# BIOGEOCHEMICAL PROCESSES OF IRON AND RELATED ELEMENTS IN TERRESTRIAL ECOSYSTEM OF AMUR RIVER 

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Terrestrial ecosystem is a one of the important sources of iron to river and ocean ecosystem. Concentration and flux of iron from terrestrial ecosystem to stream and river ecosystem are controlled by the various biogeochemical processes in the watersheds. Many external drivers (including climate, geology, hydrology and so on) and various anthropogenic disturbances (including forest fire, tree harvesting, land use change, agriculture and so on) also strongly influence the spatial and temporal pattern of iron dynamics. The comparative studies based on the monitoring of stream water and soil water in terrestrial watershed with different land-use pattern would be important to understand the natural and anthropogenic fluctuation of iron dynamics in terrestrial ecosystem. Here, we report preliminary results of some biogeochemical investigation in forest, wetland and agricultural ecosystems in terrestrial watershed of Amur River.

Table 1 List of counter-part of collaborative research in each ecosystem of China and Russia.

| Ecosystem | Country | Counter-part |
| :---: | :---: | :---: |
| Forest | China | Fuchen Shi (Nankai University) <br> Xiaoniu Xu (Anhui Agriculture University) |
| Forest | Russia | Vladimir Shamov (Institute for Water and Ecological Problem, RAS) |
| Wetland | Russia | Vladimir Shamov (Institute for Water and Ecological Problem, RAS) |
| Agriculture <br> Wetland | China | Bai Zhang (Northeast Institute of Geography and Agricultural |
| Ecology, CAS) |  |  |
| Chen Xin (Institute of Applied Ecology, CAS) |  |  |

RAS; Russian Academy of Sciences
CAS; Chinese Academiy of Sciences

## I. Characteristics of spatial pattern of iron biogeochemistry in soil and stream water in Chinese forest watershed (written by Shibata H., Shi F., Cai T. and Xu X.)

In China, we established two research region for stream chemistry in forest watershed at Liangshui and Daxing'an Mountain and one site for monitoring of river quality in Sungary (Songhua) River near Tongjiang city (Figure 1). In each site, water samples are collected monthly for analysis of concentration of iron and other solutes. In Liangshui and Daxig'an sites, we also collected soil samples to analyze the contents of iron and other elements in soil. In Liangshui site, two sub-catchments named, "Hanyue" are investigated the effect of forest harvesting on iron transport from watershed to stream. The Daxig'an Mountains is located in one of the most damaged area by forest fire in northeastern China.

Concentration of dissolved total iron in Sungary River near Tongjiang city was fluctuated seasonally (Figure 2), and mean values was 0.77 ( $\pm 0.41 \mathrm{SD}$ ) $\mathrm{mg} \mathrm{L}^{-1}$ (Figure 3). Shibata (2005) reported that the annual-mean iron concentration of Amur River in 2002 was 0.56 ( $\pm 0.17 \mathrm{SD}$ ) $\mathrm{mg} \mathrm{L}^{-1}$, suggesting the concentration of dissolved total iron in Sungary River is similar level of Amur main channel.


Figure 1. Location of three main research areas for stream chemistry in China


Figure 2. Seasonal fluctuation of dissolved total iron concentration in Sungary river near Tongjiang city in 2006 (unpublished data provided by Shi Fuchen)

Figure 3 shows mean concentration of dissolved total iron in stream water collected in each site from March to October 2006. The mean values at Daxing'an Mountains, Hanyue and Liangshui were relatively lower than that in Sungary River near Tongjiang (Figure 3). We will need to analyze detail comparison in each site to understand the effect of forest fire and tree harvesting on temporal and spatial pattern on iron dynamics in terrestrial watershed (Photo 1).


Figure 3. Mean concentration of dissolved total iron in stream water at each research site from March to October 2006 (unpublished data provided by Shi Fuchen). Each bar on box represents standard deviation. Number in each parenthesis means number of sample at each site.


Photo 1. Studied forests in Danxing'an site (Left: unburned site, Right: burned site). These photos are provided by Shi Fuchen.

Analysis of soil chemical property is important to understand the characteristics of actual iron source in ground. We are investigating the contents of iron and related solutes in soil in Lianshui, Hanyue and Daxing'an site (Photo 2). Figure 4 is an example of the preliminary analysis of soil chemical properties in each site. The total nitrogen contents in soil decreased with depth at all sites, and the values at Daxing'an site are relatively lower than those at other two sites, especially at surface soil.


Photo 2. Soil survey at studied forest (provided by Xu Xiaoniu)


Figure 4. Total nitrogen contents in soil at Daxing'an Mountain, Hanuyue and Liangshui sites (unpublished data provided by Xu Xiaoniu)

## II. Spatial distribution of dissolved iron in soil water and stream water in wetland and forest in Russia (written by YoH M., ОhJI B. and Shamov V.V.)

