



Title	Dynamics of iron in the Chikugo River Basin : Comparison of iron with nitrogen and phosphate input to the estuary
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1 **Title:** Dynamics of iron in the Chikugo River Basin: Comparison of iron with nitrogen and
2 phosphate input to the estuary

3

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19 **Keywords:** Iron, Nitrogen, Phosphate, Material dynamics, Chikugo River

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21

1 **Abstract**

2 Iron dynamics in the Chikugo River were investigated in order to understand the relationship between
3 the characteristics of iron concentrations in the basin and the river estuarine ecosystem and that of the
4 inner area of the Ariake Sea. Analysis of iron (Fe) concentration from monthly samples at 29 sites in the
5 Chikugo River from June 2011 to May 2012 was conducted together with analyses of nitrogen (N) and
6 phosphate (P) concentrations. Fe concentration changed slightly from the upstream to the middle basin,
7 whereas in the estuary it increased sharply at 10 km from the river mouth and decreased again near the
8 river mouth. This trend is different from the trends for N and P concentrations, and the Fe distribution
9 was distinctive throughout the year. Further investigation was conducted focusing on the Fe dynamics in
10 the estuary and the inner Ariake Sea. It was found that the trend of Fe concentration corresponds to the
11 trend of turbidity in the estuary. The reasons of the characteristic Fe dynamics are suggested that supplied
12 Fe is accumulated by the scavenging effect of particulate organic matter in the estuarine turbidity
13 maximum to form floccules. As these particle materials are important for forming the ecosystem in the
14 inner Ariake Sea, it is suggested that Fe dynamics have an influence in forming the ecosystem in the
15 Chikugo River and the Ariake Sea.

16

1 **1. Introduction**

2 Terrestrial materials transported through rivers, such as nutrients and organic matter, largely affect the
3 coastal and estuarine environments. The linkage between forests, rivers and the sea has been focused on
4 for conserving coastal and estuarine ecosystems in recent years (Yamashita and Tanaka, 2008; Kasai et
5 al., 2010; Shiraiwa, 2010). Especially, iron (Fe) dynamics have been focused as it is an important variable
6 in the land-ocean linkage. Thus the role of Fe in coastal ecosystems has been investigated in several
7 places (Matsunaga et al., 1984, 1998; Öztürk and Bizsel, 2003; Nagai et al., 2007; Fujii et al., 2006;
8 Shiraiwa, 2010). Although the effect of Fe on the control of phytoplankton growth in oceans has been
9 well investigated (Martin & Fitzwater, 1988; Martin et al., 1994; Nishioka et al., 2007, 2011; Gleadhill
10 and Buck, 2012; Kondo et al., 2012), investigations in estuaries and coastal areas are more limited. Fe
11 dynamics and the role of Fe in ecosystems have been a subject of considerable interest recently.

12 Matsunaga et al. (1998) firstly found that riverine input of organically bound Fe and nutrients play an
13 important role for supporting phytoplankton growth in Kesenuma Bay, Japan by culture experiments
14 using culture media prepared from bay and outer waters. Fujii et al. (2006) investigated the spatial and
15 seasonal distribution of dissolved organic matter and Fe in Matsushima Bay, Japan, and found that the
16 dissolved Fe concentration rapidly decreased with the increase in salinity from the river to the bay and
17 consequent Fe concentration was extremely low in seawater. Nagai et al. (2007) suggested that dissolved
18 Fe in Lake Kasumigaura was mainly of riverine origin and that most of the dissolved Fe in river water
19 were in the form of unstable species. The monitoring of Fe concentrations in the surface water of Lake
20 Kasumigaura indicated that most of the Fe is supplied from rivers (Tomioka et al., 2010). Öztürk and
21 Bizsel (2003) investigated the Fe speciation in four different coastal systems in order to understand the
22 controlling mechanisms on Fe speciation. The role of the Amur River in primary productivity was
23 elucidated in the Sea of Okhotsk and Oyashio region focused on dissolved Fe (Shiraiwa, 2010). It was
24 found that approximately 40% of the dissolved Fe necessary to support phytoplankton production in the
25 Oyashio region was transported through the Amur River, in which there are physical and anthropogenic

1 interactions between upstream and downstream areas. These studies pointed out the importance of
2 riverine Fe dynamics in the estuarine and coastal ecosystems.

3 The Ariake Sea is located on the western part of Kyushu Island in Japan and its area is approximately
4 1,700 km². A notable characteristic of the Ariake Sea is that the tidal amplitude (maximum: 6 m) is the
5 largest in Japan. The sea is also characterized by extensive tidal flats and an estuarine turbidity maximum
6 (ETM). The Chikugo River, which flows into the inner Ariake Sea, is the largest river in Kyushu, Japan.
7 The length is 143 km, whereas the basin area is 2,860 km². In the estuary of the Chikugo River up to 23
8 km from the river mouth, mineral particles mixed with organic matter are stirred vigorously by large tides
9 and waves. These particle materials are important for forming the ecosystem in the inner Ariake Sea,
10 because nutrients absorbed onto the particles have been shown to be important for the growth of
11 phytoplankton and bivalves (Suzuki et al., 2007). The original ecosystem including the particle species in
12 the Ariake Sea can be maintained based on this environment (Suzuki et al., 2009). However, it is pointed
13 out that the environments have gradually changed to be worse. Nori (*Porphyra*, an edible red alga)
14 aquaculture sustained enormous damage in 2000–2001 (Tsutsumi, 2012; Koriyama et al., 2013).
15 Degradation of the water environment and deterioration of ecosystems have become a serious problem in
16 the inner parts of Ariake Bay (Komiya et al., 2013). It is therefore necessary to understand the
17 ecosystem in the Chikugo River and the Ariake Sea in more detail.

18 In response to the unfavorable condition, many studies have examined the Chikugo River estuary,
19 including the movement of the estuarine turbidity maximum (ETM) and dynamics of particulate organic
20 matter (Shoji et al., 2006; Suzuki et al., 2007, 2009; Yokoyama et al., 2008), the characteristics of water
21 quality (Dong et al., 2008), and nutrients and phytoplankton (Yokoyama et al., 2010, 2011) in the estuary.
22 There is a possibility that Fe dynamics is also related to the change in the ecosystem. However, there are
23 no studies that have focused on the dynamics of Fe in the river and estuary. The relationship between Fe
24 and other factors, such as nutrients and particle organic matter, is not yet investigated in the estuary of the
25 Chikugo River. Moreover, there are few studies which deal with all the basin of a river. Therefore, the

1 objective of this study is to investigate the Fe dynamics and its relation with other factors for
2 understanding the effect of Fe on the formation of the original ecosystem in the Chikugo River and the
3 Ariake Sea.

4

5 **2. Methods**

6 **2.1 Sampling sites and methods**

7 Figure 1 shows the locations of observation sites in the Chikugo River examined in this study. Six
8 sampling sites from R2 to R7 are in the estuary and R7 is situated just at the sluice gate, which is 23 km
9 from the river mouth and the upper limit of the estuary. Twenty-three sites were in the middle and the
10 upper basin of the Chikugo River and five tributaries of the Houman, Kagetsu, Taio, Kawabaru and Kusu
11 rivers. R13 is situated in the lake behind the Matsubara Dam. Surface water sampling and water analysis
12 with multi water quality meters were operated at the spring tide once a month from the beginning of July
13 2011 to the second half of May 2012 as listed in Table 1. Surface water samples were taken from the
14 bank of the river except for the estuary in March and April, 2012. Samples were placed in plastic bottles
15 and stored in cold storage below 10 °C. Fe, total nitrogen (T-N), and total phosphorus (T-P) were
16 analyzed for each sample in the laboratory. The reason for comparing Fe, N and P is that Fe can be
17 responsible for the limitation of the phytoplankton growth as mentioned in the introduction as well as N
18 and P.

