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

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Abstract

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

1. Introduction

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

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

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

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

2. Methods

2.1 Sampling sites and methods

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

Water temperature, salinity and turbidity were measured with the multi water quality meters at the same points of water sampling. The types of the meters used were AAQ-RINKO (JFE Advantech Co., Ltd.) in July 4 and 5, 2011, DO meter 55 (YSI Nanotech) used in August 27, 30 and 31, 2011, and RINKO-Profiler (JFE Advantech Co., Ltd.) in August 27, 28 and 30, 2011 and from September 2011 to May 2012. The operations of the water quality meters as well as water sampling in the estuary were carried out within four hours before and after high tide for adjusting the observation condition. We also conducted the operations at the same place of each sampling site except for the sites of estuarine basin (R2-R7) in March 2012 and April 2012 (Table 1).

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

2.2 Analytical methods

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

3. Results

3.1 Temperature, salinity and turbidity

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

July 2011 to September 2011), autumn (from October 2011 to November 2011), winter (from December 2011 to February 2012) and spring (from March 2012 to May 2012). Averaged temperatures of all the 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 spring. Water temperature increased gradually from the upstream to the downstream except in winter. Temperatures at R13 (95 km upstream from the river mouth) and R20 (137 km) were relatively high in all the seasons, most likely because R13 is in a reservoir of the Matsubara dam, where the water can reserve more energy by the long water residence time, and R20 is in an area affected by geothermal springs. 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.

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

3.2 Nitrogen and Phosphate

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

3.3 Iron

Figure 4 indicates the relationship between averaged Fe concentrations in summer, autumn, winter and spring at all the sites with spectrometry and those with ICP-MS ($r = 0.952$).We confirmed that the Fe concentrations with spectrometry closely corresponded to those with ICP-MS. This indicates that the analytical method of Fe with spectrophotometry is qualitatively reliable. We defined analyzed values with spectrometry as dissolved Fe (D-Fe) in this paper and these data used for evaluating the Fe dynamics in the Chikugo River. Figure 5 shows the seasonal changes in D-Fe concentrations at the sampling sites analyzed with spectrometry. The dynamics of D-Fe in the river did not present a marked seasonal variation, although D-Fe concentrations in the summer were the highest. D-Fe concentrations increased gradually from the upstream to the middle basin, whereas the Fe concentration increased drastically in the estuary and concentrations at the sites of R3 or R4 were extremely high compared to those in the middle basin and upstream sites. Fe concentrations at R20 in the Kusu River were always high in the upstream region, probably because this region is a geothermal spring area.

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

4. Discussion

The Ministry of Land, Infrastructure, Transport and Tourism (MLIT) has monitored T-N and T-P concentrations in the Chikugo River and the Houman River (Water Information System: web http://www1.river.go.jp/), even though the sampling sites of the rivers are different. Fig. 7 shows T-N and T-P concentrations analyzed in this study and averaged values of annual means from 2005 to 2011 in the Chikugo River and the Houman River monitored by MLIT. The trends shown by N and P concentrations in this study were almost the same as the previous data in Figs. 7(a) and 7(b). T-N and T-P concentrations increased gradually from the upstream to the downstream and the concentrations in the Houman River were relatively high. One of the possible reasons is that the land use changed from the upstream to the downstream. The difference in the land use at all the sampling sites in the Chikugo Basin is shown in Fig. 8, which was arranged based on the data of National Land Numerical Information download service (Web http://nlftp.mlit.go.jp/ksj-e/index.html) in 2006. We calculated catchment areas of all the sampling points, and classified land uses into forest, river and lake, golf course, road and railway, building, waste land, agricultural land, paddy field, and others based on the data. The ratios of the land use at all the sampling sites were shown in Fig.8. The ratios of paddy fields, agricultural land and residential quarter in the catchment area become larger from the upstream to the downstream. Paddy fields were divided from other agricultural lands in Fig.8. It was also confirmed that the ratios of paddy fields, agricultural land and residential quarter at R8a and R8b are high, corresponding to the concentrations of T-N and T-P at R8a (29 km upstream from the river mouth) and R8b (41 km). Figure 9 shows the correlation of T-N and T-P concentrations on both paddy field and agricultural land in the middle and upstream basins (R8-R23). As Pearson's Product-moment Correlation Coefficients of T-N and T-P, and ratios of paddy field and agricultural land are 0.904 ($P < 0.01$) and 0.816 ($P<0.01$), respectively, the dynamics of N and P in the Chikugo basin can be reasonably concluded to be affected by human activities.

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

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

Suzuki et al. (2007, 2009) elucidated the dynamics of particulate organic matter (POM) in ETM in spring and in summer. The sampling sites of these studies were almost the same as those in Fig. 5 except for some additional sites in the previous studies. As turbidity showed a strong positive correlation with particle organic carbon (POC), Suzuki et al. (2007, 2009) confirmed that POC were accumulated in the estuary together with mineral particles. POM dynamics were evaluated both at neap tide and spring tide in the studies. It was found that phytoplankton was distributed from the surface and accumulated detritus in the bottom was suspended at spring tides which possessed strong-mixing and high-turbidity conditions. They also suggested that detritus was derived from both phytoplankton and terrestrial C_3 plants. As terrestrial plants are included in the particulate matter, Fe is able to adsorb onto particles and also combine with organic matter as a complex, such as iron-humate. It is suggested that the predicted mechanism is correct and the change of D-Fe concentration corresponds to that of turbidity.

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

Conclusions

Fe dynamics in the Chikugo Basin were investigated in this study for understanding the relationship between Fe and the characteristic ecosystem in the Chikugo River and the Ariake Sea. Analysis of D-Fe, T-N and T-P concentrations, and measurements of water temperature, salinity and turbidity were carried out at 29 sites of the Chikugo Basin once a month from June 2011 to May 2012. We found that D-Fe distributions in the river were specific and inherently different from N and P distributions throughout the year. Although N and P concentrations increased from the upstream region to the estuary gradually, D-Fe concentration increased sharply at the site 10 km from the river mouth and decreased again near the estuary mouth. As this trend corresponds to the trend of turbidity, supposed reason of specific Fe dynamics is that Fe is accumulated by the effect of particulate organic matter in the estuary. It is suggested that this Fe dynamics is also related to the characteristic ecosystem in the Ariake Sea.