## 1. INTRODUCTION

Dissolved iron is supplied to the Amur river at a concentration of $0.6-0.7 \mathrm{mg} / 1$ (Schesterkin, 2004) through iron dissolution processes in its watersheds. The sources of dissolved iron could be related to soil types of Gleysols, Histosols and Podsols (Yoh, 2004). The purpose of our research is to investigate the processes of iron dissolution and transport in natural watersheds in the Amur basin. Spatial distribution of dissolved iron was studied for streams and soil interstitial waters in and around Lake Gassi watershed, which was selected as a model unit that includes typical landscapes of forest, wetland and lake with little human activity.

## 2. METHODS

## 1) field survey

The Gassi watershed has an area of about $2400 \mathrm{~km}^{2}$ and a maximum height of about 950 m . Topography and vegetation of the watershed consist of steep slope (covered by forest) and flat lowland (covered by peatland). The rivers drained from the Gassi watershed flow first into the Gassi lake and then the lake water flows into the Amur river.


Figure 1 The map of Amur River (left) and Lake Gassi watershed (right) with sampling points. The latitude and longitude of the Gassi lake (center of map) is N49 ${ }^{\circ} 03.707^{\prime}$ and E136 ${ }^{\circ} 31.071$ '.

Stream water and soil water sampling was conducted preliminarily in October 2005, and in July and September 2006. The location of samplings is shown in Fig. 1 and Tab. 1.

Table 1. The sites of sampling for water and soil water

| Site No. | Name of river | Location | Site No. Name of river | Location |  |  |
| :---: | :--- | :--- | :---: | :--- | :--- | :--- |
| 1 | Polen | N49 $^{\circ} 53.155^{\prime}$ E137 $02.528^{\prime}$ | 11 | Babchi | N49 $^{\circ} 02.565^{\prime}$ | E136 |

Water samples were stored in 50 ml polyethylene containers after different treatments in situ as described in Fig. 2. For the acidification for C and $\mathrm{D}, 0.5 \mathrm{~mL}$ of conc. HCl was added to 50 mL of water samples. The pH , electric conductivity ( EC ), water temperature of stream water and lake water were measured with a $\mathrm{pH} / E C$ meter (Horiba, D-20). Duplicate soil water samples were collected from depths of 25 cm and 50 cm below the surface in the vicinity of the water sampling points with a tension lysimeter method.


Figure 2. The flow chart of the treatments for water samples.


Figure 3. Change in the absorbance after the addition of reagent in ferrozine method.

Free ferrous Fe concentration was measured by a ferrozine method (Stookey, 1970) in situ with a handy colorimeter (Tokyo Kouden, ANA-18A). Eight ml of water sample was
mixed with 2 ml of ferrozine reagent (approximately 8 mM ) in a 10 ml volumetric syringe. Because the absorbance increases with time due possibly to an interference by organic-Fe (Ohji et al., in prep), the absorbance at $\mathrm{t}=0$ was estimated by the interpolation of the curve (Fig. 3).

## 2) Laboratory analysis

All laboratory analyses of water samples were conducted in IWEP. The analytical items of water chemistry and their methods are listed in Tab. 2.

Table 2 The analytical items of water chemistry and their methods

| method | item(s) of measurement | remarks |
| :--- | :--- | :--- |
| ICP-MS | dissolved/acid leachable Fe, <br> dissolved Mn, <br> (and $\mathrm{Al}, \mathrm{Zn}, \mathrm{Ni}, \mathrm{Co}, \mathrm{Cu}, \mathrm{Mo}$ ) | The internal standard is Xe. <br> The detection limit of Fe is 1 ppb <br> (theoretically, 0.01 ppb ). <br> The calibration curves were good. |
| potassium dichromate <br> method | DOC | Not only DOC but also coexisted <br> reduced matters may be measured. <br> (samples of July, 2006) |
| TOC analyzer | DOC | (samples of September, 2006) |
| EDTA titration | $\mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}$ |  |
| atomic absorption <br> spectrometry | $\mathrm{Na}^{+}, \mathrm{K}^{+}$ |  |
| molybdenum yellow | $\mathrm{Si}^{2-}$ |  |
| barium chloride <br> spectrophotometry | $\mathrm{SO}_{4}{ }^{2-}$ |  |
| mercury nitrate <br> spectrophotometry | $\mathrm{Cl}^{-}$ |  |

## 3. RESULTS AND DISCUSSION

## (1) The spatial distribution of concentration and the source of Fe

Dissolved Fe concentrations in all samples of river and lake waters throughout three observations (October 2005, July and September, 2006) ranged between 0.04 and $5.70 \mathrm{mg} \mathrm{L}^{-1}$, having a large variation of two orders of magnitudes among the samples. The range was 0.04 to $0.73 \mathrm{mg} \mathrm{L}^{-1}$ in "forested" sites (the corresponding watersheds are presumed to be forestdominated on the basis of vegetation map), while 0.81 to $5.70 \mathrm{mg} \mathrm{L}^{-1}$ in "peatland" sites (the corresponding watersheds are presumed to be peatland-dominated on the basis of vegetation map). Thus, we found a clear tendency that peatland area has higher dissolved Fe concentrations (cf. tables in appendix).