19 Water temperature, salinity and turbidity were measured with the multi water quality meters at the
20 same points of water sampling. The types of the meters used were AAQ-RINKO (JFE Advantech Co.,
21 Ltd.) in July 4 and 5, 2011, DO meter 55 (YSI Nanotech) used in August 27, 30 and 31, 2011, and
22 RINKO-Profiler (JFE Advantech Co., Ltd.) in August 27, 28 and 30, 2011 and from September 2011 to
23 May 2012. The operations of the water quality meters as well as water sampling in the estuary were
24 carried out within four hours before and after high tide for adjusting the observation condition. We also

1 conducted the operations at the same place of each sampling site except for the sites of estuarine basin
2 (R2-R7) in March 2012 and April 2012 (Table 1).

3 Further investigation was conducted on October 18, 2012 for confirming Fe dynamics in the river.
4 Water samples were taken from both the surface and bottom layers at the sites from R7 to R2, and also at
5 the mouth of the river (R1) and 3 km (E1), 5.5 km (E2) and 20 km (E3) apart from the river mouth in the
6 Ariake Sea (Fig. 1). The sampling was examined not at the bank of the river, but at flow axis. Analysis
7 items and methods were not different from the investigations from July 2011 to May 2012.

8 **2.2 Analytical methods**

9 Fe concentration in the supernatant of the samples stored in cold storage was analyzed by the
10 spectrophotometric method that uses 1, 10-phenanthroline and a wavelength of 510 nm with a
11 spectrophotometer (Jasco, V-650) (Yamamoto et al., 2012). In addition, we also measured Fe using an
12 inductive coupling plasma mass analyzer (ICP-MS) to confirm the reliability of the detected Fe
13 concentrations, as follows. Each stored sample was filtered with 0.45 μm filter and heated after nitric
14 acid (HNO_3) addition and analyzed with the ICP-MS (Agilent Technologies, ICP7500). We defined the
15 analyzed Fe concentration with this method as dissolved Fe (D-Fe) in this study. T-N concentration was
16 analyzed with a TOC/V meter (Shimadzu, TOC-V CPN) combined with T-N unit (TNM-1), whereas T-P
17 concentration was measured using a decomposition method by potassium peroxodisulfate (JIS K0102
18 46.3.1). “JIS K0102” is the standard methods defined by the Japanese Industrial Standards
19 Committee (Web <http://www.jisc.go.jp/eng/index.html>).

20

21 **3. Results**

22 **3.1 Temperature, salinity and turbidity**

23 Figure 2 shows the seasonal change of temperature, salinity and turbidity of surface water in the
24 Chikugo River. In this study, we tracked the changing of the seasons by calculating averaged water
25 temperature in all the sampling sites, and classified the detected data into four seasons, summer (from

1 July 2011 to September 2011), autumn (from October 2011 to November 2011), winter (from December
2 2011 to February 2012) and spring (from March 2012 to May 2012). Averaged temperatures of all the
3 sites were 22.6 ± 2.18 °C in summer, 15.6 ± 3.07 °C in autumn, 8.9 ± 0.65 °C in winter, and 16.4 ± 4.43 °C in
4 spring. Water temperature increased gradually from the upstream to the downstream except in winter.
5 Temperatures at R13 (95 km upstream from the river mouth) and R20 (137 km) were relatively high in all
6 the seasons, most likely because R13 is in a reservoir of the Matsubara dam, where the water can reserve
7 more energy by the long water residence time, and R20 is in an area affected by geothermal springs.
8 Averaged values of salinity at R2 (4.5 km), R3 (10 km) and R4 (14.8 km) were over 0.1 psu in all seasons.

9 There is a typical tendency in the seasonal change of turbidity as shown in Fig. 2(c). In all seasons,
10 values in the downstream basin were higher than those in the middle and upstream basins. In the
11 downstream basin, there were no peak values in summer and winter, whereas values at R4 were the
12 highest in autumn and spring. Values at R13 in summer were extremely high (over 600 FTU). One of the
13 main possibilities is that, since R13 is in the lake behind the Matsubara dam, organic matter and a bloom
14 of phytoplankton increased drastically.

15 **3.2 Nitrogen and Phosphate**

16 Seasonal changes of T-N and T-P concentrations from July, 2011 to May, 2012 in the Chikugo River
17 are shown in Fig. 3. In all seasons, T-N and T-P concentrations increased gradually from upstream to
18 downstream. T-N and T-P concentrations in the Houman River were higher than those in the Chikugo
19 River. T-N concentrations in the Kusu River were also high. There are no evident seasonal changes of T-
20 N and T-P concentrations in summer, winter and spring. However, T-N concentrations in autumn were
21 higher than those in the other seasons.

22 **3.3 Iron**

23 Figure 4 indicates the relationship between averaged Fe concentrations in summer, autumn, winter
24 and spring at all the sites with spectrometry and those with ICP-MS ($r = 0.952$). We confirmed that the Fe
25 concentrations with spectrometry closely corresponded to those with ICP-MS. This indicates that the

1 analytical method of Fe with spectrophotometry is qualitatively reliable. We defined analyzed values with
2 spectrometry as dissolved Fe (D-Fe) in this paper and these data used for evaluating the Fe dynamics in
3 the Chikugo River. Figure 5 shows the seasonal changes in D-Fe concentrations at the sampling sites
4 analyzed with spectrometry. The dynamics of D-Fe in the river did not present a marked seasonal
5 variation, although D-Fe concentrations in the summer were the highest. D-Fe concentrations increased
6 gradually from the upstream to the middle basin, whereas the Fe concentration increased drastically in the
7 estuary and concentrations at the sites of R3 or R4 were extremely high compared to those in the middle
8 basin and upstream sites. Fe concentrations at R20 in the Kusu River were always high in the upstream
9 region, probably because this region is a geothermal spring area.

10 Figure 6 shows the analytical results of D-Fe (Fig. 6(a)) concentrations of surface and bottom waters
11 in estuary together with turbidity (Fig. 6(b)) on October, 2012. Both Fe concentrations and turbidity
12 values at R4 were higher than any other sites in the estuary.

13

14 **4. Discussion**

15 The Ministry of Land, Infrastructure, Transport and Tourism (MLIT) has monitored T-N and T-P
16 concentrations in the Chikugo River and the Houman River (Water Information System: web
17 <http://www1.river.go.jp/>), even though the sampling sites of the rivers are different. Fig. 7 shows T-N and
18 T-P concentrations analyzed in this study and averaged values of annual means from 2005 to 2011 in the
19 Chikugo River and the Houman River monitored by MLIT. The trends shown by N and P concentrations
20 in this study were almost the same as the previous data in Figs. 7(a) and 7(b). T-N and T-P concentrations
21 increased gradually from the upstream to the downstream and the concentrations in the Houman River
22 were relatively high. One of the possible reasons is that the land use changed from the upstream to the
23 downstream. The difference in the land use at all the sampling sites in the Chikugo Basin is shown in Fig.
24 8, which was arranged based on the data of National Land Numerical Information download service (Web
25 <http://nlftp.mlit.go.jp/ksj-e/index.html>) in 2006. We calculated catchment areas of all the sampling points,

1 and classified land uses into forest, river and lake, golf course, road and railway, building, waste land,
2 agricultural land, paddy field, and others based on the data. The ratios of the land use at all the sampling
3 sites were shown in Fig.8. The ratios of paddy fields, agricultural land and residential quarter in the
4 catchment area become larger from the upstream to the downstream. Paddy fields were divided from
5 other agricultural lands in Fig.8. It was also confirmed that the ratios of paddy fields, agricultural land and
6 residential quarter at R8a and R8b are high, corresponding to the concentrations of T-N and T-P at R8a
7 (29 km upstream from the river mouth) and R8b (41 km). Figure 9 shows the correlation of T-N and T-P
8 concentrations on both paddy field and agricultural land in the middle and upstream basins (R8-R23). As
9 Pearson's Product-moment Correlation Coefficients of T-N and T-P, and ratios of paddy field and
10 agricultural land are 0.904 ($P < 0.01$) and 0.816 ($P < 0.01$), respectively, the dynamics of N and P in the
11 Chikugo basin can be reasonably concluded to be affected by human activities.