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References

Dong, D., Koga, K., Ittisukananth, P., Nishimura, Y., Yamaguchi, H., 2008. Study on characteristic of water quality in down area of the Chikugo River, Environmental Systems Research, 36, 427-435.

Fujii, M., Sadaki, A., Otomo, S., Watanabe, T. and Omura, T., 2006. Spatial and seasonal distributions of dissolved organic matter and iron in Matsushima Bay, Japan, Journal of Japan Society on Water Environment, 29(3), 169-176.

Gledhill, M. and Buck, K. N., 2012. The organic complexation of iron in the marine environment: a review, Frontiers in Microbiology, 3, 69.

Kasai, A., Kurikawa, Y., Ueno, M., Robert, D. and Yamashita, Y., 2010. Salt-wedge intrusion of seawater and its implication for phytoplankton dynamics in the Yura Estuary, Japan. Estuarine, Coastal and Shelf Science, 86, 408-414.

Kondo, Y., Takeda, S. and Furuya, K., 2012. Distinct trends in dissolved Fe speciation between shallow and deep waters in the Pacific Ocean, Marine Chemistry, 134-135, 18-28.

Koriyama, M., Hayami, Y., Koga, A., Yamamoto, K., Isnasetyo, A., Hamada, T., Yoshino, K., Katano, T. and Yakaguxhi, S., 2013. Seasonal variations of water column nutrients in the inner area of Ariake Bay, Japan: the role of muddy sediments. Environmental Monitoring and Assessment, 185, 6831-6846.

Martin J. H., Coale K. H., Johnson K. H.、Fitzwater S. E., Gordon R. M., Tanner S. J., Hunter C. N., Elrod V. A., Nowicki J. L., Coley T. L., Barber R. T., Lindley S., Watson A. J., Van Scoy K., Law C. S., Liddicoat M. I., Ling R., Stanton T., Stockel J., Collins C., Anderson A., Bidigare R., Ondrusek M., Latasa M., Millero F. J., Lee K., Yao W., Zhang J. Z., Friederich G., Sakamoto C., Chavez F., Buck K., Kolber Z., Greene R., Falkowski P., Chisholm S. W., Hoge F., Swift R., Yungel J., Turner

S., Nightingale P., Hatton A., Liss P. & Tindale N. W. 1994. Testing the iron hypothesis in ecocystems of the equatorial Pacific Ocean. *Nature*, **371**, 123-129.

Martin J. H. & Fitzwater S. E. 1988. Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. Nature, **331**, 341-343.

Martin, J. H., Gordon, R. M., Fitzwater, S. E. & Broenkow, W. W. 1989. Vertex: phytoplankton/iron studies in the Gulf of Alaska, 36(5), 649-680.

Matsunaga, K., Igarashi, K., Fukase, S. and Tsubota, H., 1984. Behavior of organically-bound iron in seawater of estuaries, Estuarine, Coastal and Shelf Science, 18 (6), 615-622.

Matsunaga, K., Nishioka, J., Kuma, K., Toya, K. And Suzuki, Y., 1998. Riverine input of bioavailable iron supporting phytoplankton growth in Kesennuma Bay (Japan), Water Research, 32 (11), 3436-3442.

Nagai, T., Imai, A., Matsushige, K., Yokoi, K., Fukushima, T., 2007. Dissolved iron and its speciation in a shallow eutrophic lake and its inflowing rivers, Water Research, 41(4), 775-784

Nieldsdóttir, M. C., Bibby, T. S., Moore, C. M., Hinz, D. J., Sanders, R., Whitehouse, M., Korb. R., Achterberg, E. P., 2012. Seasonal and special dynamics of iron availability in the Scotia Sea,

Nishioka, J., Ono, T., Saito, H., Nakatsuka, T. Takeda, S., Yoshimura, T., Suzuki, K., Kuma, K., Nakabayashi, S., Tsumune, D., Mitsudera, H., Johnson, W. K., Tsuda, A., 2007. Iron supply to the western subarctic Pacific: Importance of iron export from the Sea of Okhotsk, 112, C10012.

Nishioka, J., Ono, T., Saito, H., Sakaoka, K. and Yoshimura, T., 2011. Oceanic iron supply mechanisms which support the spring diatom bloom in the Oyashio region, western subarctic Pacific, 116, C02021.

Öztürk M. and Bizsel N., 2003. Iron speciation and biogeochemistry in different nearshore waters, Marine Chemistry, 83, 145-156.

Redfield, A. C., 1958. The biochemical control of chemical factors in the environment, American Scientist, 46(3), 205-221.

Shiraiwa, T. eds., 2010. Final reports of the Amur Okhotsk project 2005-2009. Report on Amur-Okhotsk Project No.6. 3-19.

Shoji, J., Suzuki, K.W., Tanaka, M., 2006. Effect of tide and river flow on physical and biological properties in the estuarine turbidity maximum of the Chikugo River estuary during spring in 2005: evaluation as a nursery for the estuarine-dependent fish, Japanese seaperch Lateolabrax japonicas. Bulletin of the Japanese Society of Fisheries Oceanography, 70, 31-38.

Suzuki, W. K., Sugimoto, R., Kasai, A., Shoji, J., Nakayama, K., Tanaka, M., 2007. Dynamics of particulate organic matter in the estuarine turbidity maximum of the Chikugo River, Ariake Sea, in spring. Bulletin of the Japanese Society of Fisheries Oceanography, 71, 190-198.

Suzuki, W. K., Sugimoto, R., Kasai, A., Nakayama, K., Tanaka, M., 2009. Dynamics of particulate organic matter in the estuarine turbidity maximum of the Chikugo River estuary, Ariake Sea, in summer: Influence of the fluctuation of freshwater discharge. Bulletin of the Japanese Society of Fisheries Oceanography, 73, 149-160.

