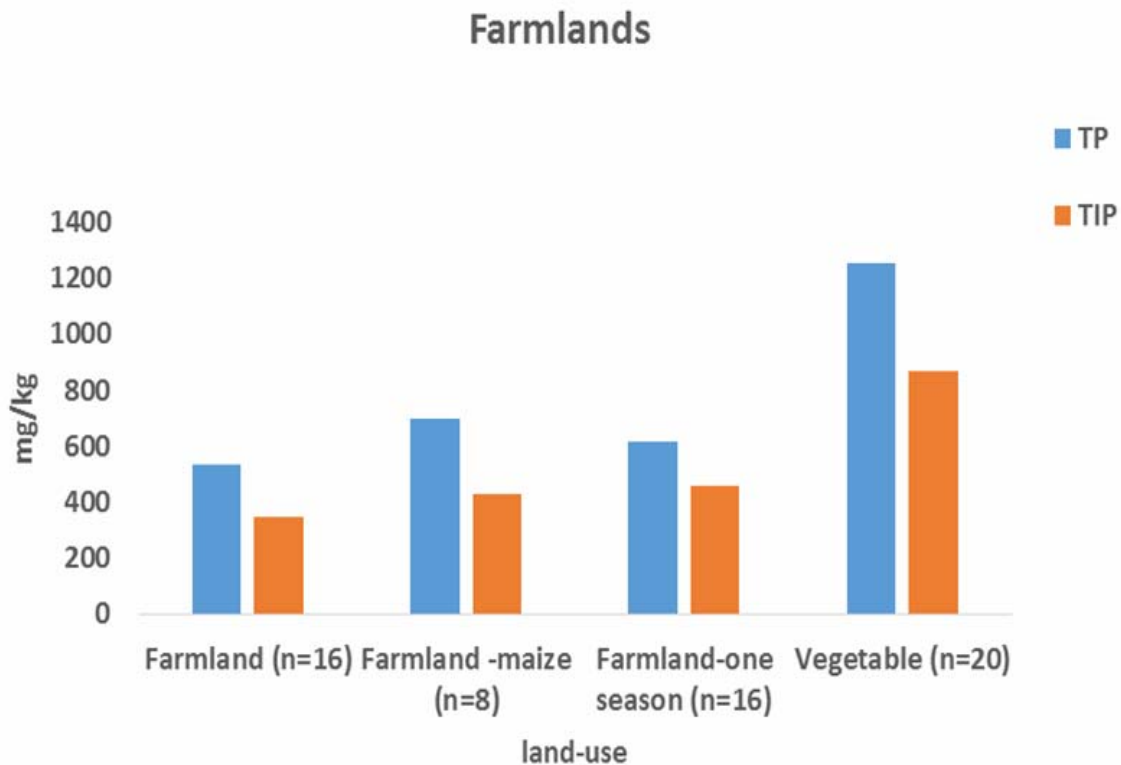
Among the different land-use in the study area vegetable fields shows the highest content of TP 0.3-3.5 g P kg<sup>-1</sup> with an average value of 1.2 g P kg<sup>-1</sup> (n=22) (Fig. 19). The variation within this land-use is mainly due to high variation with respect to TIP, which range from 0.2 to 2.5 g P kg<sup>-1</sup> with an average of 0.8 g P kg<sup>-1</sup>. Vegetable farming is extensively practiced in the region as a source of cash crop. The farmers add all types of available organic nutrients sources into their vegetable fields, such as household waste, vegetable remains, manure and P fertilizers. According to local farmer they compost all the vegetable plants after each harvest and use this organic matter for next cropping. This is done because this lead to maintain good surface soil aggregation, low bulk density and high aeration which increase production yield of vegetables (Shannon, Sen et al. 2002). Due to all the addition of organic waste the pool of TOP in vegetable farmland soils is relatively high, with an average of 0.4 g P kg<sup>-1</sup>, accounting for 40% of TP.



**Fig. 19 Phosphorus pools in Vegetable farm and Farmland**

#### 4.2.3 Phosphorous pools in farmland soils

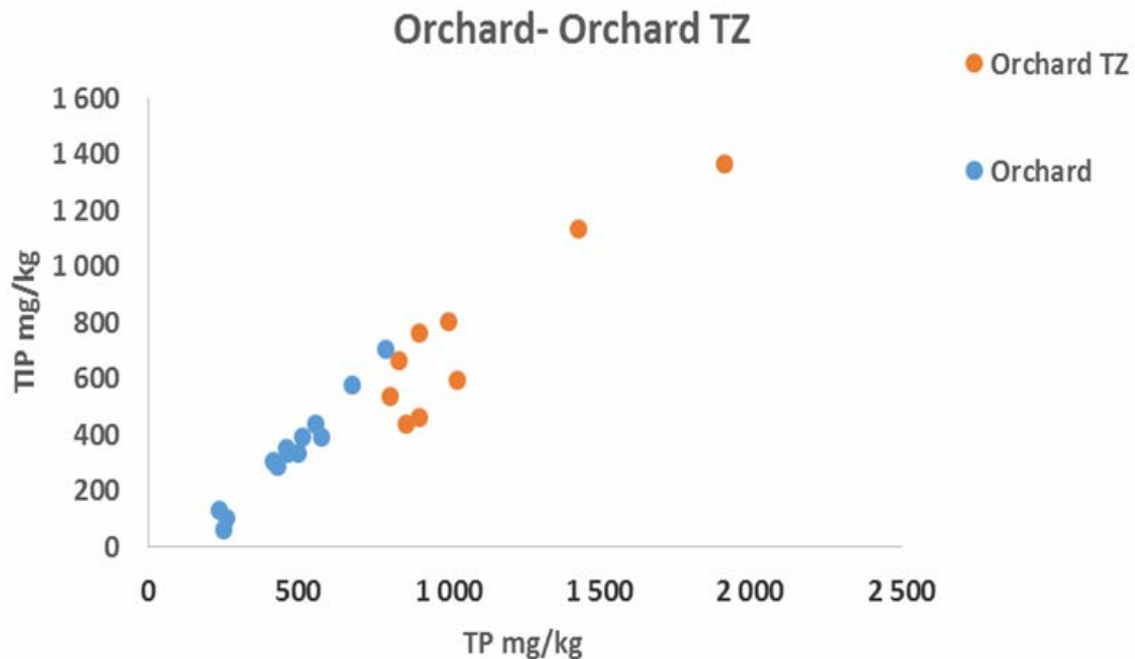
The TP in farmland soils (n=40) is found to range from 0.2 to 1.3 g P kg<sup>-1</sup>, with an average of 0.6 g P kg<sup>-1</sup>. Farmers apply inorganic fertilizers twice a year to the farmland: first during field preparation and second during crop growth (based upon interview with local farmers during field work). The TIP pool has an average of 0.4 g P kg<sup>-1</sup>, accounting for around 70% of the TP (Fig.20). The practice of applying manure on the farmland differs depending on the location of the farmland. If the farmland is located far from any livestock's shed the farmers tend to just dump the manure on wasteland and allow it to be washed away by heavy rains through surface runoff. Where the farmland is located near to livestock's the application of manure varies for different crops. Maize and wheat are the two main cereal crops in the region. Maize is planted after dry and cold season (winter) and wheat is planted after wet and rainy season (summer). The farmers apply a mixture of manure and P fertilizers during seedling of maize. During the crop growth the farmers for practical reasons only apply inorganic fertilizers. For the wheat crop the farmer only use inorganic P fertilizer as it is not practical to transport and distribute the manure onto the wet fields after the wet season. A slight difference in the TIP content of the farmland and farmland with maize (Fig. 20) is due to differences in sampling time. Some of the soil samples were collected after the farmer had planted maize while other samples were collected from the farmland with different practice of farming such as farm with crop rotation or farm with one season crop. The application of fertilizers preceding sampling of soil therefore differed as only organic manure was applied during field preparation for the maize.



**Fig. 20 Total phosphorus (TP) and total inorganic phosphorus (TIP) for different farm practice and Vegetable farm.**

#### 4.2.4 Phosphorous pools in soils from orchards

The average TP pool in the soils from Orchards (N= 22 soil samples) was found to be  $0.7 \text{ g P kg}^{-1}$  of which 71% ( $0.5 \text{ g P kg}^{-1}$ ) was accounted for by TIP. The application of a mixture of manure and inorganic fertilizers to the orchard in the study area is very similar to what is applied to the farmland. The main difference in agricultural practice is in how the fertilizers are distributed on the land. In farmland they spray the fertilizers and manure on the soil, while in the orchards the farmers apply the mixture of fertilizers and manure in ditches around the fruit tree and cover with soil and crop residue. The practice of covering manure and fertilizers with crop residue help plant root preserve moisture and accelerate the rate of nutrients dissolution. The sampling of the soil therefore included both the area near to tree trunk (Orchard TZ) and further away from the tree trunk (Orchard). As expected the samples collected near to the tree trunk show higher content of inorganic phosphorus, accounting 70 to 80% of TP, compare to area away from tree trunk (Fig.21).



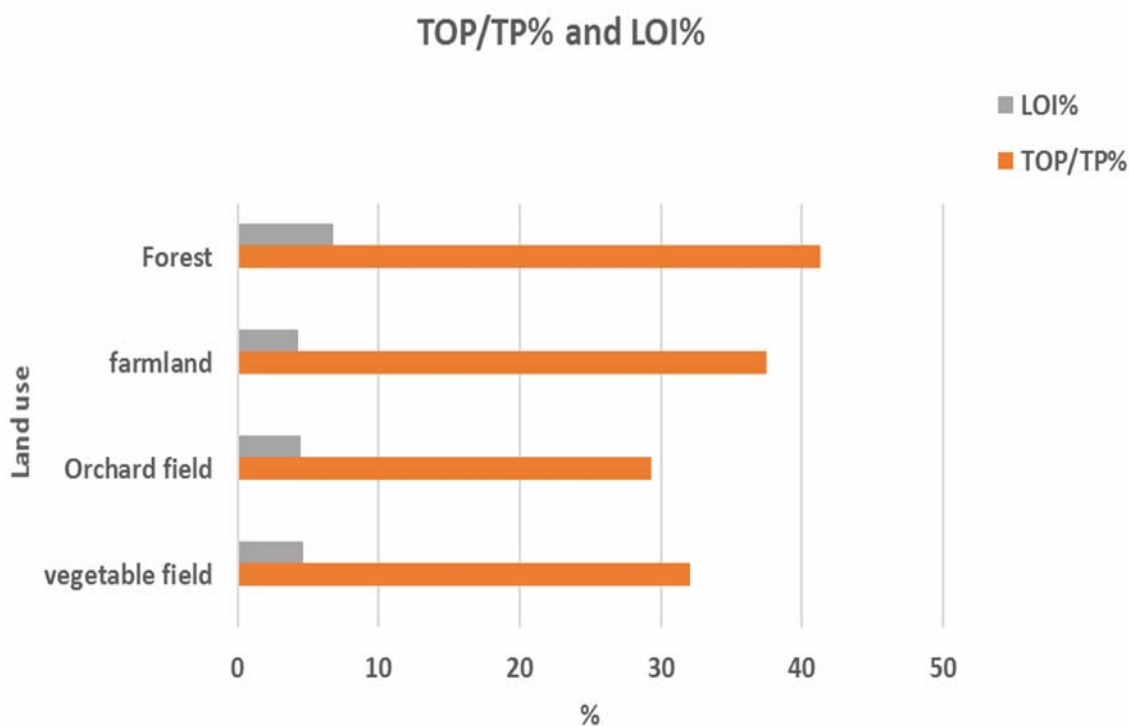
**Fig.21 Total phosphorus (TP) and total inorganic phosphorus (TIP) for Orchard- Orchard (tree zone).**

The contribution of TOP for TP is not significantly higher even for natural soil since the soils in the study area are dry with low LOI%. The majority of soil samples have  $TOP \leq 0.5 \text{ g P kg}^{-1}$  which constitute 15-25% of TP. A few soil samples from vegetable field have higher TOP compare to other land-use. This is likely due to that the farmers apply organic manure and remains of vegetable plants to the soils used for growing vegetables. Farmland samples which were collected from maize fields while the plant was growing had relatively higher TOP content compared to the other samples from farmland soils. According to local farmer they use only manure during the planting of the maize. The elevated TOP in these samples may therefore be due to the manure added to the soil short time before sampling.

#### **4.3 Organic matter (LOI %) and Total Organic Phosphorus**

There is a conceptual inherent relation between organic content (LOI %) of the soil and the total organic phosphorus content in natural soil (Fig. 22). The contribution of TOP to the TP is the highest in the forest soils from YuQiao, which is also the land-use with the highest organic content in the soil, though the differences are not large. The cultivated soil have less content of organic matter compared to natural soil due to the application of inorganic fertilizers leading to a higher decomposition rate of organic matter. The soils in the orchards resemble soils in vegetable fields with respect to LOI% and TOP. This is likely due to that

orchard fields are managed more or less in the same manner as vegetable fields. The organic matter content in the vegetable field is higher than farmland because the farmer uses manure and the plants remains of vegetables in the field in addition to inorganic fertilizers.