12 Meanwhile, the trend shown by D-Fe concentrations was different from those of T-N and T-P (Fig. 3c
13 and Fig. 5). Although T-N and T-P concentrations became relatively large in the estuary, D-Fe
14 concentrations in the estuary are extremely high, compared to those in the middle basin. The obvious
15 peak of the highest Fe concentration was also observed at R3 or R4 in each season. The possible reason of
16 specific D-Fe dynamics in the Chikugo River is that supplied D-Fe is accumulated by the effect of
17 particles, such as particulate organic matter, included in suspended solids (SS) in the estuary. The
18 mechanism could be predicted as follows. Transported Fe from the upstream is adsorbed onto particles of
19 organic matter chemically and physically in the estuary. Adsorbed Fe, defined as particulate Fe (P-Fe), is
20 accumulated by the characteristic tide and wave action in the Ariake Sea. As P-Fe concentration increases,
21 D-Fe concentration is also suggested to increase because of the equilibrium between P-Fe and D-Fe in the
22 river. The difference between P-Fe and D-Fe is defined by size of molecules and D-Fe includes inorganic
23 Fe and organic Fe. As dissolved organic Fe is flocculated and become particle organic Fe, P-Fe
24 concentrations are related to D-Fe concentrations. If this hypothesis is correct, the characteristics of the
25 D-Fe concentration in estuary correspond to that of the turbidity.

1 In order to confirm the reliability of this predicted feature, we evaluated the dependence of T-N, T-P
2 and D-Fe on turbidity in estuary as shown in Fig. 10(a), Fig. 10(b) and Fig. 10(c), respectively. Turbidity
3 is not correlated with T-N concentration as Pearson's Product-moment Correlation Coefficient (r) is 0.060,
4 and correlation in Fig. 10(a) is not statistically significant ($P > 0.05$). Furthermore, the correlation
5 coefficient between turbidity and T-P ($r = 0.419$, $P < 0.01$) was smaller than that between turbidity and D-
6 Fe ($r = 0.547$, $P < 0.01$). This result indicates that turbidity is correlated with D-Fe concentration rather
7 than with T-N and T-P concentrations. Although the distribution of N and P concentrations has
8 previously been related to turbidity (SS) (Yokoyama et al., 2011), the trends in Fig. 10(a) and Fig. 10(b)
9 were slightly different. The assumed reason is that the observation sites of N and P concentrations were
10 also in the estuary of the Chikugo River, but only narrow area, which is 9-16 km apart from the river
11 mouth in the previous work. On the other hand, the correlation coefficient between turbidity and Fe
12 concentration is not so high. One of the reasons is suggested that D-Fe concentrations in Fig. 5 are not at
13 the river flow axes but at the banks of the river. It is expected that water at the flow axis is influenced by
14 the tide and waves stronger than water at a bank. Water sampling at the flow axis is better for evaluating
15 the dependence of tide and waves on water quality. The tendency of D-Fe distribution in Fig. 6(a) is
16 similar to that of turbidity distribution in Fig. 6(b). The relationship of Fe concentration between the
17 surface and bottom layers also almost corresponds to that of the turbidity values. Figure 11 indicates the
18 relationship between turbidity and Fe concentrations at both levels of the river water in the estuary in
19 October 2012. We evaluated the relationship between the Fe concentrations and turbidity (Fig. 11). The
20 correlation coefficient was 0.767, which is higher than that in Fig. 10(c). These results indicate that the
21 distribution of Fe concentration is related to the turbidity distribution.

22 Suzuki et al. (2007, 2009) elucidated the dynamics of particulate organic matter (POM) in ETM in
23 spring and in summer. The sampling sites of these studies were almost the same as those in Fig. 5 except
24 for some additional sites in the previous studies. As turbidity showed a strong positive correlation with
25 particle organic carbon (POC), Suzuki et al. (2007, 2009) confirmed that POC were accumulated in the

1 estuary together with mineral particles. POM dynamics were evaluated both at neap tide and spring tide
2 in the studies. It was found that phytoplankton was distributed from the surface and accumulated detritus
3 in the bottom was suspended at spring tides which possessed strong-mixing and high-turbidity conditions.
4 They also suggested that detritus was derived from both phytoplankton and terrestrial C₃ plants. As
5 terrestrial plants are included in the particulate matter, Fe is able to adsorb onto particles and also
6 combine with organic matter as a complex, such as iron-humate. It is suggested that the predicted
7 mechanism is correct and the change of D-Fe concentration corresponds to that of turbidity.

8 Redfield (1958) analyzed the ratio of atoms in plankton from a variety of places. The results indicate
9 that atoms of phosphorus, nitrogen and carbon are present on the average in the ratios 1: 16: 106. We also
10 found that D-Fe did not seem to be a limiting factor for the primary production from the viewpoint of the
11 Redfield ratio (N:P:Fe = 16:1:0.05 (Marchin et al., 1989)) both in the ETM region (R4) and the middle
12 basin (R11, 76 km upstream from the river mouth) as listed in Table 2. However, as Fe dynamics in the
13 Chikugo basin are really characteristic and related to dynamics of particles in the river and estuary
14 (turbidity), it is suggested that Fe dynamics may have a large influence in forming the distinctive
15 ecosystem in the Chikugo basin. Even though we determined the characteristics of the Fe, N and P
16 dynamics in the Chikugo River, especially in the estuary, further investigation, such as the difference in
17 neap tide and spring tide and the difference in chemical forms of Fe, N and P, should be conducted in
18 future research. Furthermore, the mobilization of iron-reductive environment and the dynamics of
19 dissolved organic carbon (DOC) were not investigated in this study, although these were related to the Fe
20 dynamics directly. We should evaluate them in future work.

21

22 **Conclusions**

23 Fe dynamics in the Chikugo Basin were investigated in this study for understanding the relationship
24 between Fe and the characteristic ecosystem in the Chikugo River and the Ariake Sea. Analysis of D-Fe,
25 T-N and T-P concentrations, and measurements of water temperature, salinity and turbidity were carried

1 out at 29 sites of the Chikugo Basin once a month from June 2011 to May 2012. We found that D-Fe
2 distributions in the river were specific and inherently different from N and P distributions throughout the
3 year. Although N and P concentrations increased from the upstream region to the estuary gradually, D-Fe
4 concentration increased sharply at the site 10 km from the river mouth and decreased again near the
5 estuary mouth. As this trend corresponds to the trend of turbidity, supposed reason of specific Fe
6 dynamics is that Fe is accumulated by the effect of particulate organic matter in the estuary. It is
7 suggested that this Fe dynamics is also related to the characteristic ecosystem in the Ariake Sea.

8

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14

1 **Captions**

2 Table 1 Sampling dates

3 Table 2 Relationship of annual averaged concentrations and ratios between dissolved inorganic nitrogen
4 (DIN), phosphate (PO₄-P) and D-Fe at R4 and R11

5

6 Fig. 1 Sampling sites in the Chikugo River and the Ariake Sea. Numeric characters in each parenthesis is
7 the distance from the river mouth (km).

8 Fig. 2 Seasonal change of (a) temperature, (b) salinity and (c) turbidity along the Chikugo River and
9 tributaries.

10 Fig. 3 Seasonal changes of T-N and T-P concentrations in the Chikugo River.

11 Fig. 4 Relationship between averaged Fe concentrations in summer, autumn, winter and spring at all the
12 sites with spectrometry and those with ICP-MS.

13 Fig. 5 Seasonal changes of Fe concentrations at the sampling sites of the Chikugo River analyzed with the
14 spectrometer.

15 Fig.6 Fe concentrations and turbidity in the estuary of the Chikugo River in October, 2012. (a) D-Fe, (b)
16 Turbidity.

17 Fig. 7 Comparison of T-N and T-P concentrations analyzed in this study with the previous data (Water
18 Information System: web <http://www1.river.go.jp/>), which are averaged values of the annual mean
19 from 2005 to 2011 in the Chikugo River and the Houman River. (a) T-N, (b) T-P.

20 Fig. 8 Differences of land uses at all the sampling sites in the Chikugo basin.

21 Fig. 9 Dependence of (a) T-N and (b) T-P concentrations on the ratio of paddy field and agriculture in
22 estuary (R2-R7), and the middle and upstream basins (R8-R23, except for R18, R19 and R20).