Tomioka, N., Komatsu, K., Koshikawa, M. K., Imai, A., Matsushige, K., Inaba, K., 2010. Long-Term Monitoring of Copper and Iron in the Surface Water of Lake Kasumigaura, Japan. BUNSEKI KAGAKU, 59(12), 1169-1174.

Tsutsumi, H., 2012. Mechanism and causes of large-scale red tides in the inner part of Ariake Bay, Bulletin on Coastal Oceanography, 49(2), 165-174.

Yamamoto, M., Fukushima, M., Liu, D., 2012. The Effect of Humic Substances on Iron Elution in the Method of Restoration of Seaweed Beds using Steelmaking Slag, ISIJ International, 52, 1909-1913.

Yamashita, Y., Tanaka, M. eds., 2008. Linkage of forests, rivers and coasts and biological production in estuarine and coastal waters, Kouseisya-Kouseikaku, 147.

Yokoyama, K., Miyazaki, K., Kouno, S., 2008. Field measurement of the turbidity maximum movement in the Chikugo River estuary and the Ariake Sea, Proceedings of hydraulic engineering, JSCE, 52, 1339-1344 (in Japanese).

Yokoyama, K., Nomaguchi, Y., Yamamoto, K., Okamura, K., Kodama, M., 2010. Temporal variation of phytoplankton in the highly turbid Chikugogawa Estuary, J.JSCE, Ser.B2, Coastal Engineering, 66(1), 2006-1010 (in Japanese).

Yokoyama, K., Iwatsuki, A., Kodama, M., Okamura, K., Yamamoto, K., Ikenoya, N., 2011. Nutrient distribution in the highly turbid Chikugo River estuary in the early spring of 2010, J.JSCE, Ser.B2, Coastal Engineering, 67(2), I_901-I_905.

Captions

Table 1 Sampling dates

Table 2 Relationship of annual averaged concentrations and ratios between dissolved inorganic nitrogen (DIN), phosphate (PO_4-P) and D-Fe at R4 and R11