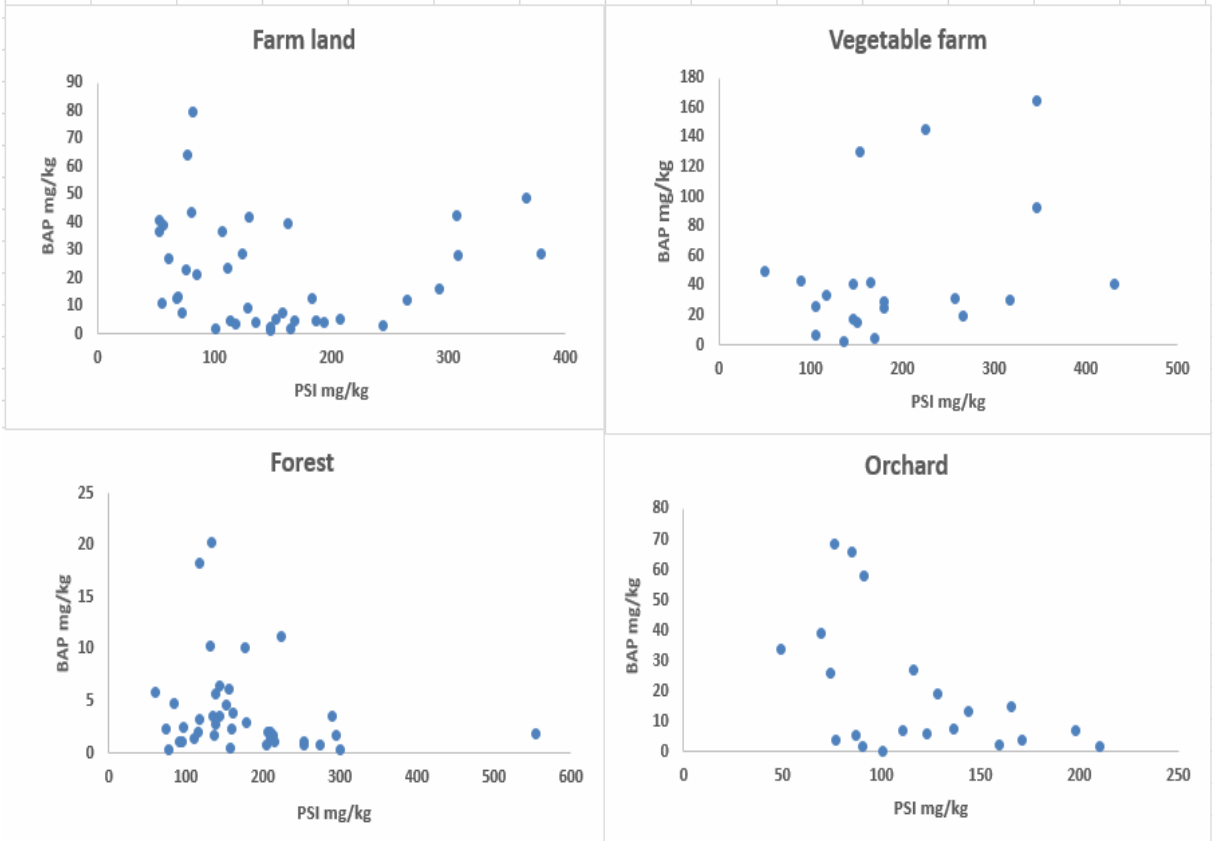


**Fig.22 Fraction of Total Organic Phosphorus and LOI%**

#### **4.4 Bioavailable Phosphorus (BAP) and Phosphorus Sorption Index (PSI)**

There are relatively large differences in bioavailable phosphorus (BAP) ranging from 0.0034 g kg<sup>-1</sup> in forest soil to 0.0558 g kg<sup>-1</sup> in soils from vegetable fields (Fig. 23). The main cause for these spatial differences is the differences in application of fertilizers. The forest area with generally uncultivated and unfertilized soil have low amount of bioavailable phosphorus (only 0.7% of the total phosphorus is available to plant uptake), while vegetable farmland where the farmers apply organic manure (vegetables remains, livestock manure and even human waste) in addition to inorganic fertilizers have relatively high BAP (0.160 g kg<sup>-1</sup>). Still, only a very small portion of the total phosphorus present in the soil from farmland and orchards is bioavailable to plants. This was surprising considering the large amount of fertilizers and manure applied to these soils. The low values may be due to that the applied labile phosphorus is lost out of the soil through leaching by surface runoff and sub-lateral flow or

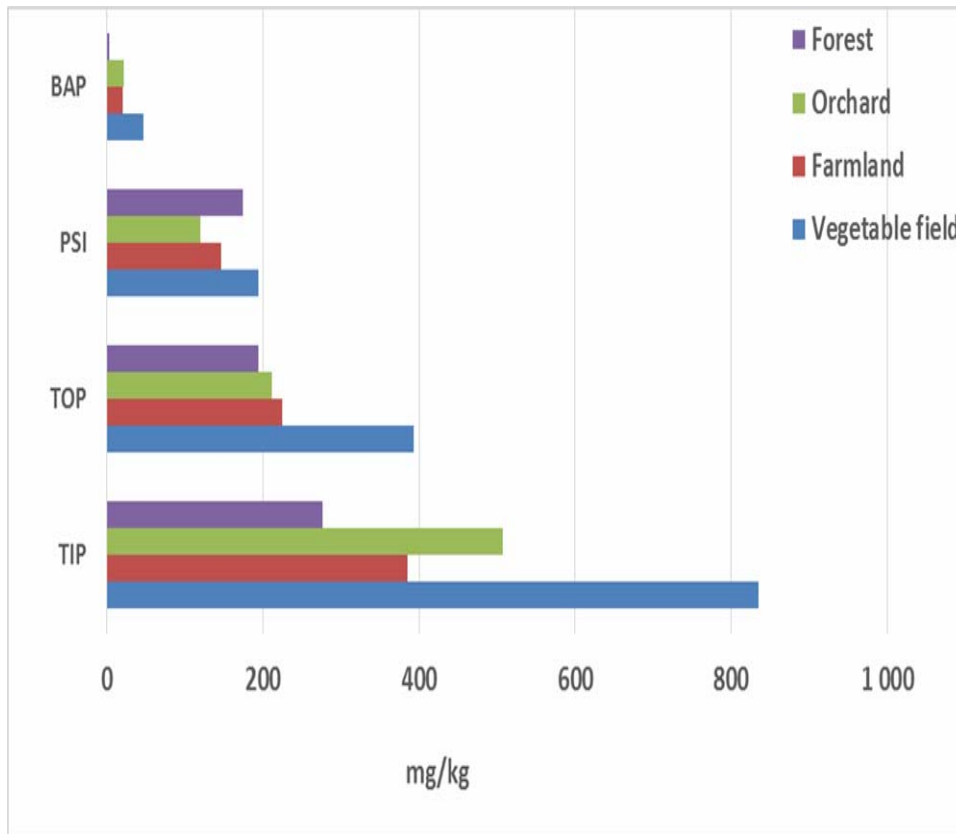
captured by the soil particles. P fixation reactions in soils allow only a small fraction of the applied phosphorus to be readily available to plants depending on the type of soil (Brady and Weil, 2010).



**Fig. 23 Bioavailable phosphorus (BAP) and phosphorus sorption index (PSI) for different land-use**

The capacity of the soil to sorb phosphorous, which is measured as phosphorus sorption index (PSI), shows that 15 to 40% of total phosphorus is adsorbed onto the soil particles. The PSI result show that 40% of TP in the forest area is adsorbed onto the soil particles. The organic matter (6.8%), and clay content of the forest soil attribute the high PSI and low BAP in the study area. However in the case of human influenced cultivated land, like farmland, orchard, and vegetable fields, the phosphorus sorption index ranges from 15 to 25% of TP and 3.3 to 4.5% of TP in the form of bioavailable phosphorus.

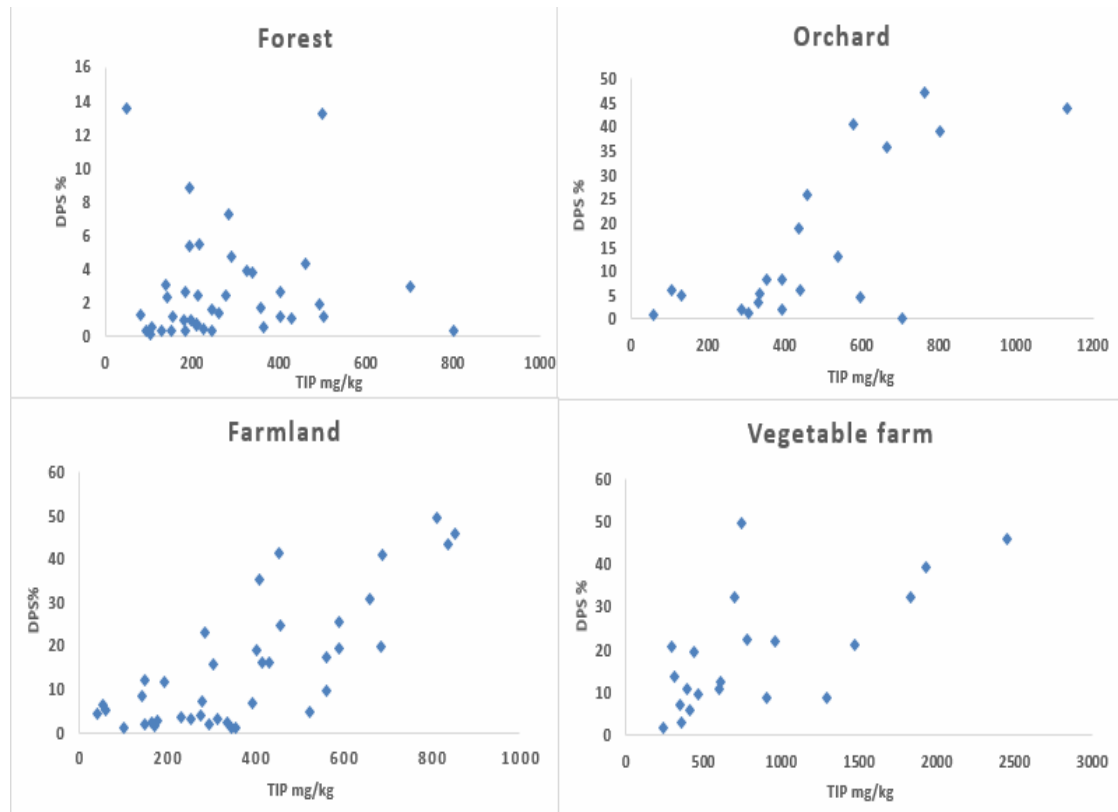




**Fig.24 Comparison of Phosphorus pools in top soil (n=126) for different land-use**

#### **4.5 Degree of Phosphorous saturation (DPS)**

The degree of P saturation (DPS %), which has been calculated using Equation 2 (page 24), reflects the capacity of the soil to adsorb more P. A high number indicates few available sites for newly added nutrients (P) and thus that the soils are more susceptible to loss via runoff. Higher P concentration then build to values that are considered very high or excessive from an agronomic perspective and soils become saturated with P (Schoumans and Groenendijk 2000). The P saturation of the soil depends on the amount of P sorbed to the soil and the soils capacity to bind P as discussed above. Soil with DPS% value of 20-40% are commonly associated with greater risks of P loss (Breeuwsma et al., 1995). Usually there is a good correlation between the DPS% and the pool of TIP.



**Fig.25 Degree of Phosphorus and TIP for different land use**

The % DPS differs mainly between the forest soil and other land-use. Natural forest soil have low DPS% ( $\approx 3\%$ ) and TIP ( $\approx 0.5 \text{ g kg}^{-1}$ ) values (Fig. 25) due to that these forests are not fertilized. This implies that they have lower risk of phosphorus loss to water because the low DPS% will maintain lower P concentration in the soil and the eroded soil particles will be less enriched with potentially desorbable P (Pautler and Sims 2000). Land-use such as farmland, orchard, and vegetable field have high TIP ( $1 - 2.5 \text{ g kg}^{-1}$ ) and DPS (14-23%) as these all receive large P input through fertilizers. The concentration of TIP and the DPS is high in the agricultural land-use soil so that the potential for release of P into solution through desorption and dissolution reactions is high leading to potentially large losses of P to runoff (Pautler and Sims 2000).