Figs. 4 and 5 show the spatial distribution of dissolved Fe concentration as the function of altitude in two observation period. A clear negative correlation exists where Fe concentrations were low at higher altitudes and high at lower altitudes.


Fe concentrations in soil water also showed a definite difference among the sites; low level in forest soils and high level in peat soils (Fig. 6). A positive correlation was found between dissolved Fe concentration in soil water and that in river water (Fig 7). It is confirmed from these results that the soil of the latter type of watershed act as the source of dissolved iron in rivers having elevated Fe concentration. Furthermore, we observed that a spray application of $2,2^{\prime}$-bipyridine solution onto peat profile produced a red color. This fact corroborates an occurrence of Fe reduction process to produce ferrous Fe in the soils.


Figure 6
Dissolved Fe concentrations in the soil waters taken from peatland and forest areas. The error bars mean the maximum and minimum levels of Fe concentration.


Figure 7
The relationship between dissolved Fe concentrations in soil water and in river waters.

## (2) Chemical forms of Fe

Fe in river water is majorly present as an organic form irrespective of its concentration level (Fig. 8). Free ferrous Fe accounted for only a small portion of dissolved Fe with a few exceptional samples.

Fe concentration in river water showed a strong relationship against DOC concentration (Fig. 9) An almost constant ratio of dissolved Fe to DOC concentration suggests the presence of organic-Fe complex with a certain composition (a molar ratio of DOC to Fe of $\sim 51.3$ ) in the river waters of the Gassi basin.


Figure 8
Concentrations of dissolved Fe, free ferrous $F$ e, and suspended Fe(Jul., 2006). Organic Fe was estimated from the difference between dissolved Fe and free


Figure 9
The relationship between DOC and dissolved Fe concentrations in river water. The slope is ~0.0907. ferrous $F$.

Although dissolved Fe concentration in soil water was positively correlated with that in river water as described above (Fig. 7), the ratio was not unity; Fe concentrations in the river water were $\sim 5$ times less than those in soil water. It was sometimes observed that river water from peatland watersheds contained a significant amount of acid leachable Fe (cf. tables in Appendix). It may be likely that dissolved Fe in soil water leads to Fe hydroxides suspended in river water.

## (3) Fe in lake water

Dissolved Fe concentration in four river waters collected just upstream of Lake Gassi varied from 0.95 to $5.18 \mathrm{mg} \mathrm{L}^{-1}$ (Table 3). The concentration in the lake water, $2.47 \mathrm{mg} \mathrm{L}^{-1}$, was within this range. A "discharge-weighted" average Fe concentration of the rivers was calculated on the basis of relative discharge rates measured on the same period (Fig. 11). The estimated average Fe concentration in river water was $2.61 \mathrm{mg} \mathrm{L}^{-1}$, in a good agreement with the concetration in lake water as above. The result suggests that the Fe concentration in Lake

Gassi, and probably that for the outflowing water to the Amur River as well, may be accounted for by the river waters of this watershed.

Table 3 Dissolved Fe concentrations and discharges of four downstream rivers in September, 2006

| Name of rivers | Dissolved Fe concentration $(\mathrm{mg} / \mathrm{l})$ | Discharge* $\left(\mathrm{m}^{3} / \mathrm{s}\right)$ |
| :--- | :--- | :--- |
| Khaso | 0.95 | 0.93 |
| Kartanga | 2.39 | 7.17 |
| Malina | 2.69 | 0.06 |
| Babchi | 5.18 | 1.20 |

Discharge-weighted average Fe concentration: 2.61 ( $\mathrm{mg} / \mathrm{l}$ )
Observed dissolved Fe concentration of the Gassi lake: 2.47 (mg/l)
*Discharge data were from Dr. Sharmov.


Figure 11
The relationship between observed discharge and catchment area in the Gassi watershed in September, 2006. The slope gives specific discharge of $1.32 \times 10^{-5}\left(\mathrm{~mm} \mathrm{~s}^{-1}\right)$. Catchment area was estimated from the map by weighing technique.
(The discharge data were from Dr. Sharmov.)