23 Fig. 10 Dependence of T-N, T-P and Fe concentrations on turbidity in estuary (R2-R7).

24 Fig. 11 Relationship between turbidity and D-Fe concentration in ETM of the Chikugo River on October,
25 2012.

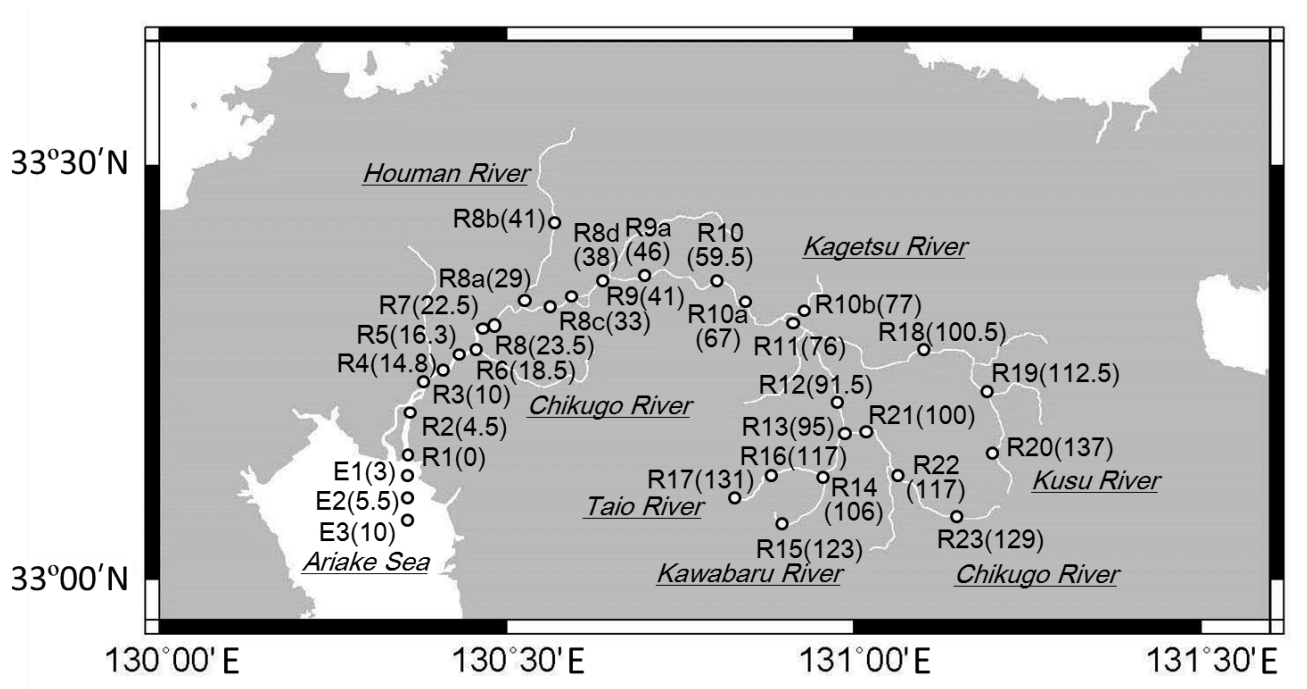
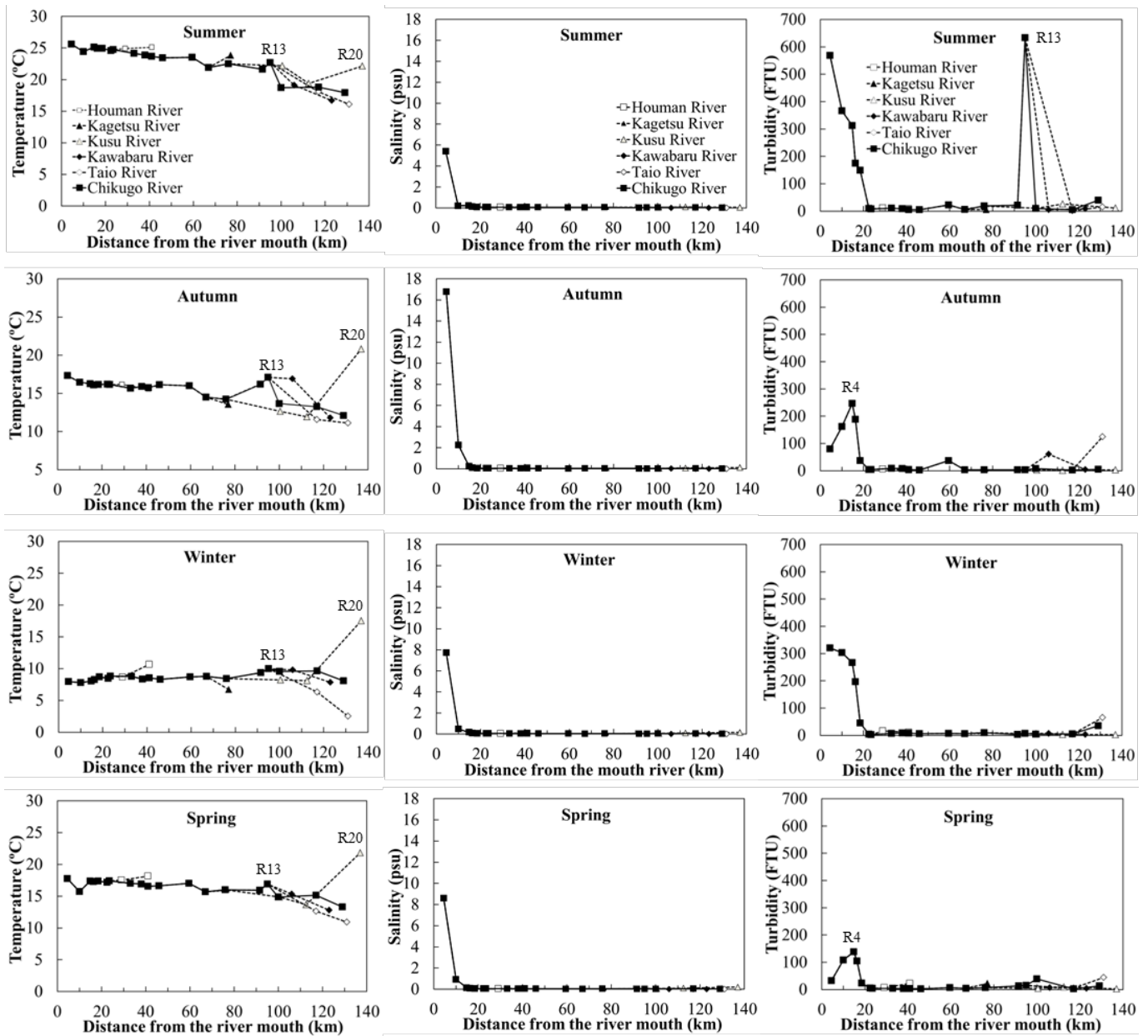