#### 4.5 Spatial Distribution of Phosphorus

The inverse distance weighted (IDW) values are interpolated for the following phosphate parameters: total phosphorus (TP), total inorganic phosphorus (TIP), total organic phosphorus (TOP), phosphorus sorption index (PSI), bioavailable phosphorus (BAP or STP), and degree of phosphorus saturation (DPS %). The spatial distribution of the values within the local watershed of the YuQiao reservoir is shown in Figs. 26 and 27. These maps are used to identify watershed areas that are potential hotspots for non-point source of

phosphorus. This is done in order to facilitate knowledge based priorities on abatement actions aimed at reducing P fluxes to the reservoir.

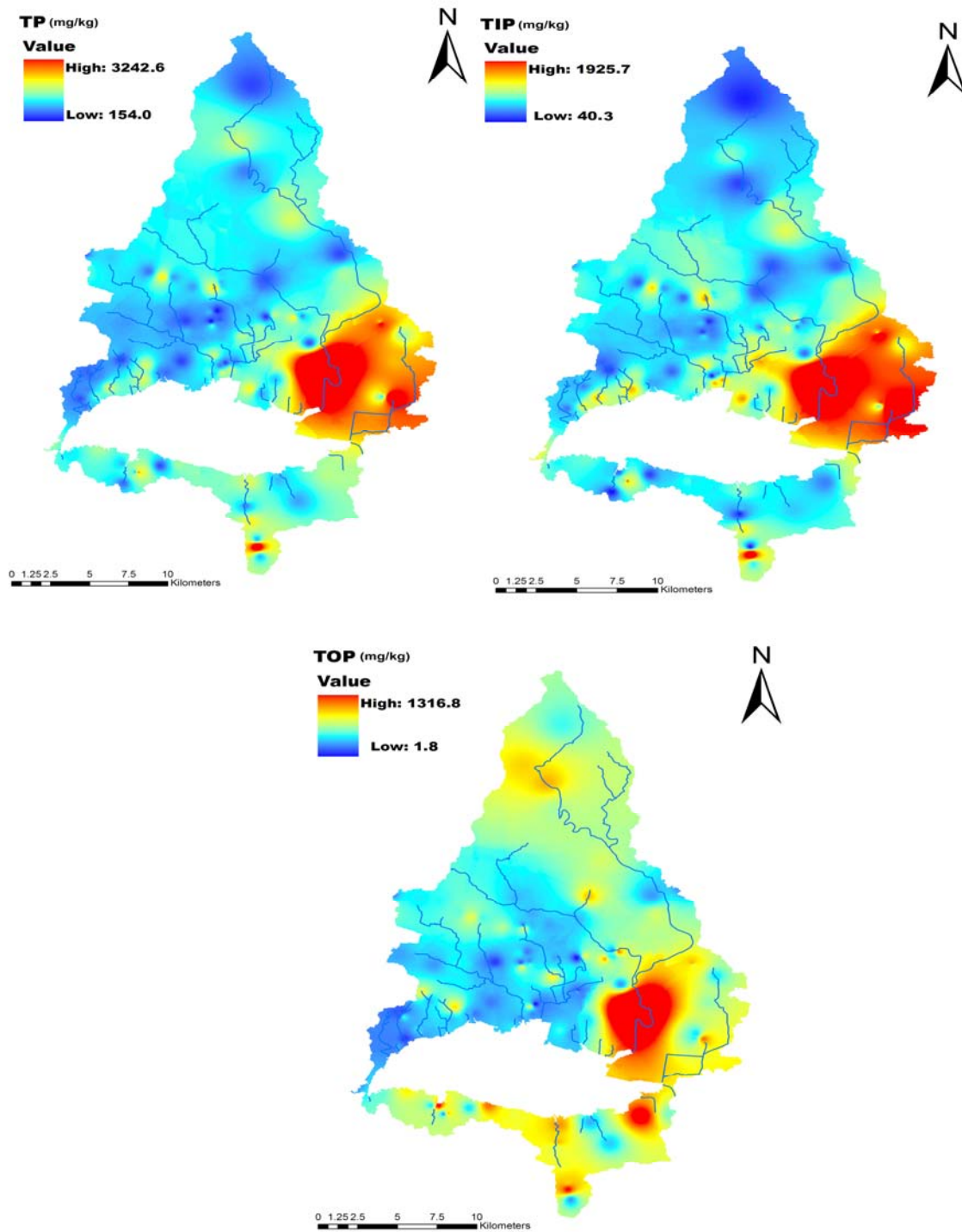
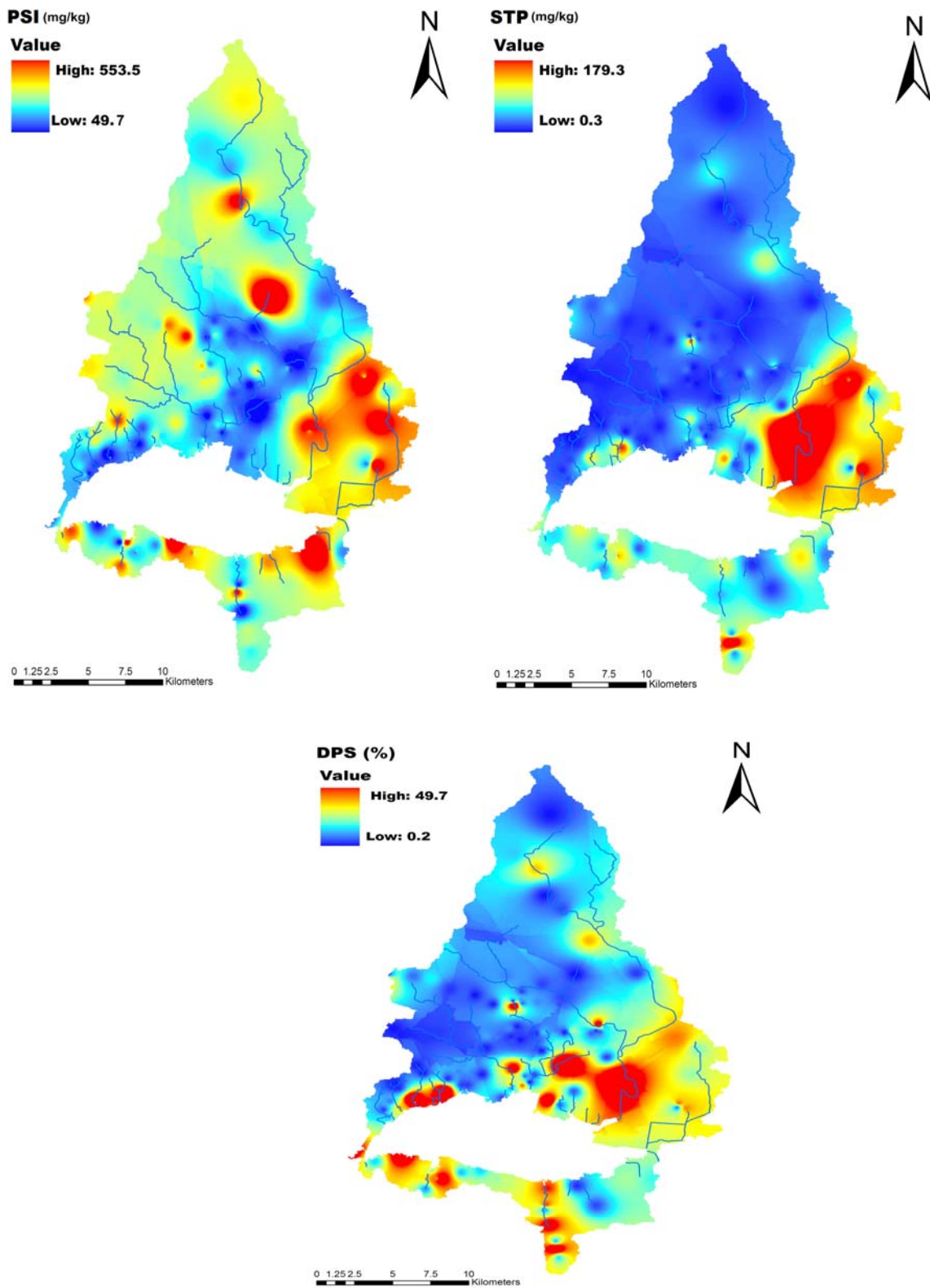


Fig.26 Spatial distribution for total Phosphorus (TP), total inorganic phosphorus (TIP) and total organic phosphorus (TOP)



**Fig.27 Spatial distribution for Phosphorus Sorption Index (PSI), Bioavailable Phosphorus or Soil Test Phosphorus (BAP or STP) and Degree of Phosphorus Saturation (DPS %)**

The spatial distribution of TP and TIP around the Yuqiao reservoir indicates high risk area in the region below where the two tributary rivers Baxianshna and Longmenkou meet and form Lin River and down to the reservoir (Fig. 26). Lin river is the main source of water inflow from local catchment to the reservoir. This area is highly susceptible to phosphorus loss because this area consist of farmland (refer to land use map Fig: 11) located close to the rivers. TIP constitutes by far the main fraction of TP, except for the natural forest located far north of the local catchment. The total organic phosphorus (TOP) shows elevated levels in the northern region since this part consists of natural forest, and large pools along with the large pools of TIP in the Middle Eastern part of the Yuqiao reservoir. A few of the samples from the north-east with relatively large pools of TOP are vegetable fields in which the farmer apply excess manure, remains of vegetable plants and household waste onto the fields.

The spatial distribution of PSI in the local watershed around the Yuqiao reservoir (Fig. 27) shows that the forest soil in the north and the clay soil in the middle-east part along the shore of Lin river (refer to land use map Fig: 11) have greatest capacity to sorb phosphorus. The PSI of the soil along the south shore of the reservoir is generally higher compared to north shore. This is mainly due to a high proportion of fine clays in the soil in the south shore (Ji county agriculture committee and soil service office, 1982). The natural forest soil in the far north and north-west have median PSI, since the natural organic matter content have high phosphorus retention capacity (Leytem and Westermann 2003).

The result for bioavailable phosphorus (Soil Test Phosphorous; STP) is low in the forests and orchards in the north and high in the predominantly farmland region in the middle-east along the lower reaches of the Lin river (refer to land use map Fig. 11). The south shore with high percentage of small farmland with intensive farming practice has moderate distribution of bioavailable phosphorus.

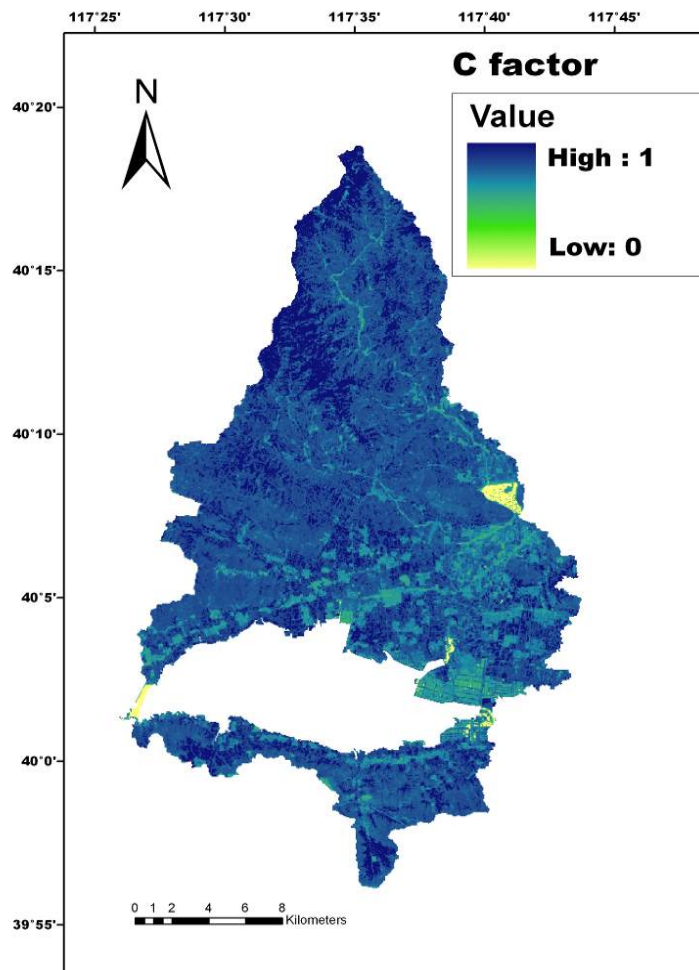
Estimating the degree of P saturation (DPS %) has been proposed as a mean to predict the potential for P losses in runoff and leaching, because high DPS% value will maintain high P concentrations in the soil solution. From the spatial distribution of DPS% (Fig. 27) it is revealed that where there is low DPS, there are moderate PSI and vice-verse. The main critical areas with high TP and DPS% is again the lower reaches of Lin river, in addition to other small local hotspots. The critical region has a large number of agricultural channels and river. This increases the risk of P loss in the form of soluble and particulate form.