## 4. PERSPECTIVE FOR FURTHER RESEARCH

Our field survey in the Gassi basin revealed that peatland (wetland) is important area as the source of dissolved Fe and that dissolved Fe is probably organic-complexed form.

In addition, our results suggested that the concentration of dissolved Fe in river waters might be controlled by DOC concentration. To predict dissolved Fe concentration and Fe flux from a catchment to the Amur river, the estimation of DOC concentration and DOC flux from a catchment is considered to be necessary. To make DOC concentration linked with its catchment characteristics can be an important issue for further research.

# III. Dissolved iron concentration in soil water with and without land use change in sanjiang plain, china (written by Yoh M., Guo Y., Wang D. and Yan B.) 

## 1. INTRODUCTION

Sanjiang plain is a vast flat area in the northeast end of China, encircled by Amur River, Songhua River, and Ussuri River. The area is one of the largest wetland in the Amur Basin so that it could be a typical source of iron to this river and the ocean. However, land use change for recent decades has turned that area mostly into agricultural fields, which may lead to significant changes in the biogeochemical cycling and the transport of Fe . The purpose of this subject is to know the Fe behavior in areas with different land use; the concentration and chemical forms of dissolved iron were studied for soil interstitial water in wetland, paddy field and upland field.

## 2. MATERIALS AND METHODS

## Sites and field research

The research sites in Sanjiang plain include three types of landscape (wetland, paddy field, and upland field) of the Sanjiang wetland ecological experimental station $\left(47^{\circ} 35^{\prime} \mathrm{N}\right.$, $133^{\circ} 31^{\prime} \mathrm{E}$ ), a wetland near Bielahonghe River ( $47^{\circ} 31^{\prime} 57.6^{\prime \prime} \mathrm{N}, 133^{\circ} 52^{\prime} 53.2^{\prime \prime} \mathrm{E}$ ), and a wetland in Honghe Sanctuary Natural Researve ( $47^{\circ} 49^{\prime} 45.8^{\prime \prime} \mathrm{N}, 133^{\circ} 41^{\prime} 38.2^{\prime \prime}$ E), in the Heilongjiang province, China. The upland field was planted with soy bean. The average elevation of Sanjiang plain is 56 m , and the mean annual precipitation is 600 mm and the mean annual temperature is $1.9^{\circ} \mathrm{C}$ (Chen et.al., 1996). Water and soil in the wetland are completely frozen in October and begin to melt in late April. The highest and lowest temperatures occur in July and January, respectively.

The soil interstitial water was collected seven times (June, August, September, 2005 and May, July, August, October, 2006) at the Sanjiang wetland ecological experimental station, and four times (May, July, August, and October, 2006) at the Bielahonghe wetland. The soil interstitial water was collected from tree depths $(10 \mathrm{~cm}, 50 \mathrm{~cm}$, and 60 cm$)$ with a tension lysimeter technique, and surface water $(0 \mathrm{~cm})$ was collected by a plastic bottle directly. The sites for soil water collection had an impermeable formation around a depth of 60 cm .
$\mathrm{pH}, \mathrm{EC}$ and water temperature were measured by a pH meter and an EC meter in situ. Soil Eh was measured by an Eh meter for one depth $(10 \mathrm{~cm})$ in the sites of wetland, paddy field and upland field of Sanjiang experimental station as above. The Eh probe was installed in May with a replication of 3 or 4 .

## Chemical analyses

Free ferrous Fe was analyzed colorimetrically by a ferrozine method immediately after soil water collection. Dissolved iron and dissolved manganese were analyzed with an atomic absorption photometer (HITACHI, Ltd.Tokyo Japan. Z-8000) for a sample which was acidified ( 1 mL conc. $\mathrm{HCl} / 100 \mathrm{ml}$ ) after a filteration with a $0.45 \mu \mathrm{M}$ disposable filter
(ADVANTEC DISMIC-25cs). For the analysis of acid soluble iron, water sample is acidified ( 4 mL conc. $\mathrm{HCl} / 100 \mathrm{ml}$ ), heated to boil, and then filtered in the same way (APHA 1998). Dissolved organic carbon was analyzed with a TOC analyzer (SHIMADZU TOC-500) for a sample which was filterated and preserved frozen in a glass vial pre-burnt at $550^{\circ} \mathrm{C}$.

## 3. RESULTS AND DISCUSSION

Soil water dissolved iron profiles in the wetland site (station)(a), the Bielahonhe wetland site (b), and the paddy field site (station) (c) are shown in Fig. 1. Considerable seasonal variation in dissolved Fe concentration was observed in these landscapes. As a whole, dissolved Fe concentration level was relatively low in spring (May), but increased with season. The concentration level was largest in summer in the wetland site and in the paddy field site, but in October in the Bielahonhe wetland site; their maxima amounted to 5.0 mg L-1, 3.4 mg $\mathrm{L}-1$, and 17 mg L-1, respectively.