Fig. 1

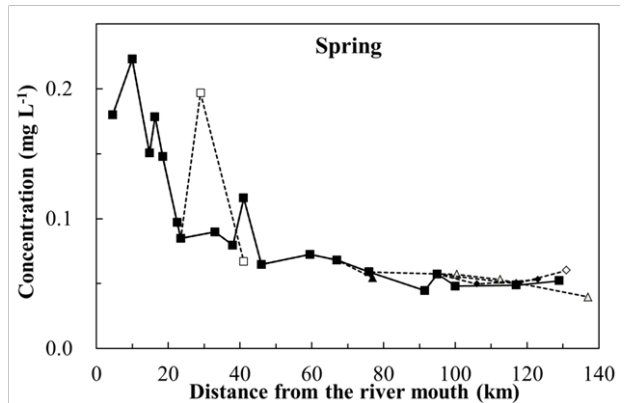
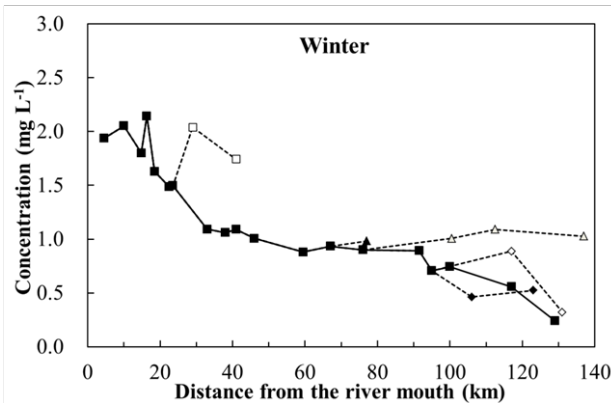
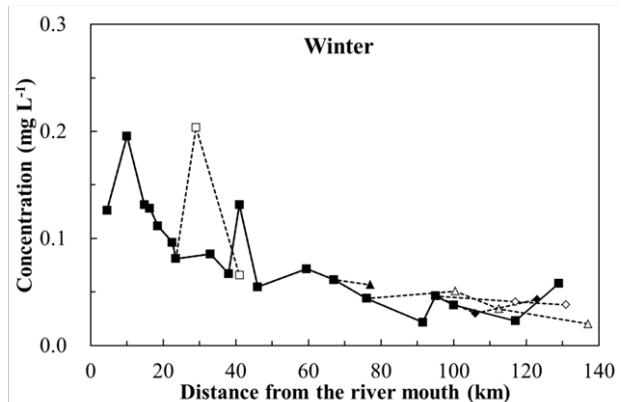
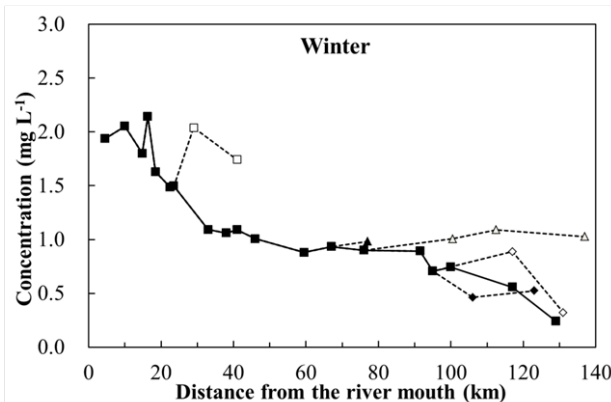
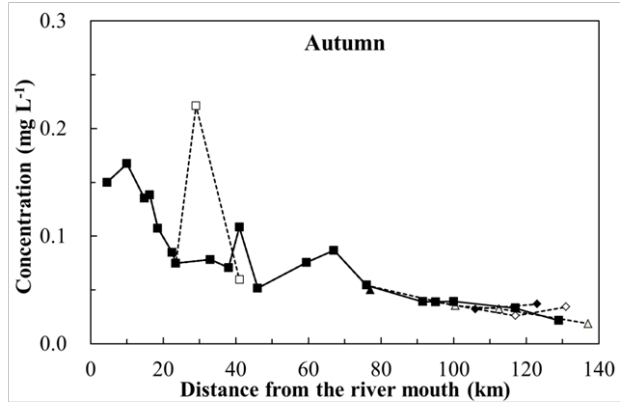
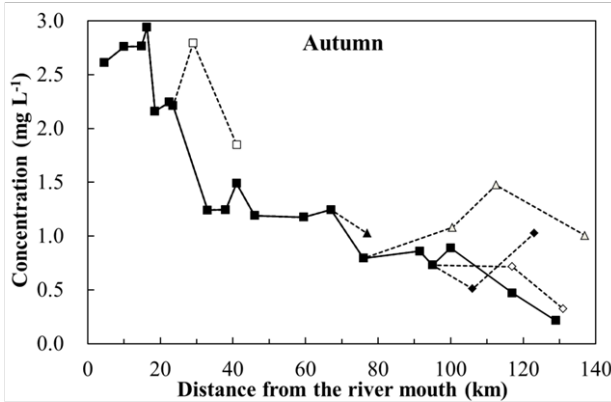
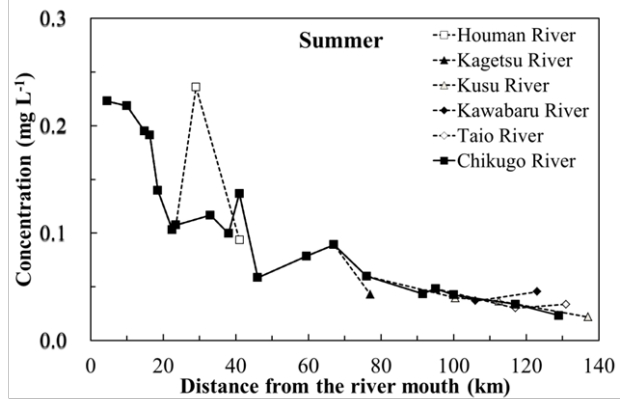
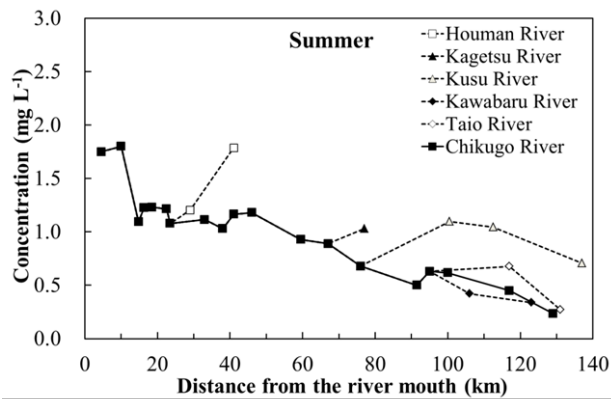