## **4.6 Evaluating risk of potential soil P losses**

Phosphorous bound to particles constitute the main fraction of the P flux to the reservoir. There are several mechanisms governing the flux of soil particles in nature. The main process is soil erosion, especially in the plough layer. As outlined in Chapter. 2.4 and 3.5.3 the transport of particles is mainly influenced by six factors: rainfall erosivity factor (R), soil erodibility factor (K), slope length (L) and slope steepness (S) (LS), vegetation cover management practices (C), and support conservation practices (P). The calculation of different USLE factor has been discussed in appendix E. The combined product of these factors (USLE) gives the erosion factor. Combining the USLE parameters in an ArcGIS platform provides the spatial distribution in the potential for soil loss (T) in the local catchment of Yuqiao reservoir. The map obtain is used to identify the critical area for soil erosion potential in the local catchment of Yuqiao reservoir.

### **4.6.1 C factor**

The vegetation cover and management factor (C) play an important role in determining the intensity of water flow during rainfall. The extent of erosion will be significantly decreased with increase in the amount of vegetation due to ability to bind the soil. The data for the C factor are based on NDVI data through the equation given in Appendix E. The major vegetation cover in the local catchment is 43% forest area, 20% for shrub area and 31% farmland. In general the vegetation cover is thin so that the C factors in the local watershed are high (i.e. close to 1) (Fig. 28).

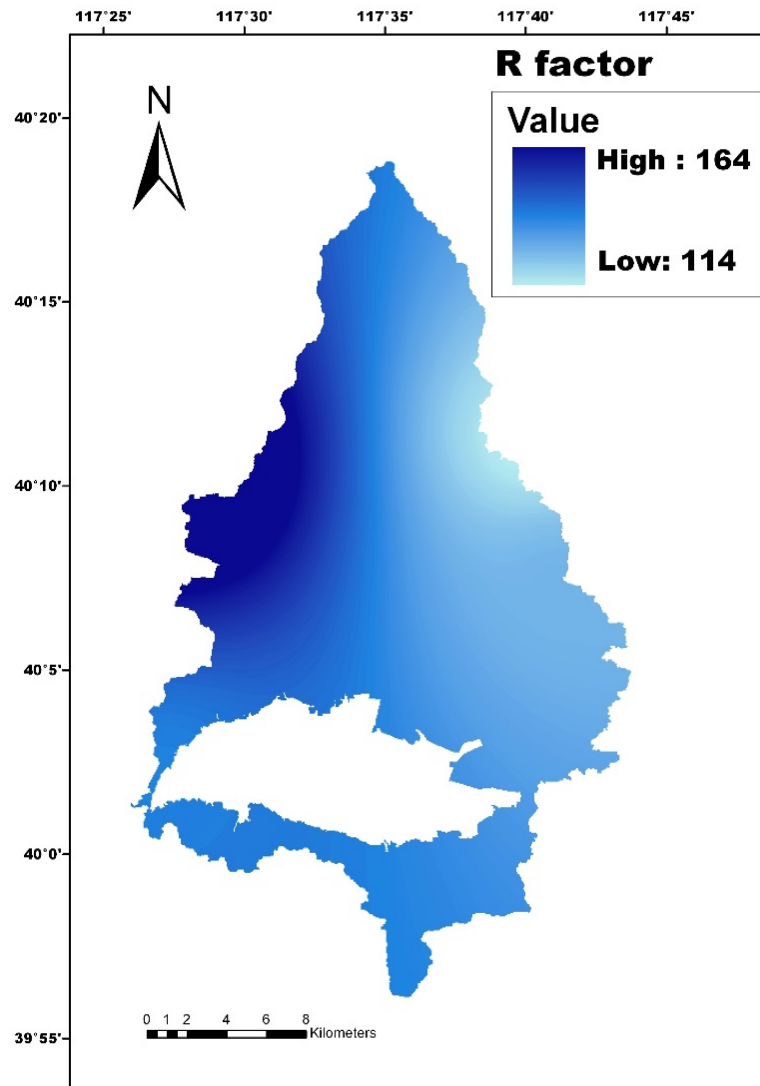


**Fig.28 Spatial distribution of C factor**

#### **4.6.2 R factor**

The erosivity factor (R), providing relative information on the erosive power of the runoff, is based mainly on meteorological rainfall data as described in Chapter. 3.5.3. The R factor does not include the erosive forces of runoff from thaw, snow-melt or irrigation. The middle-west part of local catchment, which consists of high rocky mountains with steep slope, have high annual R index (164) (Fig. 29). During the field work it was observed that dry streams open with high flow only during the rainy session. During the rainfall with high flow these streams carry a significant particle loading.



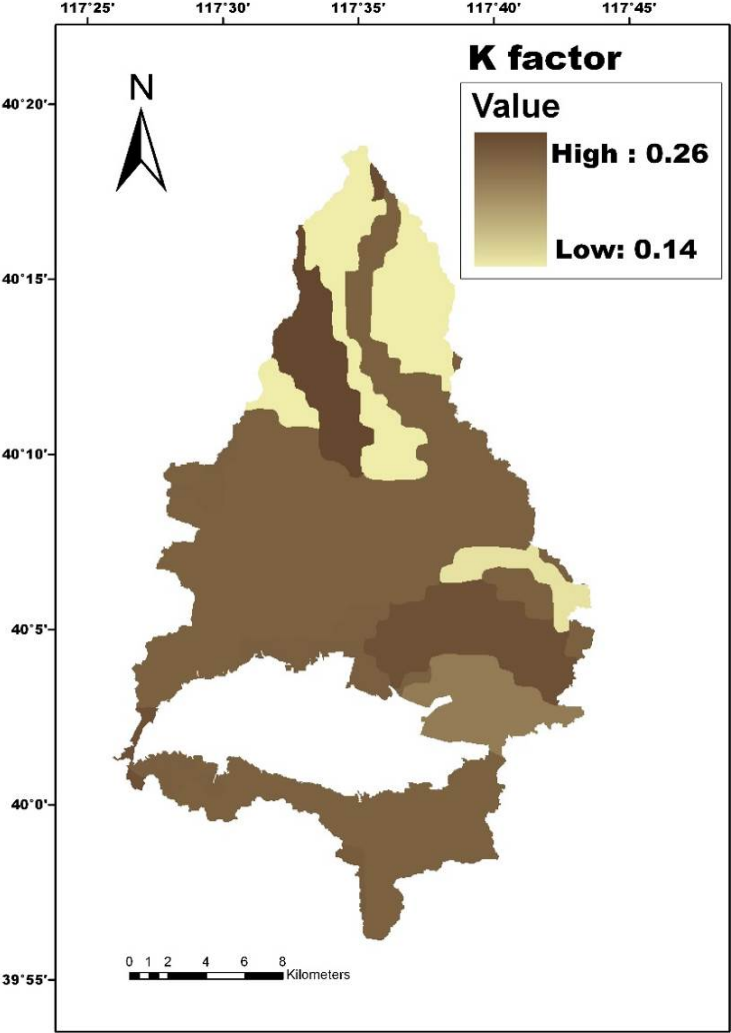


**Fig.29 Spatial distribution of R factor**

#### **4.6.3 K factor**

The soil erodibility factor (K) is mainly based on the soil texture (Ji county soil database, 1982) and organic matter content of the soils. The K is high along the Lin river (Fig. 30) due to clay rich soils. The north part consists mainly of rocky mountain with large coarse soil particle and low organic matter content. The middle north and north-west part of the local catchment with steep sides and high stream flow has high to extremely high soil erodibility factor. However this part is situated long way from the reservoir. The practice of orchard farming in these highlands also play a key role for high soil erodibility factor. The lowland area near the shore of Yuqiao reservoir and along the basin of Lin river has soil that are rich in fine particles which makes them more prone to be eroded during surface flow. Also the

south part, with mountains and low lying farmland, has high risk of soil erodibility compare to farmland in the north-central part of the local catchment.

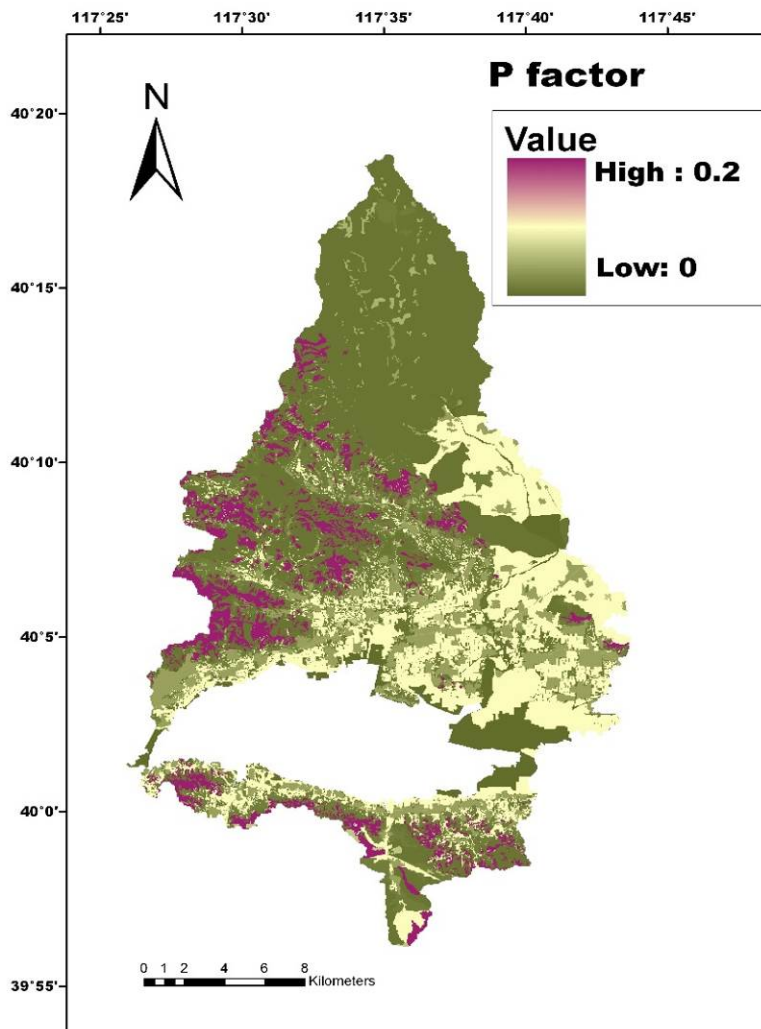


**Fig.30 Spatial distribution of K factor**

**4.6.4 P factor**

The support practice factor (P) (based on remote sensing image) is based on management practises reducing the runoff velocity. The P factor in the central-west and the south part of Yuqiao reservoir is high (0.2) compared to the northern and eastern part (Fig. 31). The south part with high mountains have high P factor which can contribute with high erosion because this part consists of low lying intensive agricultural land and is situated close to the reservoir. The central-east with residential area, farmland and numerous agricultural channels have low practice factor and contribute high soil erosion. However the central-west part of the local

catchment has orchard farming with terracing and step-farming. This slows the runoff water and thus reduces the amount of soil it can carry.



**Fig.31 Spatial distribution of P factor**

#### **4.6.5 LS factor**

Both the length and the steepness of the land slope (LS factor) (based on Digital Elevation Model, DEM) have a substantial effect on the rate of soil erosion by water. A high LS factor (25) is found around the periphery of Baxianshna river in the north-east of the local catchment (Fig. 32). This region has steep slopes which drain into rivers allowing a high rate of soil erosion. The mountainous area with steep slope in the north-west part of the catchment, generate rapid runoff which drain through the low lying plain land give high risk of

P transport along with surface runoff. In the south the steep slopes along the catchment boundary and short distance to the reservoir also contribute to high risk of P transport.