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

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

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

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

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

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

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

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

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

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

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

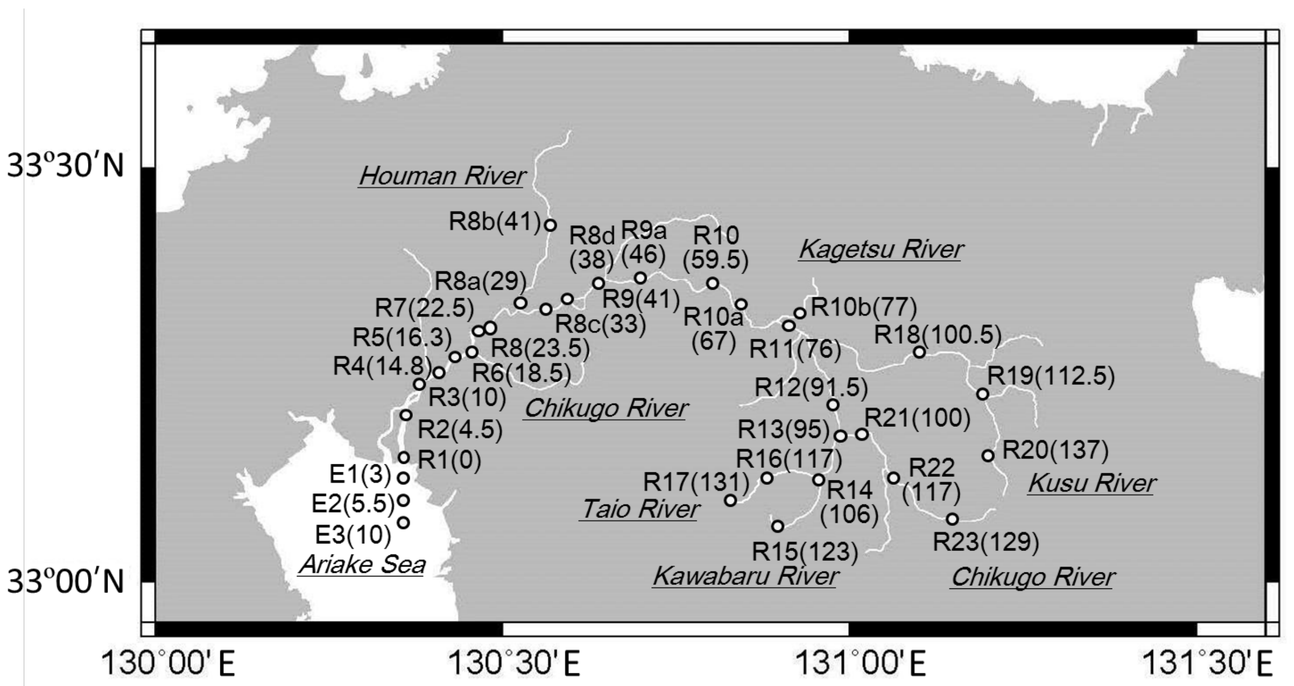
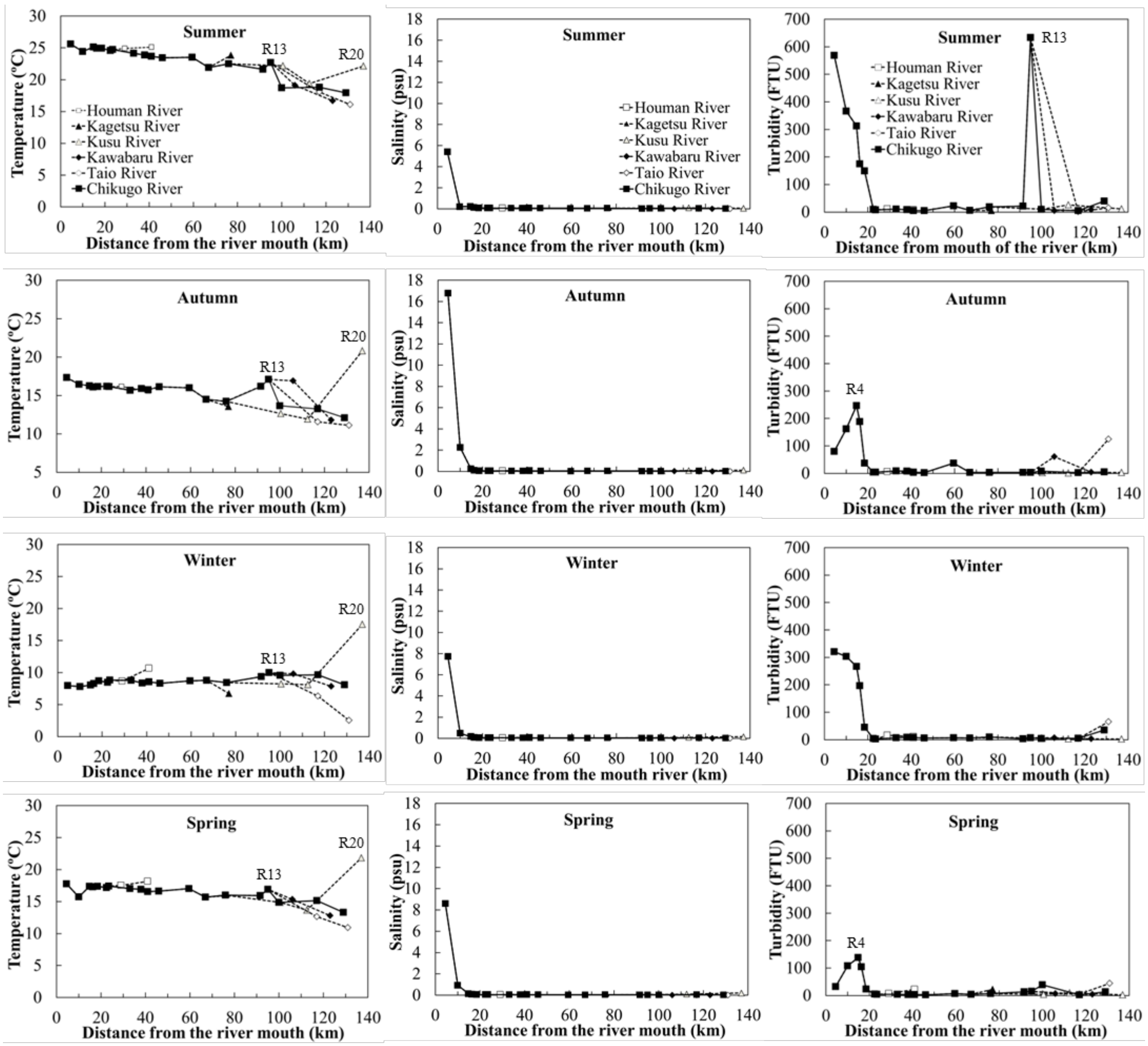
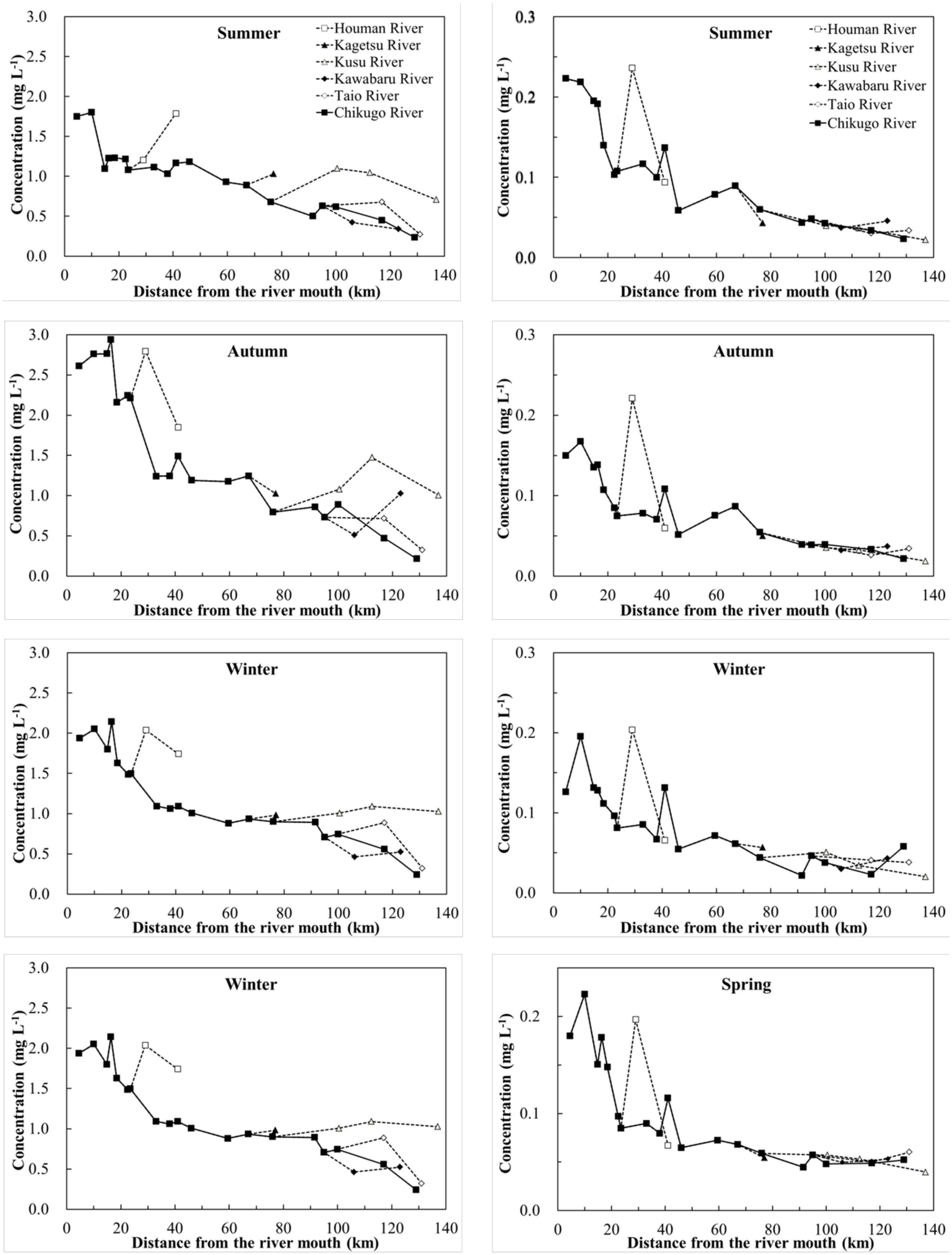