In Fig. 1(d), the concentration levels of dissolved Fe in July are compared among these sites. The profile obtained from Honghe Sanctuary wetland site is also shown in the figure, which is the most preserved wetland area in Sanjiang plain. The result showed that the profile and the dissolved Fe level in the station wetland site was very similar to those in Honghe Sanctuary wetland site. Larger concentration level was observed in the Bielahonhe wetland site on every period (Fig 1 d). In the paddy field (Fig 1c), dissolved Fe levels were consistently somewhat small compared to three natural wetland sites.


Fig. 1 Vertical distribution of total dissolved iron in the wetland and paddy field of sanjiang plain in 2006

It is interesting to note that these profiles of dissolved Fe concentration had a common feature. The concentrations were nearly stable in deeper horizon in all observations. The maximum concentration often occurred at a depth of 10 cm below soil surface. In addition, the surface water ( 0 cm depth) invariably showed remarkably low concentrations compared with deeper layers. Although the reason for such steep decreases in surface water is unknown, this phenomenon deserves attention in view of the biogeochemical cycling of Fe .


Fig. 2
Vertical distribution of different forms of dissolved iron in different seasons for wetland of station, wetland of BieLaHongHe, paddy field of station

The chemical form of Fe in the soil waters of three landscapes on different periods is shown in Fig. 2. Free ferrous Fe generally accounted for $20 \%$ or less of dissolved Fe ; i.e., organic iron was the main fraction of dissolved Fe in each site. Relative proportion of organic Fe showed no significant difference between the wetland site and the Bielahonhe wetland site. The soil water in the wetland of Bielahonghe had invariably higher organic Fe concentration than that in the wetland site.

A striking difference found for the paddy field site was that a large amount of Fe was present as acid leachable form, probably Fe hydroxide. Acid leachable Fe was also the major form of Fe in the surface water of two wetland sites, which probably resulted from oxidation




Fig. 3
Vertical distribution of dissolved organic carbon in the wetland and paddy field of sanjiang plain in 2006
(a)Wetland of station, (b) Wetland of BieLaHongHe, (c) paddy field of station
of dissolved iron. Precipitaion of Fe by this process partly explains low concentrations of dissolved Fe observed in the surface waters as described above.

The concentration of the dissolved organic carbon often showed a maximum at a 10 cm depth and a significant decrease in the surface waters (Fig. 3), analogous to the profiles of dissolved Fe as shown in Fig. 1. Higher concentrations at 10 cm depth may be associated with a peat accumulation observed in that layer in the wetland site. Again, the whole level of DOC concentration were relatively low in spring and tended to increase with season. Although the change of DOC concentration with depth and with season is not completely identical to those of dissolved Fe , a similarity exists in their spatial and temporal changes between these components. There appears no significant difference in DOC concentration level among three landscapes.

Fig. 4 compares the seasonal variation in dissolved Fe concentration in 10 cm and 50 cm depths among wetland, paddy field, and upland field. The data for upland field are hypothetical but realistic as this soil was completely oxic throughout the season. The redox potential in these fields is shown in Fig. 5. Significant amounts of dissolved Fe were detected in warm season for both wetland and paddy field as opposed to upland field. It is obvious that the concentration was constantly higher in both depths in wetland than those in paddy field. Especially, a distinct difference exists for 50 cm depth in late May between both sites, where little dissolved Fe was detected in the soil water of paddy field. Water management is common in paddy field; irrigation in May and drainage in September in this field. This farming practice affected decisively the soil redox condition in paddy field as demonstrated in the Eh value in Fig. 5 (the Eh had positive values in May and October), and consequently the seasonal variation in dissolved Fe concentration in the soil of this site. In addition to the concentration level of dissolved Fe in warm periods, the period itself during which Fe solubilization takes place is suggested to be largely shortened in paddy field, which is also considered as a factor related to the biogeochemical role of this Fe source.


Fig. 6
Seasonal change in dissolved Fe concentration at 10 cm depth (upper) and 50 cm depth (lower) in upland field ( ), paddy field ( $\mathbf{(}$ ) and wetland $(\boldsymbol{)}$ ). The arrows denote the period of water drainage management in this paddy field. Dotted lines and the data for upland field are presumptive.




Fig. 5
Seasonal change in Eh at 10 cm soil depth in upland field, paddy field and wetland

## 4. SUMMARY AND FUTURE PERSPECTIVES

The present study has demonstrated a considerable change in both the concentration and the chemical forms of Fe among wetland, paddy field and upland field. It was also found
that dissolved Fe concentration is significantly decreased in surface water compared to deeper soil horizons. This finding is not only interesting in the behavior of Fe but of an important implication in considering the iron transport from land regions to river. The discharge process of soil water in wetland and paddy field and their quantitative importance for the iron transport are unknown yet, being an question on this subject to be investigated next year.