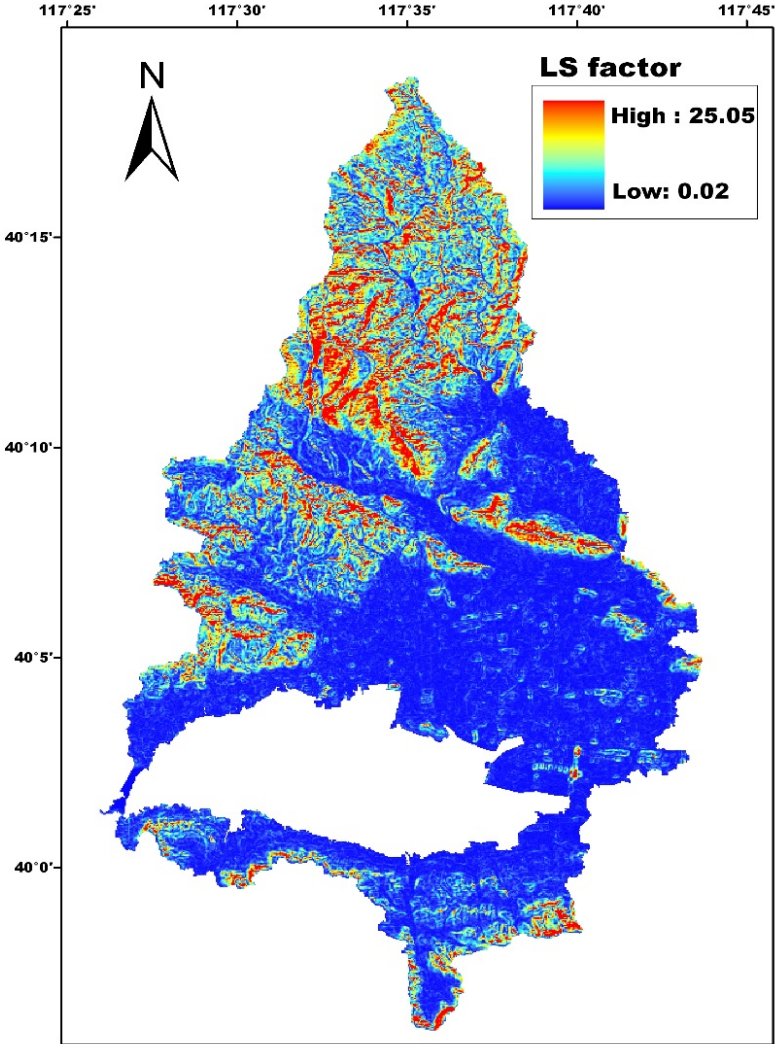


Fig.32 Spatial distribution of LS factor

#### 4.6.6 Soil erosion

The final soil erosion map of the local catchment (Fig. 33) was obtained based on USLE model and the interpolation of its six soil erosion factors. The highest soil loss value (26.0 tons.hm<sup>-2</sup>.year<sup>-1</sup>) was found in the north-west and along the river basin in the west. The area in the basin of Lin river, with high content of clay soil (Ji county agriculture committee and soil service office, 1982), is also susceptible to high soil erosion. For the compact clay in the subsoil the soils have a very low infiltration capacity and the soil particles are transported either as overland flow or laterally above a dense plough layer (Lundekvam and Skoien

1998). The far north part of the local catchment with steep slopes bring eroded soil into the Longmenkou river which finally deposits its load in the Longmenkou reservoir. The particle loading of this river is therefore of little interest with respect to sediment loading in the Yuqiao reservoir. However, dissolved nutrients from the outlet of Longmenkou reservoir can significantly contribute, since this reservoir is the source of water for Lin river in the local catchment. The south part with mountains very near to the reservoir can produce high flow during the rainfall which can easily erode the fine clay soil from the low lying vegetable and farmland. This can contribute high flux of particulate phosphorus. Soil erosion and surface runoff play an important role in the transport of P from local catchment to the YuQiao reservoir due to heavy application of P through fertilizers to the soil in the study area relative to their moderate capacity to bind the P (Fig.24). The P is transported via surface runoff to agricultural channel and ultimately to the reservoir. The flux is especially large from the upper plough layer, since the concentration of P is higher in A-layer compared to the impermeable lower B-layer (Fig.17). The agricultural land around the reservoir, accounting for the largest soil losses, are associated with intensively cultivated lowland catchments with a combinations of vulnerable soils, land-use, cultivation frequency, timing and method and high population density. Together this causes significant erosion and impacts for the P flux to the reservoir.

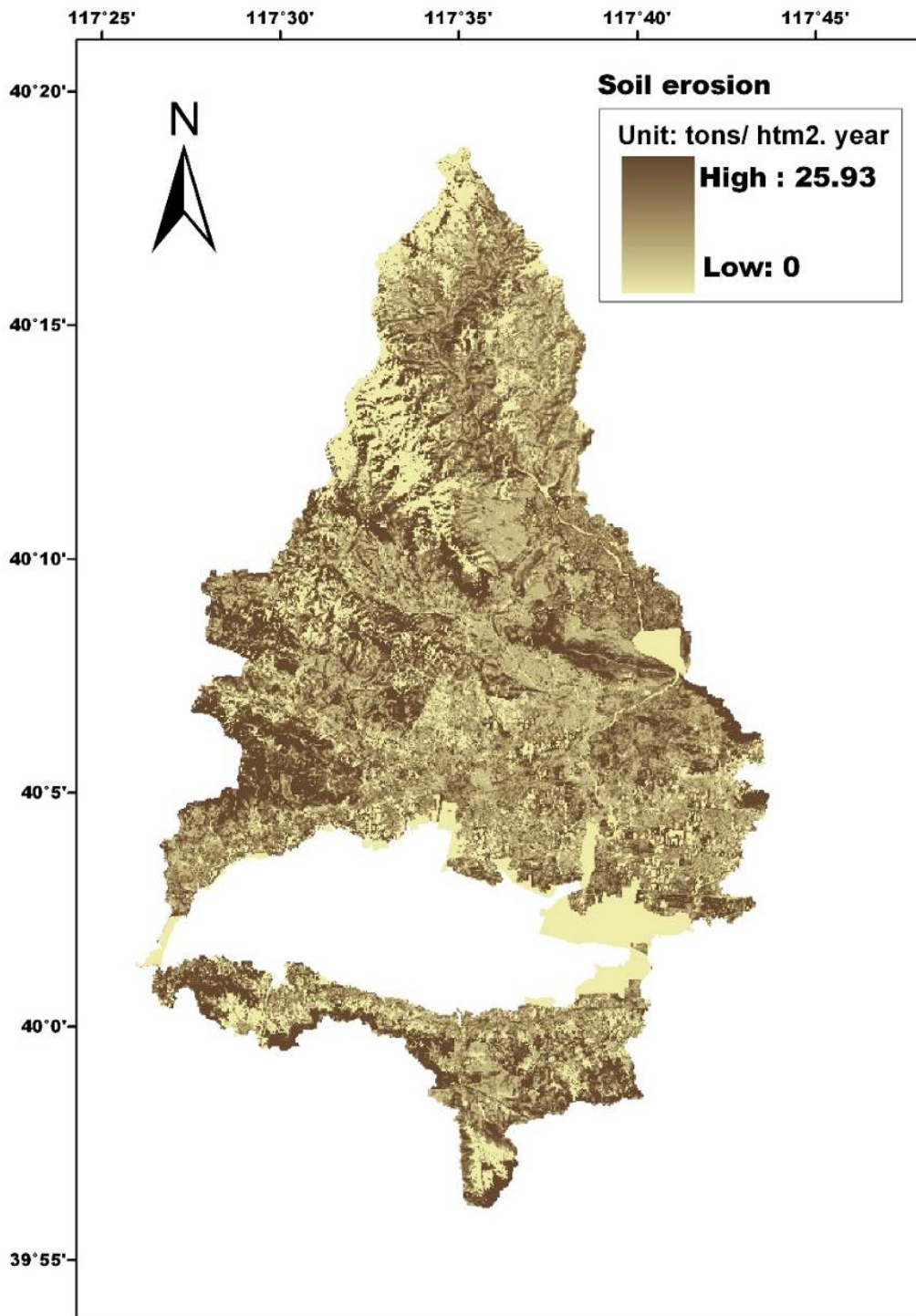


Fig.33 Spatial distribution of soil erosion

#### 4.6.7 Identification of Critical Source Area's (CSA's)

Coupling the source part (chemical analysis) and the transportation part (using USLE) in the local catchment of Yuqiao reservoir, using spatial analysis based on ArcGIS, reveal high risk area with respects to phosphorus loss (Fig. 34).

The human dwellings around the north and south shore of Yuqiao reservoir have been identified as critical areas with respect to phosphorus flux. The south shore, with large nutrients pools in the soil and close proximity to the reservoir, also play an important role for the phosphorus load to the reservoir. This is in contradiction to what was previously hypothesized for south part. This south part has mountains in the catchment boundary which provides high flow of stream during rainfall. This rapid water flow washes out the nutrients from the downstream farmland resulting in a large flux of phosphorus to the reservoir. The central-eastern part of the reservoir, with dense population and high percentage of agricultural land, is the most critical area with respect to phosphorus loss. The sensitivity of this area is also high from the point of view of transport, since the large Lin river provides the media for the transport of phosphorus from low lying area during rainfall.

The north-western part with perennial vegetation cover and moderately high PSI ( $300 \leq \text{PSI} \leq 560$ ) contributes limited phosphorus flux to the reservoir, mainly due to low erosion rate and lower fertilizers P input. However the west part close to reservoir with high phosphorus pools and large number of agricultural channels have high risk of phosphorus loss during the surface runoff.

The far north part of the local watershed is also identified as CSA's, but these area contributes less to the phosphorus flux to the reservoir due to relatively low phosphorus pools and long distance to the reservoir. Furthermore, the particle loading from this region is low due to that the stream releases its load of particle bound P in the Longmenkou reservoir.

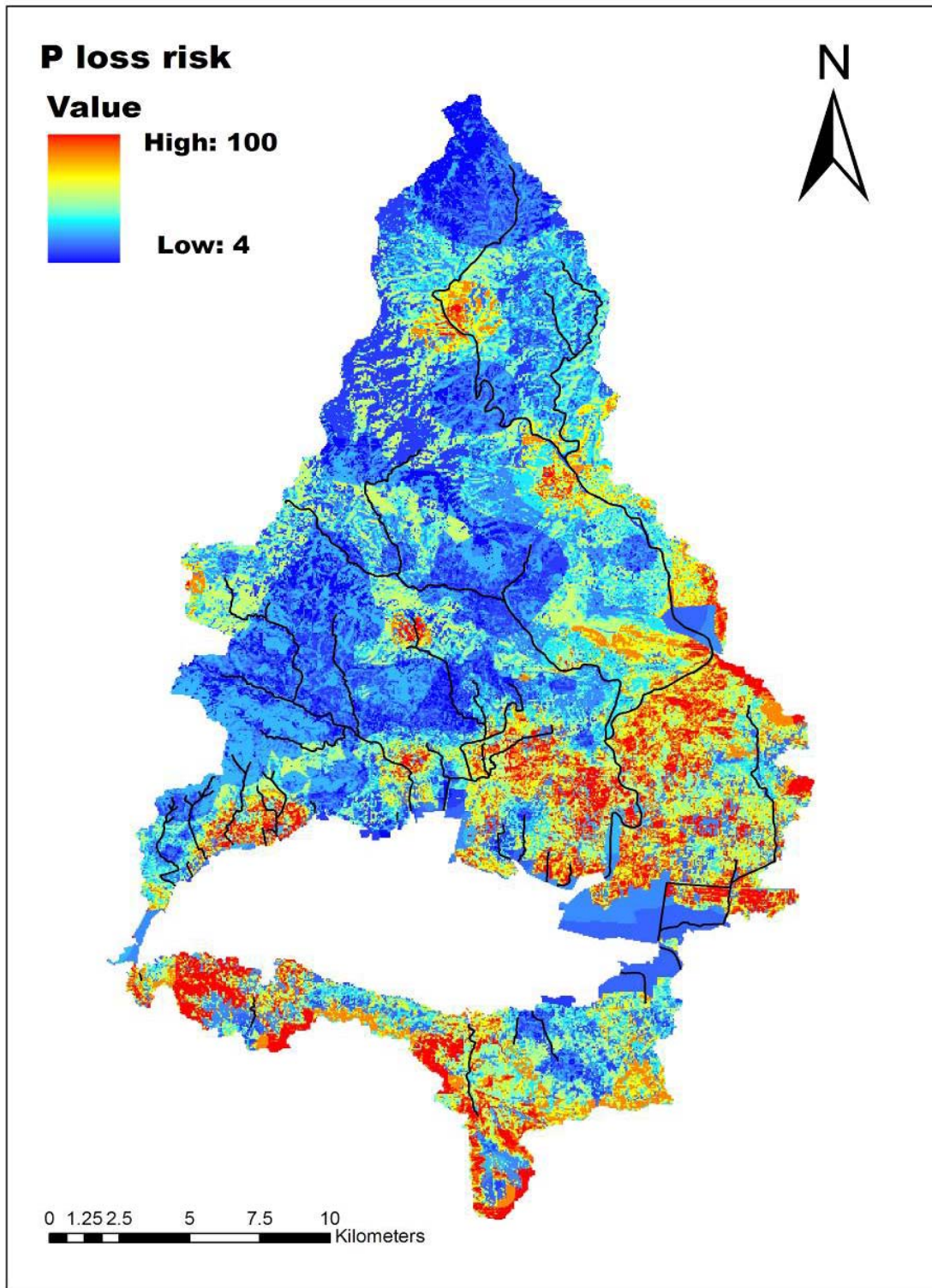


Fig.34 Spatial distribution of source part and transportation factor



## 5. Conclusions and Outlook

This thesis took the local catchment of Yuqiao reservoir as the case study area, and analysed the spatial distribution characteristic of Non-Point Source (NPS) phosphorus loss risk to the Yuqiao reservoir. The assessment of NPS phosphorus transfer from different land-use practices identified the Critical Source Area's (CSA's) with respect to source and transport factor. In order to identify the CSA's of P loss, information about the source and transport factors have been integrated.