(a) temperature

(b) salinity

(c) turbidity

Fig. 2



(a) T-N

(b) T-P

Fig. 3

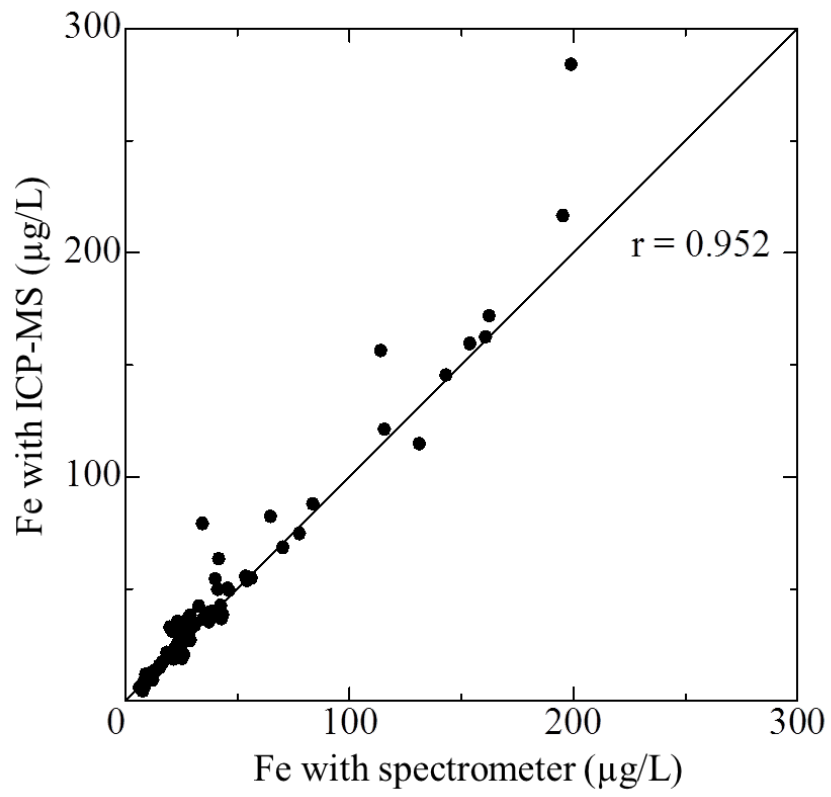


Fig. 4

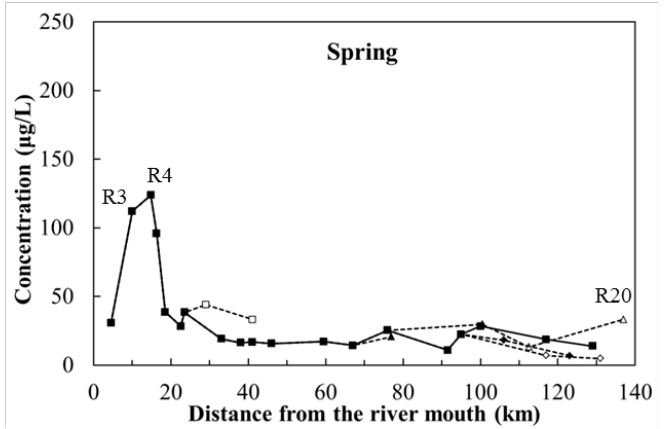
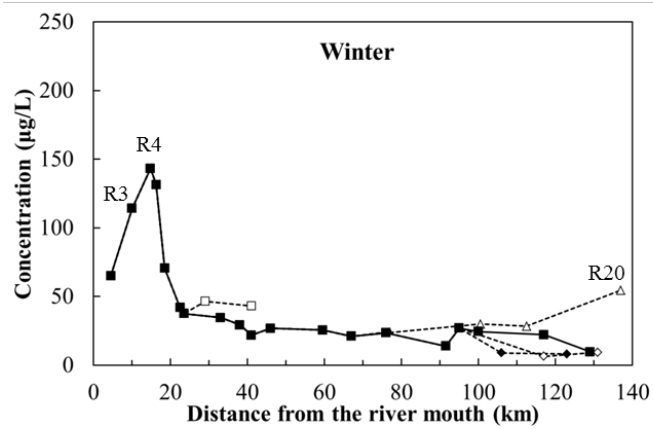
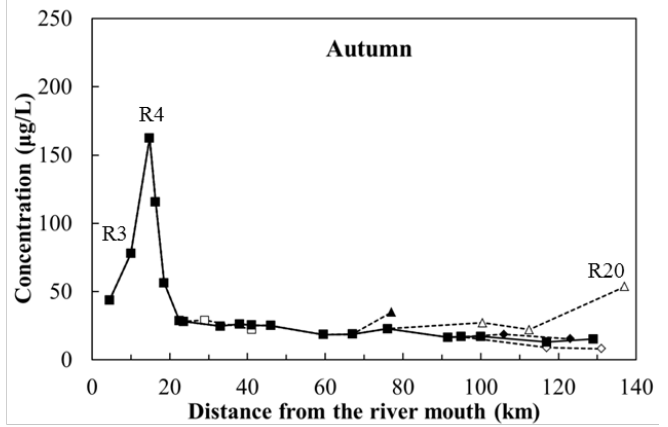
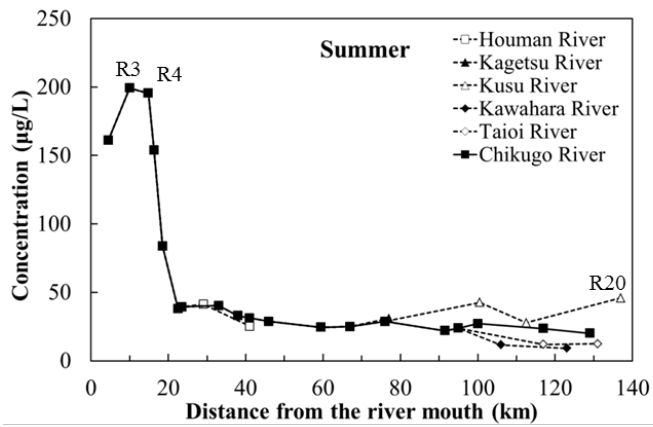
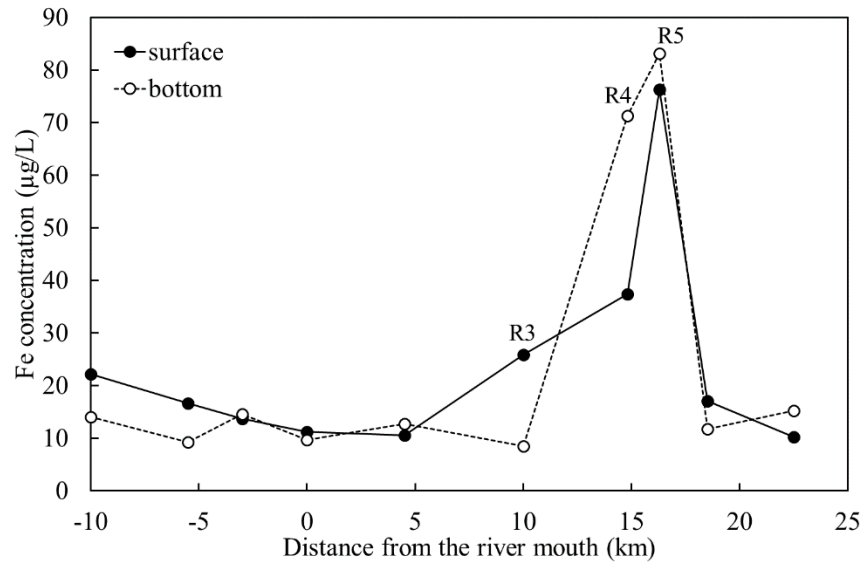
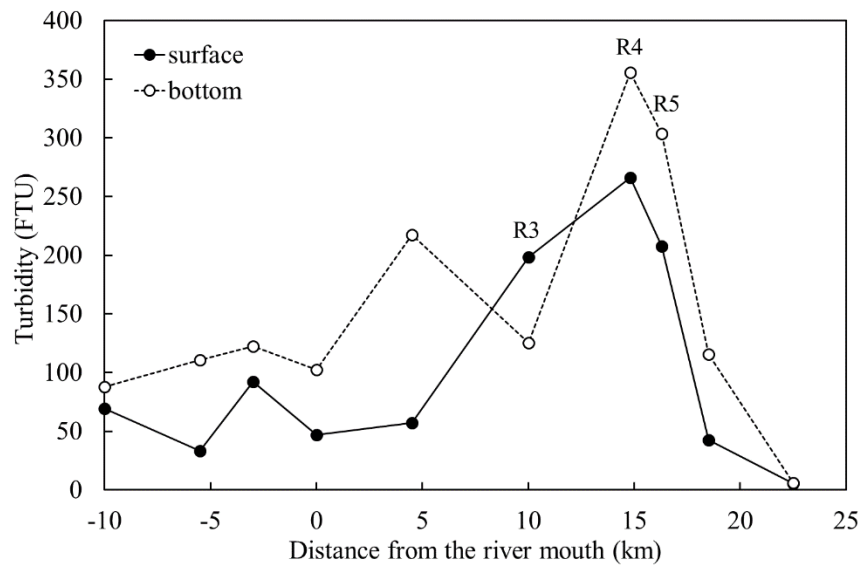


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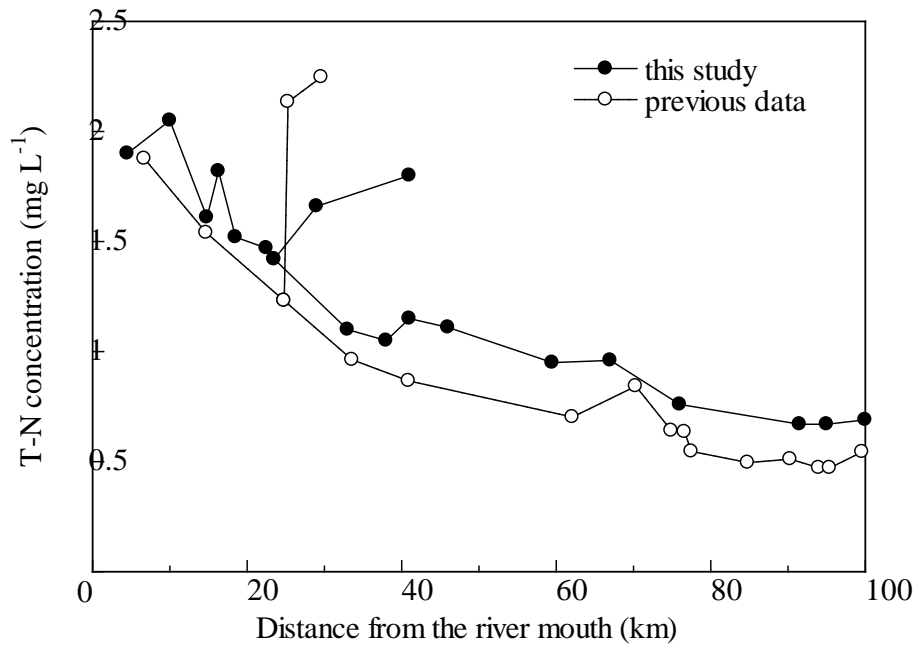