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## REFERENCES

American Public Health Association (APHA): 3500.Fe, In, Standard Methods for the Examination of Water and Wastewater (1998)
GangQi Chen. Brief introduction of the Ecological Experimental Station of mire-wetlands in the Sanjiang plain. In, Study in the Wetland of Sanjiang Plain, 1-4. (1996)
Lenore S. Clesceri, Arnold E. (1998) Greenberg and Andrew D. Eaton, Standard Methods For The Examination of water and wastewater, 3: 75-78
Leopold L. B. (1994): A view of the river, Harvard University Press, p.99.
Schesterkin V. P. (2004): Iron content in the middle Amur in winter low water period. Report on Amur-Okhotsk Project, No.2, 67-70.
Schlesinger, W.H. (1997) Biogeochemistry, An Analysis of Global Change, 224-260.
Shibata, H. (2005) Processes of iron transport from terrestrial ecosystem to river: Preliminary analysis of spatial and temporal patterns of iron concentrations in Amur River. In 'Report on Amur-Okhotsk Project No. 3: Proceedings of the International Kyoto Symposium 2005', Research Institute for Humanity and Nature, 97-104. Kyoto.
Stookey L. L. (1970): Ferrozine-a new spectrophotometric reagent for iron. Anal. Chem., 42, 779-781.
Yoh M. (2004): Possible fundamental sources of Dissolved iron in terrestrial environments: their mechanisms, presumed anthropogenic impact, and research needs. Report on Amur-Okhotsk Project, No.2, 81-86.

## Appendix:

Appendix 1. Results at river and lake sites in October, 2005

| Date of sampling | $\begin{aligned} & \text { Site } \\ & \text { No. }{ }^{1} \end{aligned}$ | Name of river/lake | Dominant landscape of catchment ${ }^{2}$ | Fe concentration (mg/l) |  | $\mathrm{pH}^{5}$ | $\begin{gathered} \mathrm{EC} \\ (\mu \mathrm{~S} / \mathrm{cm}) \end{gathered}$ | Water temperature $\left({ }^{\circ} \mathrm{C}\right)$ | Altitude ${ }^{6}$ (m) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Dissolved ${ }^{3}$ | $\begin{gathered} \text { acid } \\ \text { leachable } \end{gathered}$ |  |  |  |  |
| 10/5 | 1 | Polen river | peatland | 1.95 | 6.12 | 6.7-7.5 | 55 | 4.2 | 24 |
| 10/5 | 2 | Nyura river | peatland | 1.24 | 1.81 | 7.2 | 63 | 6.5 | 22 |
| 10/5 | 3 | Elman river | forest | 0.73 | 0.96 | 7.1 | 36 | 6.1 | 137 |
| 10/5 | 4 | Manoma river | forest | 0.23 | 0.31 | 7.4 | 44 | 7.1 | 138 |
| 10/6 | 8 | Zabyty river | forest | 0.05 | 0.07 | 6.9-7.3 | 75 | 5.1 | 359 |
| 10/6 | 7 | Gabilli river | forest | 0.06 | 0.12 | 7.0-7.3 | 58 | 4.0 | 365 |
| 10/6 | 6 | Koopturkoo river | forest | 0.04 | 0.09 | 6.7-7.2 | 25 | 6.1 | 257 |
| 10/6 | 5 | Anuy river | forest | 0.11 | 0.06 | 7.3-7.7 | 44 | 7.0 | 200 |
| 10/7 | 9 | Anuy river mouth | forest | 0.11 | 0.15 | 7.2 | 53 | 7.2 | 26 |
| 10/7 | 12 | Kartanga river | peatland | 1.22 | 1.37 | 6.8-7.5 | 68 | 6.3 | 32 |
| 10/7 | 16 | Oota river | forest | 0.05 | 0.07 | 7.2-7.7 | 52 | 6.7 | 78 |
| 10/7 | 11 | Babchi river | peatland | 1.53 | 2.18 | 7.0-7.3 | 51 | 7.3 | 30 |
| 10/7 | 10 | Gassi lake | - | 1.66 | 2.84 | 7.4-7.7 | 82 | 10.9 | 23 |

${ }^{1}$ The site numbers correspond to those in Table 1.
${ }^{2}$ These are decided by vegetation in map.
${ }^{3}$ Dissolved Fe means the iron fraction that pass through Whatman GF/F filter.
${ }^{4}$ Acid leachable Fe means the iron fraction that pass through Whatman GF/F filter after acidifying samples to $\sim \mathrm{pH} 2$ : dissolved $\mathrm{Fe}+$ acid leachable suspended Fe
${ }^{5}$ Two values at one site means the pH values measured with different two pH meters.
${ }^{6}$ The sea level is zero.