(1) Inorganic P is the primary soil P pool in the study zone, even in the natural forest soil.  
(2) Soil P in the vegetable and orchard fields show higher bio-availability due to possessing relatively high BAP. While, the forest soil represent higher phosphorus sorption capacity (PSC) than other land-use types, which implied soil bound to natural background has lower P loss risk due to relatively lower DPS%(lower BAP and higher PSC) as compare to human influenced land-use types. This supports the use of P sorption index, testing methods as a proxy for not only the quantity of P present in a soil but also the capacity to retain additional P.

(3) The area at vicinity of Yuqiao reservoir have relatively high DPS%, in which human influenced land-use are main land-use types (such as farmland and orchard). The zone closing to river and agricultural channel also has higher susceptibility for P flux to the reservoir, mainly due to the close proximity. However the soil samples from far north with relatively higher PSI ( $\leq 200.0$  mg/kg) and low BAP ( $< 0.32$  mg/kg) contribute only a minor flux of dissolved phosphorus. The contribution of particulate phosphorus is also not significant due to perennial vegetation cover, long distance to the reservoir, and sedimentation in the Longmenkou reservoir.

The regions with extremely high and high risk of phosphorus loss comprise 18 % of the local catchment. The rest of the local catchment represent medium to low risk areas. The area with highest risk, which covers only 4% of the local catchment, is located around the shore of Yuqiao reservoir and in the central-east part of the local catchment along the Basin of Lin River. This part is heavily populated and characterized by abundant intensive agriculture practices.

Further research is needed in order to determine which chemical processes are governing the mobility of phosphorous in the soils, including specific binding creating phosphate esters, precipitation and dissolution reactions with Al, Fe, Mg and Ca, and adsorption/desorption by anion exchange. Information of the particle size distribution (PSD) is needed in order to

acquire information regarding the soil texture. This will allow us to get a better understanding of the hydrological flow and thus the transport mechanism.

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## 7. Appendix

### Appendix-A

**Table A-1. Types of water**

The following table describes the types of ion-exchanged water used in the preparation of reagents and standards according to the Millipore purification specifications

Parameter/criteria	Type I water (ultra-pure )	Type II water (pure)
Resistivity MΩ .cm at 25 °C	> 18.0	> 1.0
TOC(ppb)	< 10	< 50
Sodium (ppb)	< 1	< 5
Chloride (ppb)	< 1	< 5
Silica (ppb)	< 3	< 3
Bacteria (CFu/ml)	< 10	< 100

**Appendix-B: Preparation of samples, standards and P determination by MBM (Møberg and Petersen Method) for the determination of tot-phosphorus, tot-inorganic phosphorus and tot-organic phosphorus.**

<b>Table B-1. Reagents used in the molybdate blue method and their preparation</b>	
<b>Reagent(s)</b>	<b>Preparation</b>
Ascorbic acid (reducing agent)	5 g of L-ascorbic acid dissolved in 100 mL of water
Sulphuric acid	120 mL of concentrated H <sub>2</sub> SO <sub>4</sub> (95-97 %) was added to 170 mL water in 500mL flask with stirring

Potassium antimony tartrate (catalyst)	0.35 g K (SbO) C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · ½H <sub>2</sub> O was dissolved in 100 mL water and filled to the mark
Ammonium molybdate	13.00 g ammoniumheptamolybdate tetra hydrate (NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> · 4H <sub>2</sub> O into 100 mL flask, dissolved in water and filled to the mark
Molybdate reagent	The ammonium molybdate solution was added to the sulfuric acid solution, on stirring the tartrate reagent and finally water to the mark

## B-2 Phosphate determination by MBM

The determination of phosphorus fraction in the soil following Møberg and Petersen Method was carried out to estimate total phosphorus, inorganic phosphorus and organic phosphorus. For the determination of total-phosphorus 1gm ignited sample was taken oak ridge tube and digested at 70°C for 10 min using 5ml of 6M H<sub>2</sub>SO<sub>4</sub>. The digested sample on cooling was mixed with 5ml 6M H<sub>2</sub>SO<sub>4</sub> and whole mass was transferred in 250ml volumetric flask and diluted with DI water. The diluted sample was filtered in 50ml tube using Whatman 42 filter paper. The 5 ml final filter solution was taken in 25ml volumetric flask for the color development in MBM. The process for sample preparation for the determination of inorganic-phosphorus was same as total-phosphorus determination except 1 gm. oven dried sample was taken instead of ignited sample. The P content in the extracts and known solutions was then quantified spectrophotometrically at 880 nm wavelength after development of blue color. Samples were prepared in duplicate and the reagents were added in the same manner as for the standards. A linear calibration curve, absorption versus concentration of the standard solutions, was obtained (Figure A-3). Unknown concentrations were then calculated from the curve. The tot-organic phosphorus was calculated using the equation 6.

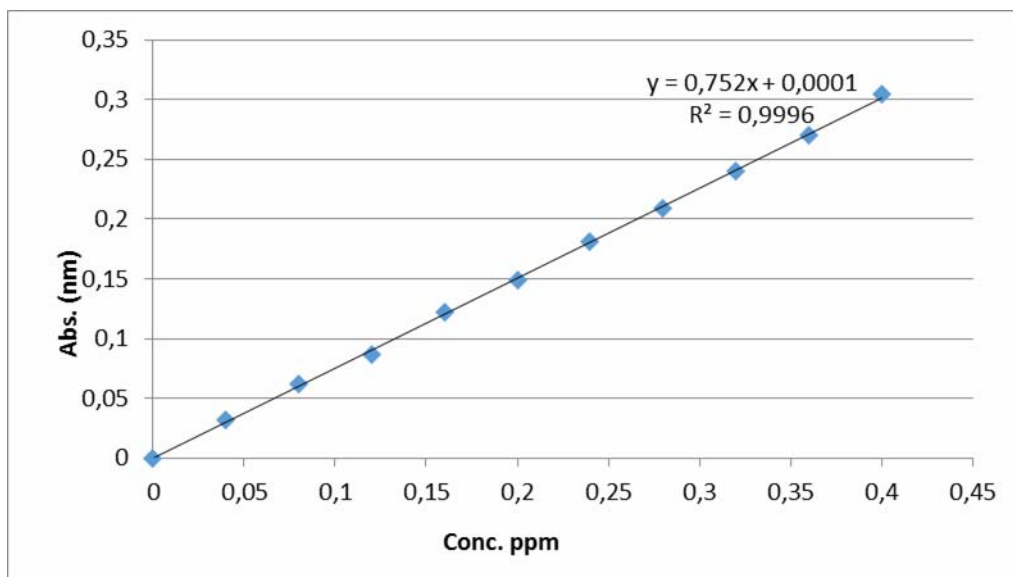
## B-3. Preparation of phosphate calibration standards for MBM

In the analyses of phosphorus fractions using molybdenum blue method, there was a need for the preparation of a standard calibration curve which establishes a relationship between absorbance and the concentration of the desired P. For this purpose, a series of 11 different P concentration standard solutions were prepared according to Norwegian standard NS4724. The following dilution equation was used during the preparation of reagents and for all diluting solutions when the concentration level of samples felt beyond the working range of the calibration curve and the instrument.

$$C_1 V_1 = C_2 V_2$$

Equation 8

Where C is concentration and V is volume, 1 and 2 signify for initial and final respectively.



**Figure B-3. Calibration standard curve for phosphorus**

The concentration is calculated from the equation of the calibration line by;

$$X = (Y - 0,0001) / 0,752;$$

Equation 9

Where x is the concentration and y is absorbance.

### **C Procedure for Phosphorus Sorption Index (PSI).**

### Phosphorus Sorption Solution (75ppm)

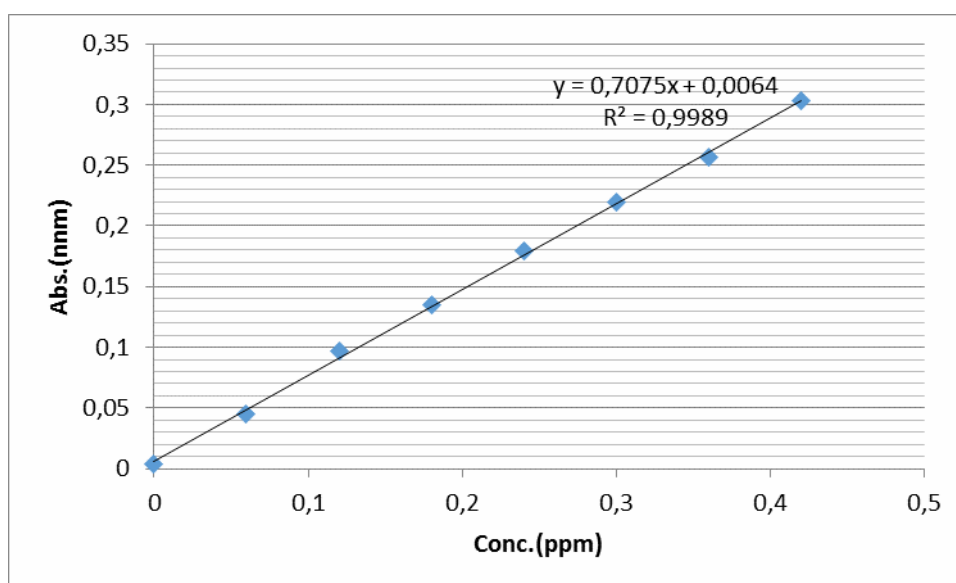
0.659 gm. of oven dried monobasic  $\text{KH}_2\text{PO}_4$  was placed in 2liter volumetric flask and diluted with DI water and kept in the freeze.

For the determination of phosphorus sorption index (PSI), 1 g of OD sample was placed in 80ml oak ridge tube and dissolves in 20 ml of 75 ppm phosphorus sorption solution (Note: This provides a ratio of 1.5 g P/kg soil), two drops of chloroform was added to inhibit the microbial activity and shake in end to end shaker for 18 h at  $25\pm 2^\circ\text{C}$ . Centrifuge the samples at 2000 rpm using Jouan B4i (Thermo Fisher scientific Inc.) for 30 minutes. The sample obtain after centrifuge was filtered through  $0.45\mu\text{m}$  filters using vacuum pump. The filtered sample was further diluted taking 1 ml to 100 ml volumetric flask with type-2 water and unabsorbed phosphorus was measured by MBM as described in section----

To minimize the error from the water extractable phosphorus from the soil one blank sample of soil with 20ml of type-2 water was taken in the same way and the amount of phosphorus extracted from the soil in the solution was measured. This value was subtracted from each sample.

#### **C-1 Preparation of phosphate calibration standards curve for PSI**

For the preparation of standard calibration curve 1.5 ppm phosphorus solution was prepared from the stock phosphorus solution of 75ppm. 8 solutions with different concentration ranging from 0.0 ppm to 0.420ppm were prepared and the absorbance was measured using MBM.



**Figure B-1. Calibration standard curve for phosphorus (PSI)**

The concentration is calculated from the equation of the calibration line by;

$$X=(Y-0.0064)/0.7075; \quad \text{Equation 10}$$

Where x is the concentration and y is absorbance.

#### **D- Procedure for Bioavailable phosphorus (BAP) or Soil Test phosphorus (STP)**

For the determination of soil test phosphorus or bioavailable two methods were employed based on the pH of the soil. For the acidic soil with pH less than 6.8 Bray and Kurtz P-1 and for alkaline soil with pH higher than 6.8 Olsen P was used to determine bioavailable phosphorus.