(a) D-Fe

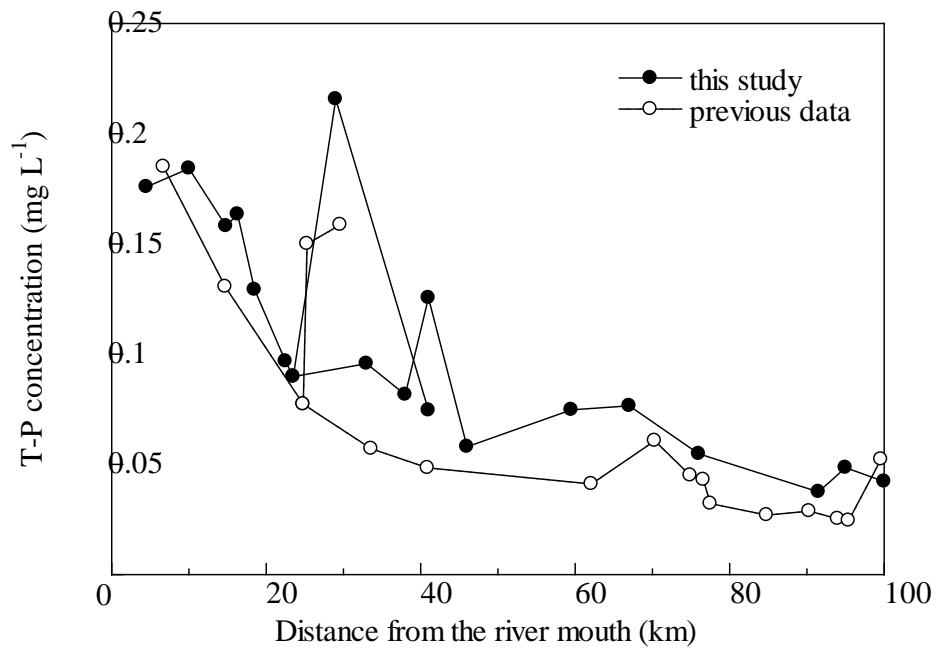


(b) Turbidity

Fig.6



(a) T-N



(b) T-P

Fig. 7

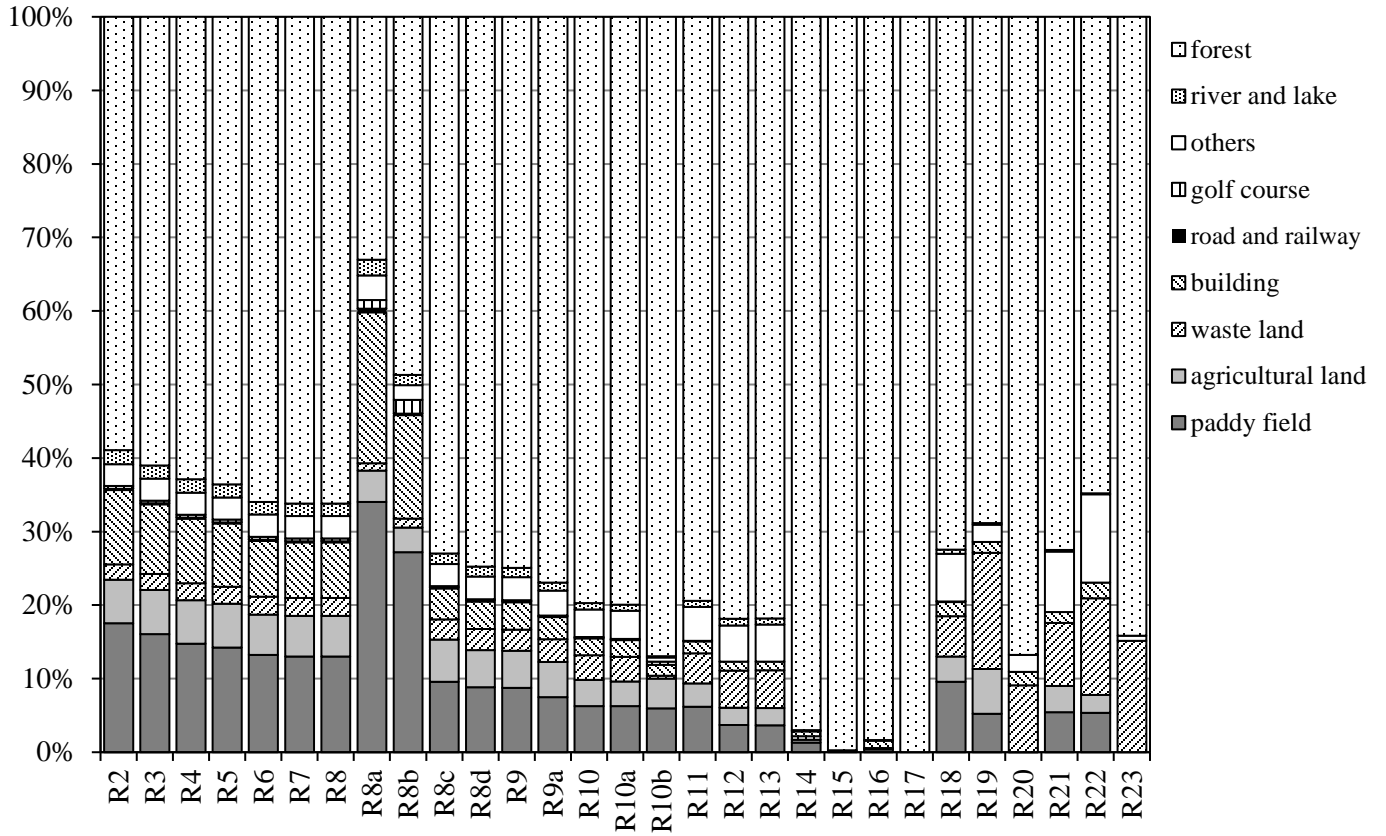
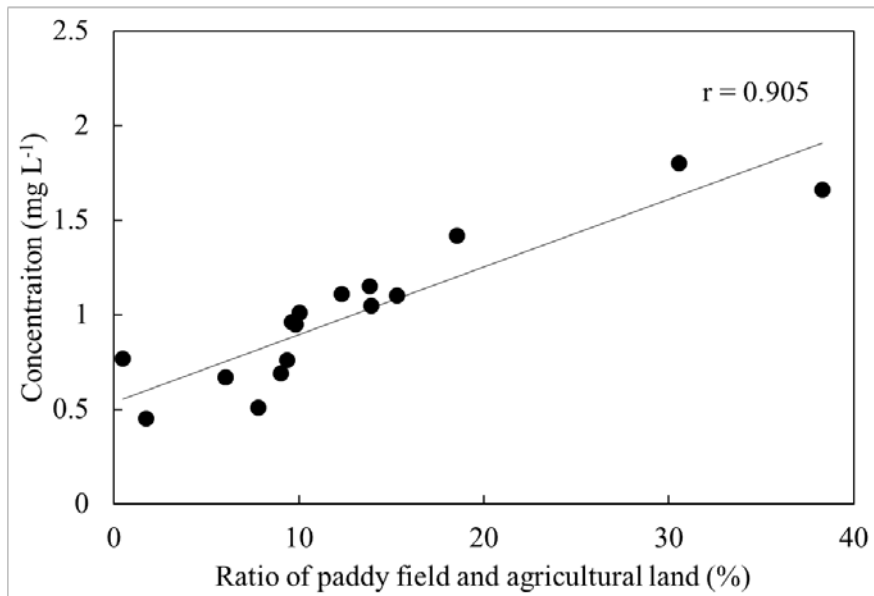
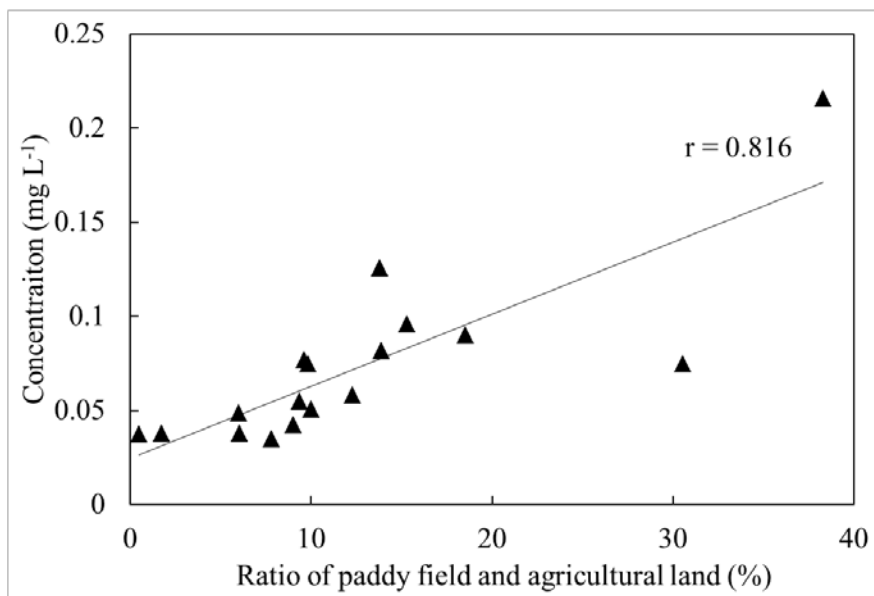