Appendix 2. Results at river and lake sites in July, 2006.


* pH values were not obtained successfully in this survey.
${ }^{1}$ The site numbers correspond to those in map.
${ }^{2}$ These are decided by vegetation in map.
${ }^{3}$ Dissolved Fe means the iron fraction that pass through GF/F filter.
${ }^{4}$ Acid leachable Fe means the iron fraction that pass through GF/F filter after acidifying samples to $\sim \mathrm{pH} 2$ : dissolved $\mathrm{Fe}+$ acid leachable suspended Fe
${ }^{5}$ The sea level is zero.

Appendix 3. Concentration of chemical components in rivers and lake in July, 2006.

| Date of <br> Sampling | Site No. | Name of river/lake | Concentration $(\mathrm{mg} / \mathrm{l})$ |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :--- | ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{Ca}^{2+}$ | $\mathrm{Mg}^{2+}$ | $\mathrm{Na}^{+}$ | $\mathrm{K}^{+}$ | $\mathrm{Cl}^{-}$ | $\mathrm{SO}_{4}{ }^{2-}$ | Si | Mn |  |  |
| $7 / 18$ | 12 | Kartanga river | 4.2 | 2.3 | 2.51 | 0.50 | 1.3 | 2.78 | 1.93 | 0.028 |  |  |
| $7 / 18$ | 13 | Khaso river (lower) | 3.9 | 2.6 | 2.53 | 0.36 | 0.9 | 3.23 | 7.68 | 0.233 |  |  |
| $7 / 18$ | 15 | Khaso river (middle) | 5.3 | 2.0 | 2.34 | 0.22 | $-*$ | 3.11 | 8.06 | 0.010 |  |  |
| $7 / 18$ | 16 | Oota river | 4.2 | 2.2 | 1.89 | 0.24 | 0.5 | 2.43 | 6.71 | 0.005 |  |  |
| $7 / 19$ | 17 | Boorga river | 3.3 | 3.0 | 2.35 | 0.41 | 0.6 | 3.07 | 5.82 | 0.032 |  |  |
| $7 / 19$ | 14 | Malina river | 5.6 | 4.2 | 1.91 | 0.60 | 1.2 | 1.45 | 7.90 | 0.068 |  |  |
| $7 / 19$ | 11 | Babchi river | 5.6 | 3.3 | 1.55 | 0.37 | 0.9 | 5.73 | 4.69 | 0.903 |  |  |
| $7 / 19$ | 10 | Gassi lake |  | 5.6 | 4.2 | 1.50 | 0.66 | 1.0 | 6.68 | 7.30 |  |  |

Appendix 4. Results at river and lake sites in September, 2006.

| Date of sampling | $\begin{aligned} & \text { Site } \\ & \text { No. }{ }^{1} \end{aligned}$ | Name of river/lake | Dominant landscape of catchment ${ }^{2}$ | Fe concentration (mg/l) |  | $\begin{gathered} \mathrm{Fe}^{2+} \\ (\mathrm{mg} / \mathrm{l}) \end{gathered}$ | $\begin{gathered} \mathrm{DOC} \\ (\mathrm{mgC} / \mathrm{l}) \end{gathered}$ | pH | $\begin{gathered} \mathrm{EC} \\ (\mu \mathrm{~S} / \mathrm{cm}) \end{gathered}$ | Watertemperature$\left({ }^{\circ} \mathrm{C}\right)$ | Altitude (m) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Dissolved ${ }^{3}$ | acid <br> leachable ${ }^{4}$ |  |  |  |  |  |  |
| 9/6 | 12 | Kartanga | peatland | 2.39 | 3.22 | 0.06 | 27.1 | 7.05 | 51 | 13.8 | 32 |
| 9/6 | 11 | Babchi | peatland | 5.18 | 9.94 | 0.27 | 33.6 | 6.29 | 57 | 15.8 | 30 |
| 9/6 | 16 | Oota | forest | 0.19 | 0.35 | 0.00 | 2.4 | 7.15 | 58 | 11.8 | 78 |
| 9/6 | 17 | Boorga | forest | 0.30 | 0.54 | 0.06 | 6.0 | 7.13 | 59 | 13.4 | 93 |
| 9/7 | 15 | Khaso (middle) | forest | 0.25 | 0.39 | 0.05 | 5.1 | 4.62 | 55 | 13.2 | 61 |
| 9/7 | 19 | Khaso (upper) | forest | 0.05 | 0.13 | 0.01 | 4.2 | 5.05 | 49 | 10.4 | 235 |
| 9/8 | 18 | Khalgoso | forest | 0.24 | 0.41 | 0.02 | - | 6.94 | 61 | 15.8 | 71 |
| 9/8 | 14 | Malina | peatland | 2.69 | 3.30 | 0.01 | 33.6 | 6.50 | 62 | 15.0 | 35 |
| 9/8 | 13 | Khaso (lower) | peatland | 0.95 | 1.05 | 0.20 | 12.2 | 6.74 | 56 | 14.7 | 32 |
| 9/8 | 10 | Gassi lake | - | 2.47 | 3.95 | 0.04 | 28.0 | 7.00 | 56 | 20.2 | 23 |