##### **D-1 Bray and Kurtz P-1**

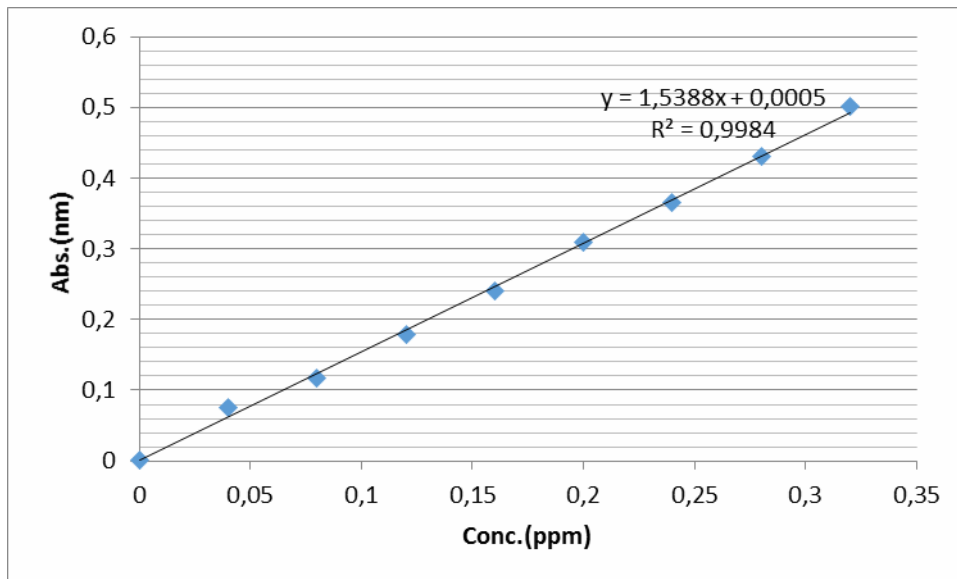
Preparation of Bray and Kurtz P-1 extracting solution (0.025 M HCL in 0.03M NH<sub>4</sub>F): 2.222 g of reagent grade ammonium fluoride (NH<sub>4</sub>F) was taken in 2 L flask and dissolved in 1500 ml DI water. To the resulting solution 50 ml of previously standardized 0.025 M HCl was added and the pH was adjusted to 2.6 ± 0.05 with HCl or ammonium hydroxide. The final solution was transfer to 2l volumetric flask and the volume was made with DI water and solution was store in refrigerator.

To determine bioavailable phosphorus for acid soil 2 gm. of oven dried soil samples were weighted in 50 ml Erlenmeyer flask and dissolve in 20ml of Bray and Kurtz P-1 extracting solution, the flask was fitted with rubber cork and shake in rotator shaker for 5 min at 200 rpm. The extract was filter through Whatman No. 42 filter paper to obtain the colorless filtrate. 2ml of final filtrate was taken for color development in 25 ml volumetric flask and the bioavailable phosphorus was determined from MBM

##### **D-1.1 Preparation of phosphate calibration standards curve for BAP (Bray and Kurtz P-1)**

0.2208 gm. of oven dried monobasic KH<sub>2</sub>PO<sub>4</sub> was placed in 500ml volumetric flask and dissolved in DI water to obtained the 500ml stock solution. From the stock solution 2ml was diluted to obtain 100ml, from this solution different 9 calibration solutions ranging from 0.0 ppm to 0.32 ppm was prepared and the absorbance was measure from MBM. 4 ml of

extracting solution was added to final color development solution to match the matrix as in sample solution.



**Figure C-2.1. Calibration standard curve for phosphorus (BAP)**

The concentration is calculated from the equation of the calibration line by;

$$X = (Y - 0.0005) / 1.5388; \quad \text{Equation}$$

11

Where x is the concentration and y is absorbance.

### **D-2 Olsen P**

Preparation of Olsen-P extracting solution (0.5 M NaHCO<sub>3</sub>, pH 8.5): 84.0 gm. of commercial grade sodium bicarbonate (NaHCO<sub>3</sub>) was dissolved in DI water to obtain 2L. The pH was maintained to 8.5 with 50% NaOH.

2 g. of air-dried sample was weighted in 50 ml Erlenmeyer flask and dissolved in 20ml Olsen-P extracting solution, the flask was fitted with rubber cork and shake in rotator shaker for 30 min at 200 epm. The extract was than filtered using Whatman No. 42 filter paper to obtain the colorless filtrate. The 2 ml of filtrate solution was diluted to 25 volumetric flasks to determine the phosphorus in the extract by MBM.

### D-2.1 Preparation of phosphate calibration standards curve for BAP (Olsen-P)

0.2208 gm. of oven dried monobasic  $\text{KH}_2\text{PO}_4$  was placed in 500ml volumetric flask and dissolved in DI water to obtained the 500ml stock solution. From the stock solution 2ml was diluted to obtain 100ml, from this solution different 9 calibration solutions ranging from 0.0 ppm to 0.32 ppm was prepared and the absorbance was measure from MBM. 4 ml of extracting solution ( $\text{NaHCO}_3$ ) was added to final color development solution to match the matrix as in sample solution.

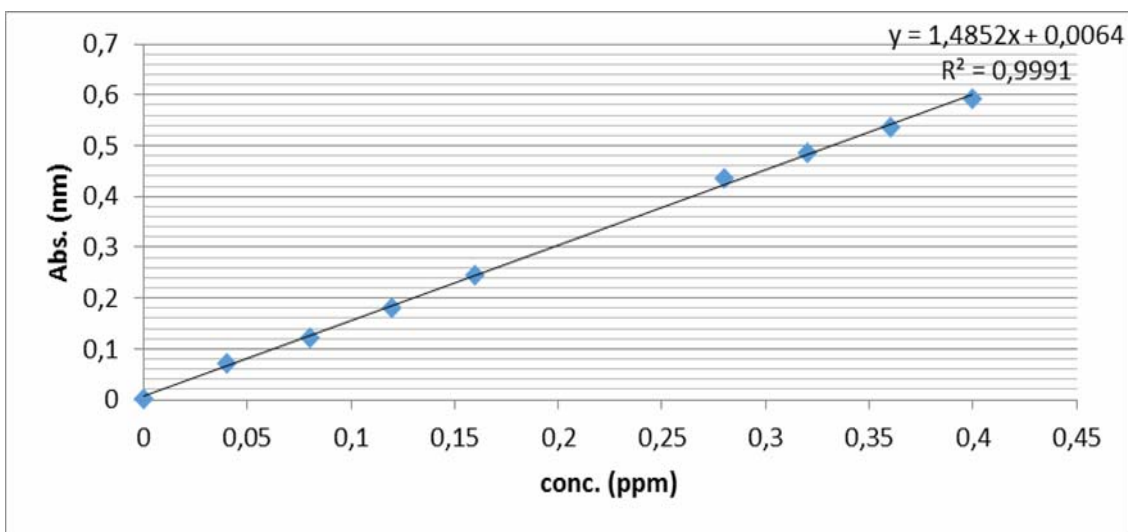


Figure C-3.1 Calibration standard curve for phosphorus (Olsen-P)

The concentration is calculated from the equation of the calibration line by;

$$X = (Y - 0.0064) / 1.4852;$$

Where x is the concentration and y is absorbance.

### E- Calculation of different USLE factors

#### R factor

Based on monthly data the value for 12 months of each year were summed:

$$E_j = \alpha \left[ 1 + \eta \cos(2\pi f_j + \omega) \right] \sum_{d=1}^N R_d^\beta \quad R_d > R_0$$

Equation 12

Where,

$E_j$  = the monthly rainfall erosivity (MJ mm ha<sup>-1</sup> h<sup>-1</sup> year<sup>-1</sup>)

$R_0$  = the daily rainfall threshold causing erosion (in general,  $R_0$  is 12.7 mm)

$N$  = the number of days on which the precipitation corresponds to a monthly rainfall  $\geq 12.7$  mm

$f = 1/12$  (the frequency)

$\omega = 5\pi/6$

$\alpha$ ,  $\beta$ , and  $\eta$  are the model parameters

The  $\beta$  value ranges from 1.2 to 1.8 and  $b$  is taken as 1.5

(Note: Relevant daily weather data from Ji County weather station).

### **LS factor**

$$LS = \left( \frac{\lambda}{22.1} \right)^m \times (65.41 \times \sin^2 \theta + 4.56 \times \sin \theta + 0.065)$$

Equation 13

$$\begin{cases} m = 0.2 & \text{slope} < 1\% \\ m = 0.3 & 1\% \leq \text{slope} \leq 3\% \\ m = 0.4 & 3\% < \text{slope} < 5\% \\ m = 0.5 & \text{slope} \geq 5\% \end{cases}$$

### **K factor**

$$K = \left\{ 0.2 + 0.3 \exp \left[ -0.0256 SAN \left( 1 - \frac{SIL}{100} \right) \right] \right\} \times \left[ \frac{SIL}{CLA + SIL} \right]^{0.3} \\ \times \left\{ 1 - \frac{0.25C}{C + \exp(3.72 - 2.95C)} \right\} \times \left[ 1 - \frac{0.7S_n}{S_n + \exp(-5.51 + 22.9S_n)} \right]$$

Equation 14

Where,

SAN= Sand (%), CLA= Clay (%)

SIL= Silty (%), C= Organic matter (%) and  $S_n = 1 - \frac{SAN}{100}$



### C Factor

The Normalised Difference Vegetation Index (NDVI) grids and maps are derived from satellite data. The data provides an overview of the status and dynamics of vegetation across the study area, providing a measure the amount of live green vegetation. The satellite data comes from the Advanced Very High Resolution Radiometer (AVHRR) instruments on board the National Oceanic and Atmospheric Administration (NOAA) series of satellites that are operated by the US (<http://noaasis.noaa.gov/NOAASIS/ml/avhrr.html>).

Live green vegetation absorbs visible light (solar radiation) as part of photosynthesis. At the same time plants scatter (reflect) solar energy in the near infrared. This difference in absorption is quite unique to live vegetation and provides a measure of the greenness of the vegetation. NDVI is an index which measures this difference, providing a measure of vegetation density and condition. It is influenced by the fractional cover of the ground by vegetation, the vegetation density and the vegetation greenness. It indicates the photosynthetic capacity of the land surface cover.

NDVI is calculated from the red and near-infrared reflectance's  $r_{Red}$  and  $r_{NIR}$  as

$$NDVI = (r_{NIR} - r_{Red}) / (r_{NIR} + r_{Red})$$

Its value is always between -1 and +1, substituting the value obtained for NDVI in the following equation 15.

$$I_c = 108.49NDVI + 0.717$$

Equation 15

$$C = 1 \quad I_c = 0$$

$$C = 0.6805 - 0.343 \log I_c \quad 0 < I_c < 78.3$$

$$C = 0 \quad I_c > 78.3$$

### **F- Inverse Distance weighted (IDW) Interpolation**

The value for the parameter in question at any point (x, y) is calculated using Equation 16

$$f(x, y) = \sum_{i=1}^n w_i f_i$$

Equation

16

where  $n$  is the number of data points in the set,  $f_i$  are the prescribed function values at the scatter points (e.g. the data set values), and  $w_i$  are the weight functions assigned to each scatter point. The classical form of this weight function is given in Equation 17:

$$w_i = \frac{h_i^{-p}}{\sum_{j=1}^n h_j^{-p}}$$

Equation

17

Where  $p$  is an arbitrary positive real number called the power parameter (typically,  $p=2$ ) and  $h_i$  is the distance from the scatter point to the interpolation point as:

$$h_i = \sqrt{(x - x_i)^2 + (y - y_i)^2}$$

Equation 18

Where  $(x, y)$  are the coordinates of the interpolation point and  $(x_i, y_i)$  are the coordinates of each scatter point. The weight function varies from a value of unity at the scatter point to a value approaching zero as the distance from the scatter point increases. The weight functions are normalized so that the weights sum to unity. The effect of the weight function is that the surface interpolates each scatter point and is influenced most strongly between scatter points by the points closest to the point being interpolated.

Although the weight function shown in Equation 17 is the classical form of the weight function in inverse distance weighted interpolation, the Equation 19 is used in SMS.

$$w_i = \frac{\left[ \frac{R - h_i}{Rh_i} \right]^2}{\sum_{j=1}^n \left[ \frac{R - h_j}{Rh_j} \right]^2}$$

Equation 19

Where  $h_i$  is the distance from the interpolation point to scatter point  $i$ ,  $R$  is the distance from the interpolation point to the most distant scatter point, and  $n$  is the total number of scatter points. This equation (Eqn. 19) has been found to give superior results to the classical equation (Eqn. 17) (Franke & Nielson, 1980).