33°30′N
33°00′N
130°00′E
130°30′E
131°00′E
131°30′E
Houman River
Kagetsu River
Chikugo River
Taio River
Kawabaru River
Kusu River
Chikugo River
Ariake Sea
R8b(41)
R8d (38)
R9a (46)
R10 (59.5)
R8a(29)
R7(22.5)
R9(41)
R8c(33)
R10a (67)
R10b(77)
R5(16.3)
R8(23.5)
R11(76)
R18(100.5)
R4(14.8)
R6(18.5)
R3(10)
R12(91.5)
R19(112.5)
R2(4.5)
R13(95)
R21(100)
R1(0)
R16(117)
R20(137)
E1(3)
R17(131)
R14 (106)
R22 (117)
E2(5.5)
E3(10)
R15(123)
R23(129)

Fig. 1



(a) temperature (b) salinity (c) turbidity

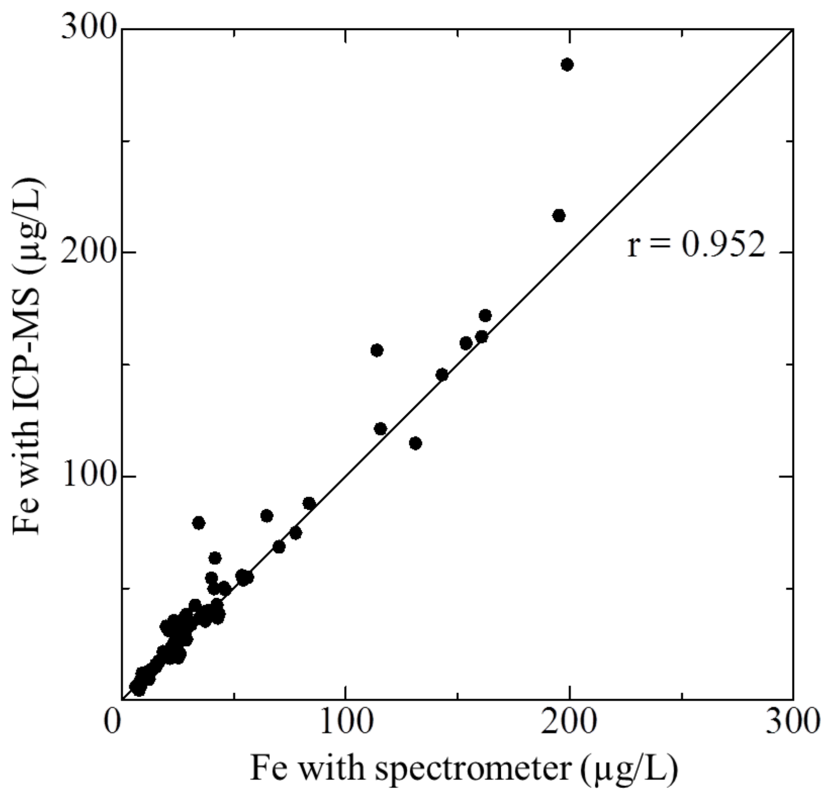
Fig. 2


Summer
Houman River
Kagetsu River
Kusu River
Kawabaru River
Taio River
Chikugo River
Autumn
Winter
Winter
Spring
Concentration (mg L-1)
Distance from the river mouth (km)