${ }^{1}$ The site numbers correspond to those in Table 1.
${ }^{2}$ These are decided by vegetation in map.
${ }^{3}$ Dissolved Fe means the iron fraction that pass through Whatman $\mathrm{GF} / \mathrm{F}$ filter.
${ }^{4}$ Acid leachable Fe means the iron fraction that pass through Whatman GF/F filter after acidifying samples to $\sim \mathrm{pH} 2$ : dissolved $\mathrm{Fe}+$ acid leachable suspended Fe
${ }^{5}$ The sea level is zero.

Appendix 5. Concentration of chemical components in rivers and lake in September, 2006.

| Date of Sampling | Site No. | Name of river/lake | Concentration (mg/l) |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{Ca}^{2+}$ | $\mathrm{Mg}^{2+}$ | $\mathrm{Na}^{+}$ | $\mathrm{K}^{+}$ | $\mathrm{Cl}^{-}$ | $\mathrm{SO}_{4}{ }^{2-}$ | Si | Mn |
| 9/6 | 12 | Kartanga river | 4.6 | 3.3 | 3.05 | 0.70 | 0.9 | 5.38 | 8.06 | 0.080 |
| 9/6 | 11 | Babchi river | 4.6 | 3.1 | 3.07 | 0.83 | 1.7 | 4.77 | 6.34 | 2.106 |
| 9/6 | 16 | Oota river | 4.9 | 3.0 | 3.04 | 0.59 | 0.9 | 2.02 | 7.46 | 0.015 |
| 9/6 | 17 | Boorga river | 6.4 | 2.3 | 4.63 | 0.54 | 0.9 | 3.35 | 7.46 | 0.017 |
| 9/7 | 15 | Khaso river (middle) | 4.6 | 2.7 | 2.95 | 0.66 | 1.1 | 2.45 | 8.96 | 0.015 |
| 9/7 | 19 | Khaso river (upper) | 3.8 | 2.6 | 4.53 | 0.98 | 0.7 | 2.41 | 8.96 | 0.001 |
| 9/8 | 14 | Malina river | 5.9 | 4.2 | 3.76 | 1.00 | 1.7 | 6.49 | 9.33 | 0.063 |
| 9/8 | 13 | Khaso river (lower) | 4.9 | 3.0 | 2.85 | 0.69 | 1.0 | 4.69 | 8.96 | 0.065 |
| 9/8 | 10 | Gassi lake | 5.2 | 2.9 | 3.44 | 0.87 | 1.2 | 5.33 | 7.84 | 0.241 |

*The sample of the Khalgoso river was not analyzed because of the lack of water.

## Appendix 6. Results of Fe concentration in soil water

| Date of sampling | $\begin{aligned} & \text { Site } \\ & \text { No. }{ }^{1} \end{aligned}$ | Name of sites | Dominant landscape of catchment ${ }^{2}$ | Fe concentration (mg/l) |  |  |  | Average Fe concentration (mg/l) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | 25 cm depth |  | 50 cm depth |  |  |
| 9/6 | 17 | Boorga | forest | - | - | 0.10 | 0.45 | 0.28 |
| 9/6 | 16 | Oota | forest | 3.39 | 0.11 | 0.02 | 0.08 | 0.90 |
| 9/7 | 15 | Khaso (middle) | forest | - | - | 0.21 | - | 0.21 |
| 9/6 | 12 | Kartanga | peatland | 37.2 | 6.26 | 1.93 | - | 15.1 |
| 9/8 | 13 | Khaso (lower) | peatland | 33.4 | 9.95 | 0.13 | 0.28 | 10.9 |
| 9/6 | 11 | Babchi | peatland | 35.8 | 8.38 | 35.8 | - | 26.7 |
| 9/8 | 10 | Gassi | - | - | 0.07 | 0.06 | 0.15 | 0.09 |

*The data of DOC concentration in soil water are not obtained yet.
${ }^{1}$ The site numbers correspond to those in Table 1.
${ }^{2}$ These are decided by vegetation in map.