Fig. 8

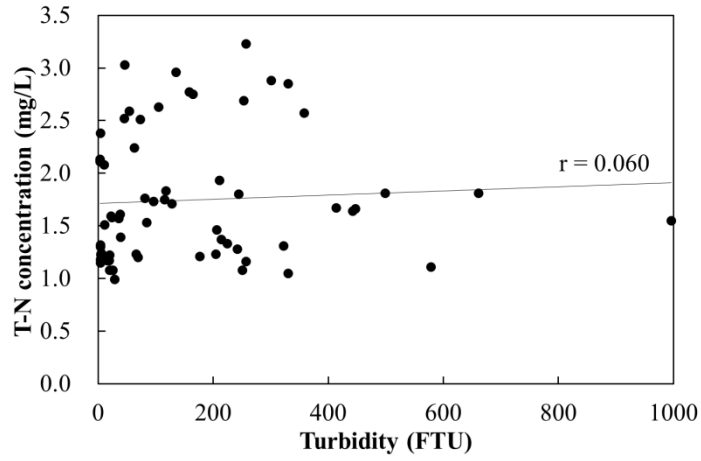


(a) T-N

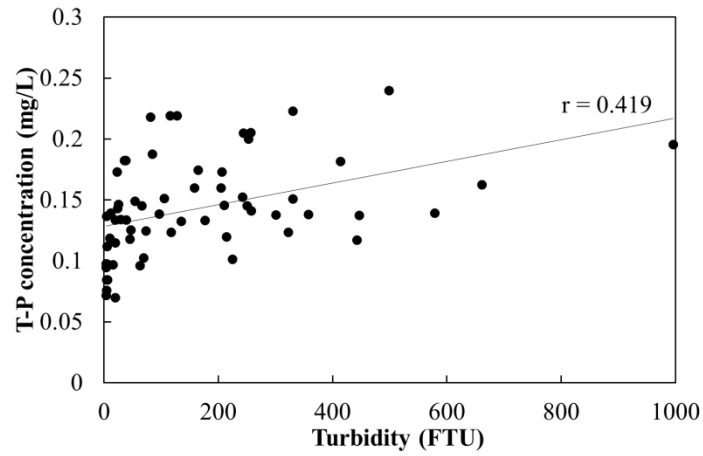


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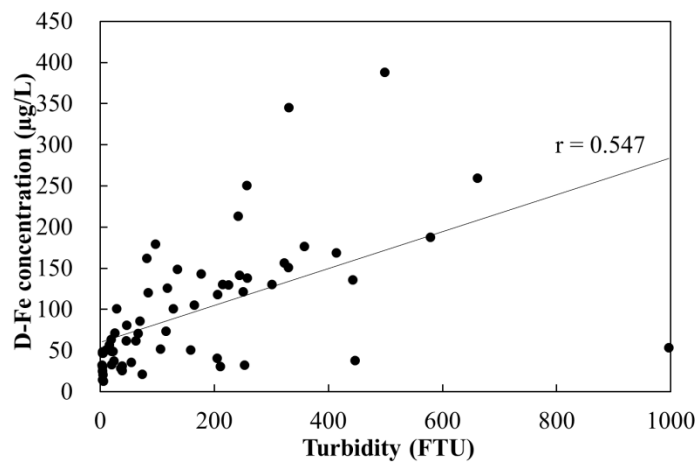
Fig. 9



(a) T-N



(b) T-P



(c) D-Fe

Fig. 10

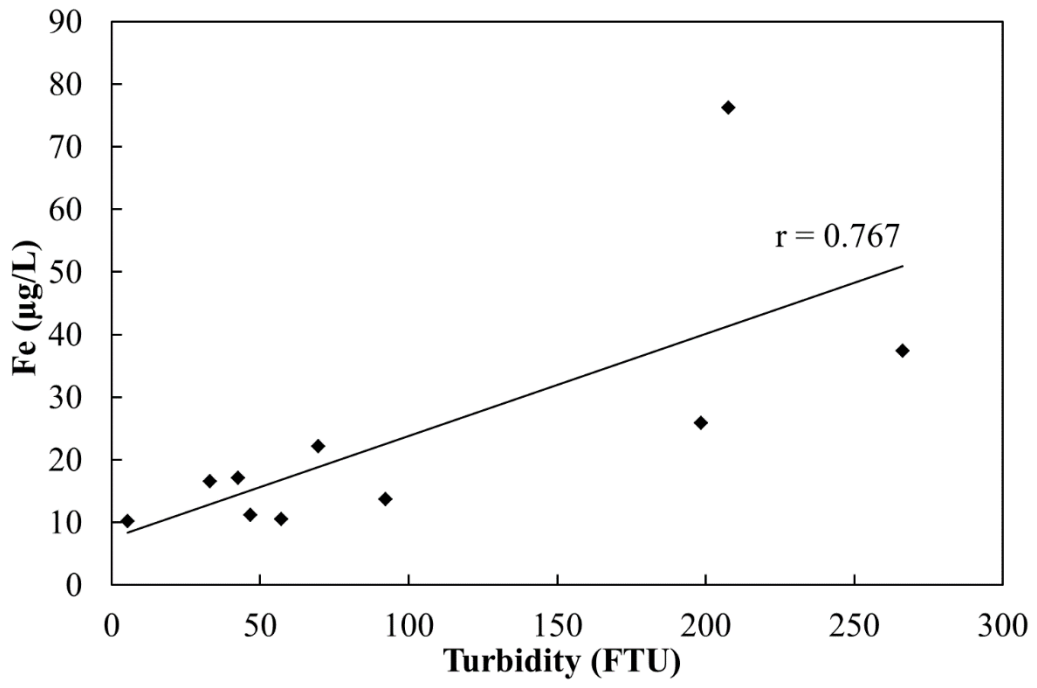


Fig. 11