(a) T-N

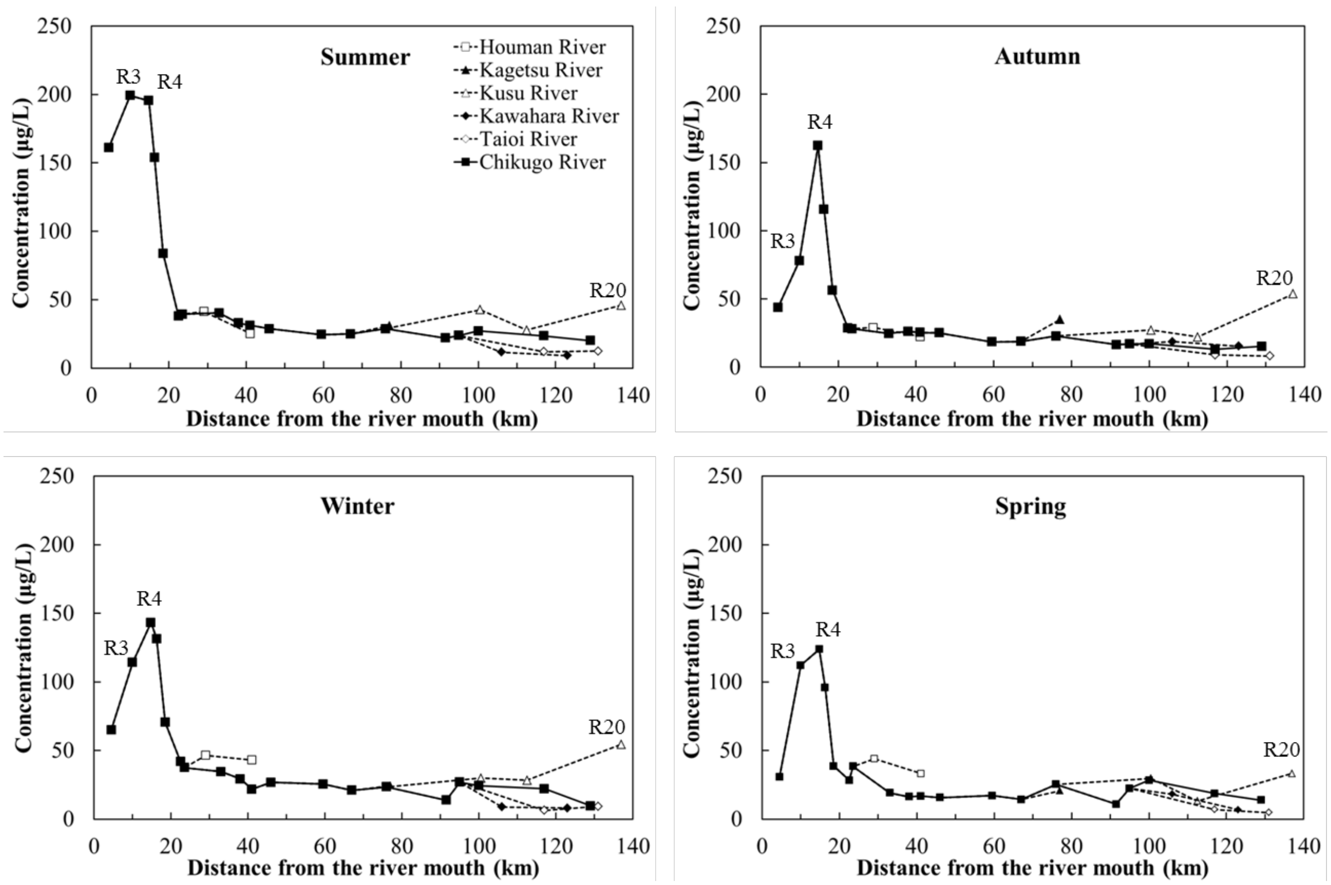
(b) T-P

Fig. 3



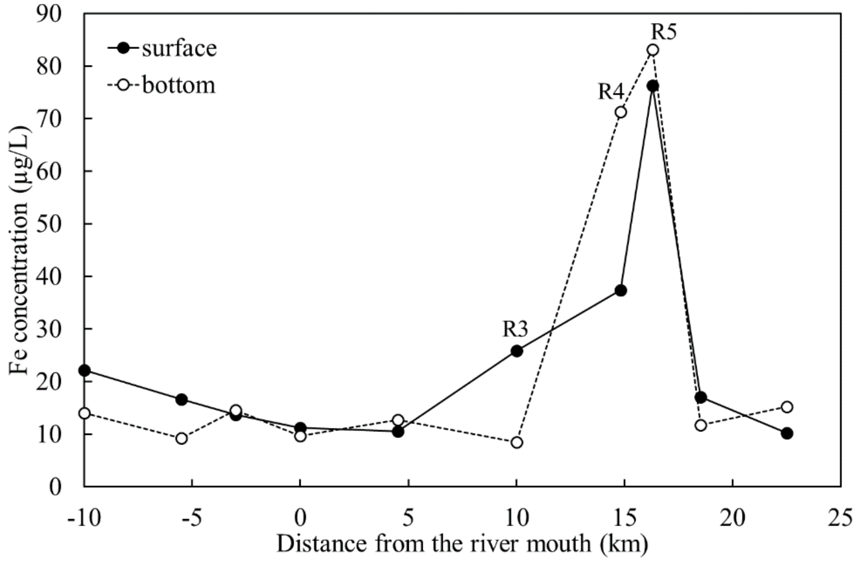
300
200
100
0
100
200
300
r = 0.952
Fe with ICP-MS (μg/L)
Fe with spectrometer (μg/L)

Fig. 4

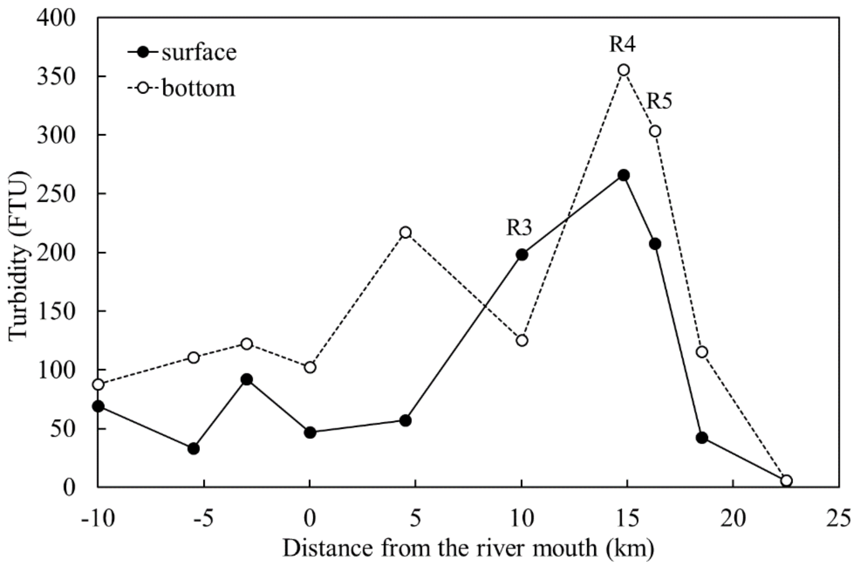


Summer
Autumn
Winter
Spring
Houman River
Kagetsu River
Kusu River
Kawahara River
Taioi River
Chikugo River
R3
R4
R20
Concentration (µg/L)
Distance from the river mouth (km)
0
50
100
150
200
250
0
20
40
60
80
100
120
140