## E- Chemical Analysis Data

### a. Farmland

Serial No. (check)	TP	TIP	TOP	pH water	LOI %	STP (Olsen) (ppm)	STP(+Bray)(ppm)	PSI	DPS (oslen) (%)	DPS (Bray) (%)
SS002	234,20	232,10	2,10	7,54	2,83	5,37	5,37	152,08	3,53	3,41
SS007	264,40	172,90	91,50	7,68	3,20	2,41	2,41	147,52	1,63	1,61
SS010	480,90	294,60	186,30	8,09	5,09	4,05	4,05	193,47	2,09	2,05
SS016	999,60	836,80	162,80	8,04	4,59	40,59	40,59	53,06	76,49	43,34
SS017	701,00	688,40	12,60	7,21	3,85	38,85	38,85	55,75	69,69	41,07
SS018	618,60	524,60	94,00	7,63	3,78	7,61	7,61	157,68	4,83	4,60
SS026	547,60	415,10	132,50	8,18	2,53	13,15	13,15	68,28	19,26	16,15
SS028	709,10	683,20	25,90	7,73	3,87	21,08	21,08	85,32	24,71	19,81
SS029	437,00	313,20	123,80	7,94	3,48	4,38	4,38	135,38	3,23	3,13
SS031	743,60	590,20	153,40	7,65	3,44	36,69	36,69	106,58	34,43	25,61
SS032	368,70	252,90	115,80	8,52	2,23	3,71	3,71	117,84	3,15	3,05
SS034	370,90	275,10	95,80	9,14	2,85	4,62	4,62	112,99	4,09	3,93
SS045	480,90	356,00	124,90	8,08	6,05	1,28	1,28	148,22	0,87	0,86
SS050	1270,20	812,30	457,90	8,11	9,54	79,77	79,77	81,16	98,29	49,57
SS053	660,90	336,60	324,30	7,73	9,37	5,28	5,28	207,56	2,54	2,48
SS057	153,30	102,70	50,60	6,92	4,84	1,28	2,10	165,16	0,77	1,26
SS058	277,40	177,10	100,30	6,58	5,72	3,04	5,00	168,22	1,81	2,89
SS061	1191,20	852,80	338,40	5,75	6,51	70,71	64,51	76,87	91,99	45,63
SS072	743,40	560,40	183,00	7,53	6,27	7,85	7,85	72,59	10,82	9,76
SS073	513,68	393,80	119,88	7,80	9,52	9,45	9,45	127,99	7,38	6,87
SS085	891,05	590,33	300,72	6,05	6,12	38,40	39,55	162,51	23,63	19,57

SS087	800,51	453,45	347,06	5,71	3,71	34,60	36,85	52,38	66,05	41,30
SS088	447,66	431,96	15,70	6,2	2,33	8,90	10,76	55,50	16,04	16,24
SS089	272,57	165,15	107,42	6,21	2,6	3,50	4,66	187,28	1,87	2,43
SS090	319,10	229,63	89,47	8,16	3,83	12,13	12,13	264,61	4,58	4,38
SS091	723,21	404,14	319,07	8,34	3,20	42,40	42,40	307,43	13,79	12,12
SS092	755,16	454,55	300,61	8,00	5,66	28,55	28,55	379,66	7,52	7,00
SS093	358,99	241,30	117,69	7,44	2,04	16,23	16,23	292,73	5,55	5,25
SS094	570,72	298,44	272,28	7,88	4,23	28,28	28,28	308,22	9,18	8,41
SS095	441,81	203,56	238,25	8,03	3,56	12,70	12,70	182,88	6,95	6,50
SS097	800,12	368,70	431,42	8,13	4,26	48,96	48,96	367,06	13,34	11,77
SS133	773,20	408,57	364,63	7,88	3,85	43,79	43,79	79,93	54,79	35,40
SS134	465,04	304,80	160,24	7,63	3,36	12,57	12,57	67,80	18,54	15,64
SS135	494,05	402,24	91,81	8,45	2,93	28,89	28,89	123,95	23,31	18,90
SS142	899,24	457,65	441,59	7,45	3,75	41,95	41,95	129,31	32,44	24,50
SS143	700,21	286,01	414,20	7,72	3,41	22,86	22,86	75,52	30,27	23,23
SS144	999,79	660,20	339,59	7,49	3,71	27,28	27,28	61,13	44,63	30,86
SS147	473,58	346,13	127,46	8,04	3,48	2,82	2,82	244,59	1,15	1,14
SS150	787,47	561,54	225,92	7,17	3,40	10,70	23,40	110,68	9,67	17,45

**b. Forest**

Serial No. ( check)	TP	TIP	TOP	pH water	LOI %	STP (Olsen) (ppm)	STP(+Bray)(ppm)	PSI	DPS (oslen) (%)	DPS (Bray) (%)
SS004	311,40	139,70	171,70	5,93	3,52	1,23	2,36	74,65	1,65	3,06
SS006	888,10	799,70	88,40	7,44	3,68	0,29	0,29	77,68	0,38	0,38
SS012	370,70	243,90	126,80	7,70	3,66	2,94	2,94	179,07	1,64	1,61
SS019	507,30	337,90	169,40	6,66	4,37	3,25	6,20	155,61	2,09	3,83
SS023	653,50	193,50	460,00	6,80	10,34	3,84	5,90	60,82	6,32	8,84
SS027	289,20	213,20	76,00	8,53	3,51	3,55	3,55	143,51	2,47	2,41
SS030	484,60	326,80	157,80	6,37	6,46	3,92	5,67	139,18	2,82	3,91
SS033	434,50	277,20	157,30	8,52	2,05	2,42	2,42	96,17	2,52	2,46
SS035	383,90	181,20	202,70	7,95	6,48	2,00	2,00	210,61	0,95	0,94
SS036	291,30	244,80	46,50	7,69	8,33	0,48	0,48	157,27	0,31	0,31
SS039	232,50	94,60	137,90	8,05	5,40	0,86	0,86	274,02	0,31	0,31
SS040	497,00	152,00	345,00	7,72	7,06	0,80	0,80	205,11	0,39	0,39
SS041	878,90	501,90	377,00	7,38	10,73	1,14	1,14	94,80	1,20	1,18
SS042	354,90	262,70	92,20	8,33	2,90	2,32	2,32	159,45	1,45	1,43
SS044	249,80	217,60	32,20	7,95	8,49	10,11	10,11	176,18	5,74	5,43
SS046	418,30	156,00	262,30	5,30	8,29	2,12	3,49	289,40	0,73	1,19
SS047	418,60	224,80	193,80	7,90	8,03	1,18	1,18	254,01	0,46	0,46
SS048	1025,00	701,60	323,40	8,22	8,35	4,60	4,60	152,87	3,01	2,92
SS049	351,50	143,70	207,80	5,84	11,85	2,26	3,88	161,48	1,40	2,35
SS051	253,90	182,70	71,20	7,74	6,17	0,87	0,87	253,55	0,34	0,34
SS052	480,70	363,80	116,90	8,32	7,95	1,10	1,10	214,79	0,51	0,51
SS054	198,90	104,80	94,10	7,46	8,23	0,42	0,42	300,96	0,14	0,14
SS055	391,60	209,20	182,40	6,25	6,05	0,87	1,71	213,66	0,41	0,79
SS056	400,70	197,90	202,80	6,45	8,28	0,79	2,06	205,71	0,38	0,99
SS059	475,20	291,80	183,40	7,43	8,18	11,21	11,21	223,71	5,01	4,77
SS060	167,50	81,00	86,50	6,17	4,88	0,80	1,46	111,38	0,72	1,29
SS066	371,90	195,20	176,70	6,90	7,54	2,20	4,80	84,62	2,60	5,37

SS067	577,90	401,40	176,50	5,93	7,37	1,09	1,65	135,95	0,80	1,20
SS068	210,70	209,00	1,70	5,90	6,08	0,93	1,35	210,33	0,44	0,64
SS069	815,40	498,50	316,90	6,82	10,68	18,36	20,30	133,15	13,79	13,23
SS070	531,40	128,40	403,00	5,91	11,55	1,14	1,85	553,85	0,20	0,33
SS071	781,70	428,00	353,70	6,18	9,08	0,62	1,05	91,93	0,68	1,13
SS074	507,80	357,00	150,80	6,27	5,00	1,40	2,00	116,46	1,20	1,69
SS076	577,80	401,70	176,10	6,16	5,19	2,18	3,25	117,96	1,85	2,68
SS077	599,10	493,70	105,40	7,60	4,91	2,78	2,78	139,06	2,00	1,96
SS078	594,40	462,20	132,20	7,82	7,96	6,52	6,52	144,25	4,52	4,33
SS080	676,29	284,25	392,04	6,24	4,5	9,42	10,34	131,92	7,14	7,27
SS082	361,68	106,12	255,56	6,01	6,71	1,17	1,68	295,37	0,40	0,57
SS083	456,70	183,55	273,15	6,13	5,13	3,00	3,62	134,76	2,23	2,62
SS096	361,32	194,73	166,59	8,85	5,22	18,32	18,32	117,12	15,64	13,52

### c. Orchard Farm

Serial No. (check)	TP	TIP	TOP	pH water	LOI %	STP (Olsen) (ppm)	STP(+Bray)(ppm)	PSI	DPS (oslen) (%)	DPS (Bray) (%)
SS003	833,20	664,10	169,10	7,86	4,41	38,98	38,98	69,67	55,96	35,88
SS005	237,80	132,40	105,40	5,92	2,87	1,99	4,08	76,80	2,59	5,04
SS009	899,70	762,70	137,00	8,14	4,32	68,20	68,20	76,41	89,26	47,16
SS011	414,60	306,40	108,20	7,78	5,30	2,35	2,35	159,60	1,47	1,45
SS014	575,40	392,10	183,30	7,72	3,53	15,02	15,02	165,48	9,08	8,32
SS015	515,10	392,70	122,40	8,34	5,47	1,79	1,79	90,78	1,97	1,93
SS020	1000,00	803,70	196,30	7,76	4,58	57,89	57,89	91,14	63,52	38,85
SS022	678,40	579,10	99,30	6,92	2,99	29,86	33,60	49,23	60,66	40,57
SS024	501,10	331,90	169,20	7,75	4,02	7,05	7,05	197,77	3,57	3,44
SS063	791,70	702,90	88,80	7,70	5,56	0,33	0,33	100,28	0,33	0,32
SS064	463,30	333,30	130,00	6,68	6,94	7,28	7,70	136,19	5,35	5,35
SS065	1028,60	597,20	431,40	5,62	9,32	3,53	6,02	122,63	2,88	4,68
SS075	558,40	438,70	119,70	6,56	4,21	4,24	5,50	87,04	4,87	5,94
SS079	251,86	59,63	192,23	5,87	4,59	0,94	1,53	210,03	0,45	0,72
SS081	859,46	436,77	422,69	5,69	4,97	26,34	26,92	116,37	22,64	18,79
SS084	804,17	538,53	265,65	6,31	4,67	16,86	19,03	128,12	13,16	12,93
SS136	1430,87	1131,02	299,85	7,50	3,75	65,79	65,79	85,07	77,33	43,61
SS138	263,06	103,84	159,22	8,04	2,06	7,09	7,09	111,01	6,39	6,00
SS140	902,22	459,41	442,81	7,51	3,43	25,92	25,92	74,54	34,77	25,80
SS145	1915,20	1363,50	551,70	5,56	5,73	97,34	97,34	177,04	54,98	35,48
SS146	460,21	353,36	106,85	7,07	2,96	12,59	13,10	143,83	8,76	8,35
SS149	429,94	286,85	143,09	8,02	2,50	3,72	3,72	171,05	2,17	2,13



#### d. Vegetable Field

Serial No. (check)	TP	TIP	TOP	pH water	LOI %	STP (Olsen) (ppm)	STP(+Bray)(ppm)	PSI	DPS (oslen) (%)	DPS (Bray) (%)
SS001	874,10	780,50	93,60	8,40	2,35	33,85	33,85	117,01	28,93	22,44
SS008	899,40	743,30	156,10	7,86	3,71	50,04	50,04	50,40	99,30	49,82
SS013	322,70	241,00	81,70	7,83	3,98	2,16	2,16	135,50	1,60	1,57
SS021	589,50	408,90	180,60	6,74	4,43	4,37	6,70	105,75	4,13	5,96
SS025	791,50	697,00	94,50	8,47	2,99	42,79	42,79	90,06	47,52	32,21
SS062	489,90	354,50	135,40	7,89	5,56	4,88	4,88	169,11	2,89	2,81
SS099	966,50	439,44	527,06	6,32	5,60	25,54	25,54	105,16	24,29	19,54
SS105	3462,61	2454,76	1007,85	8,05	7,79	129,72	129,72	153,43	84,53	45,81
SS107	765,05	466,16	298,89	7,75	3,36	15,64	15,64	150,33	10,40	9,42
SS109	1602,89	1289,45	313,45	6,86	3,75	113,49	41,30	431,16	26,32	8,74
SS111	1041,83	605,51	436,32	7,20	2,62	49,71	25,40	179,50	27,69	12,40
SS113	773,35	603,96	169,39	7,46	4,32	17,54	17,54	146,59	11,97	10,69
SS118	1145,95	902,28	243,67	6,74	3,52	40,66	29,90	317,84	12,79	8,60
SS122	1112,43	956,67	155,76	7,48	3,13	41,01	41,01	145,73	28,14	21,96
SS125	1946,33	1470,17	476,16	8,19	4,45	92,38	92,38	347,09	26,61	21,02
SS128	3245,12	1927,10	1318,02	5,85	12,85	145,79	145,79	224,61	64,91	39,36
SS130	3068,37	1832,92	1235,45	5,13	11,00	164,54	164,54	346,36	47,51	32,21
SS132	560,13	348,83	211,30	8,21	2,74	20,00	20,00	265,52	7,53	7,01
SS137	732,11	291,77	440,34	7,85	3,80	42,66	42,66	165,07	25,84	20,53
SS139	639,06	312,47	326,59	7,79	2,61	28,71	28,71	179,39	16,00	13,80
SS141	756,11	394,97	361,14	7,78	3,24	31,05	31,05	256,73	12,10	10,79