Fig. 5

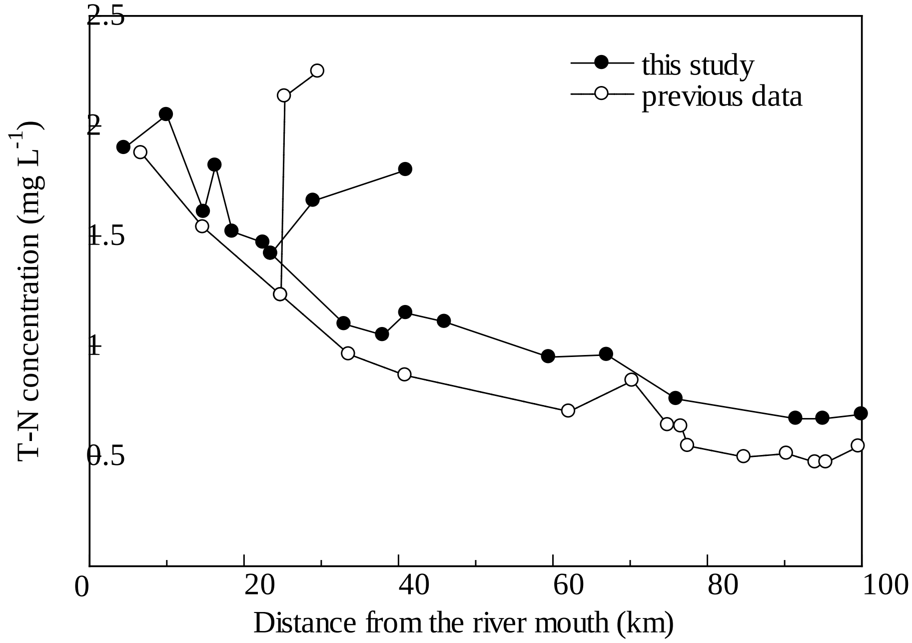


(a) D-Fe



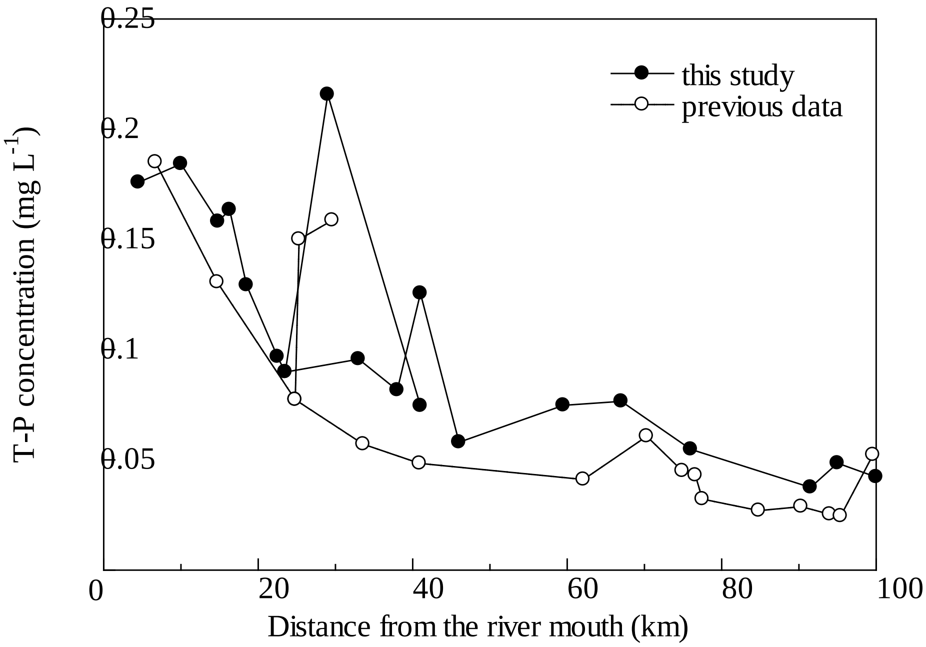
(b) Turbidity

Fig.6



this study
previous data
2.5
2
1.5
1
0.5
0
20
40
60
80
100
T-N concentration (mg L-1)
Distance from the river mouth (km)

(a) T-N



this study
previous data
0.25
0.2
0.15
0.1
0.05
0
20
40
60
80
100
T-P concentration (mg L-1)
Distance from the river mouth (km)

(b) T-P

Fig. 7

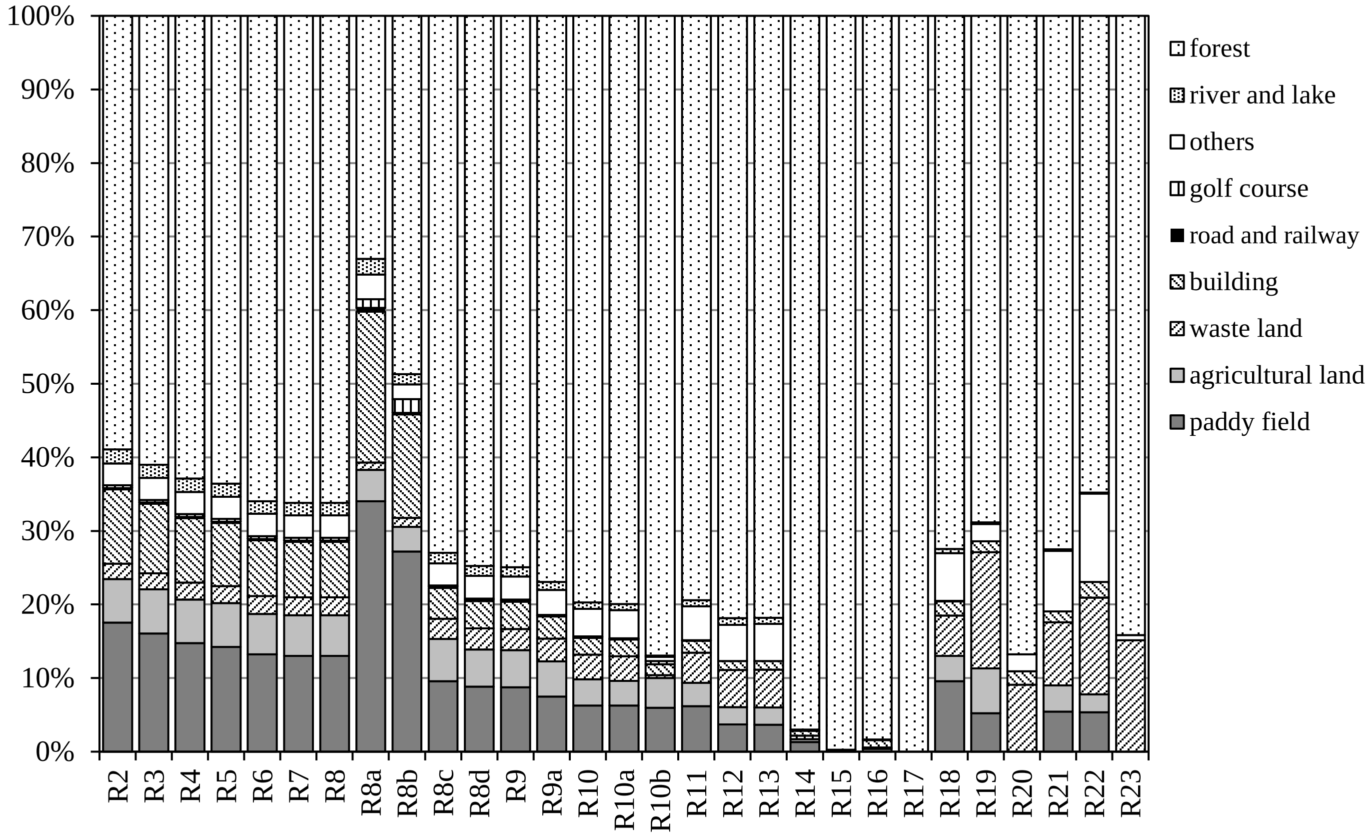
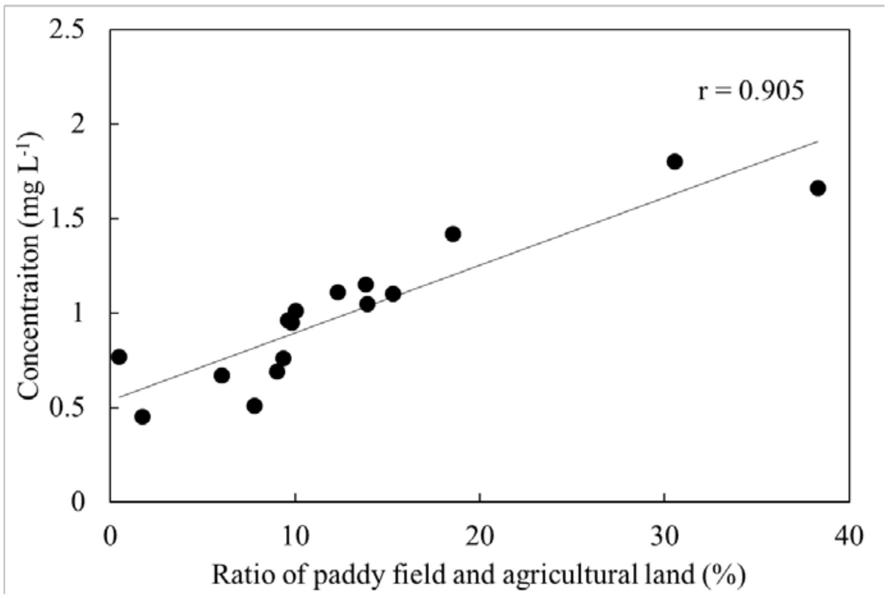
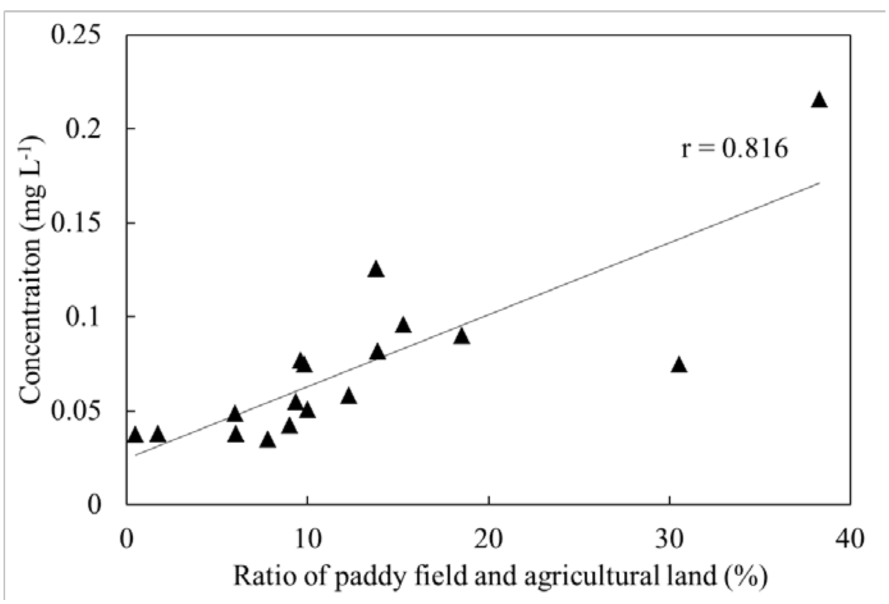

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
R2
R3
R4
R5
R6
R7
R8
R8a
R8b
R8c
R8d
R9
R9a
R10
R10a
R10b
R11
R12
R13
R14
R15
R16
R17
R18
R19
R20
R21
R22
R23
forest
river and lake
others
golf course
road and railway
building
waste land
agricultural land
paddy field

Fig. 8



r = 0.905
Concentraiton (mg L-1)
Ratio of paddy field and agricultural land (%)

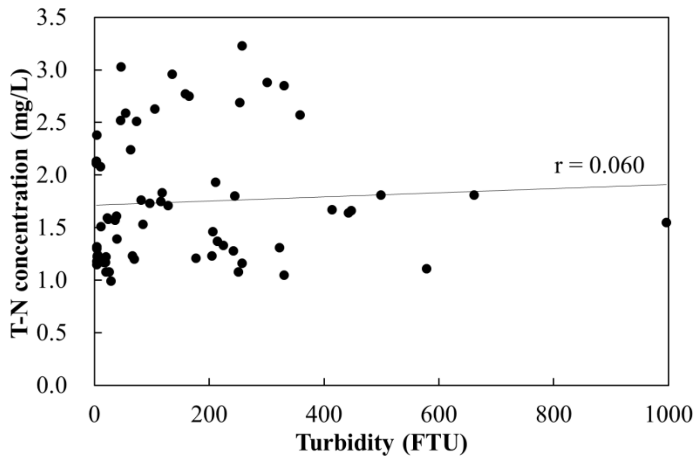
(a) T-N



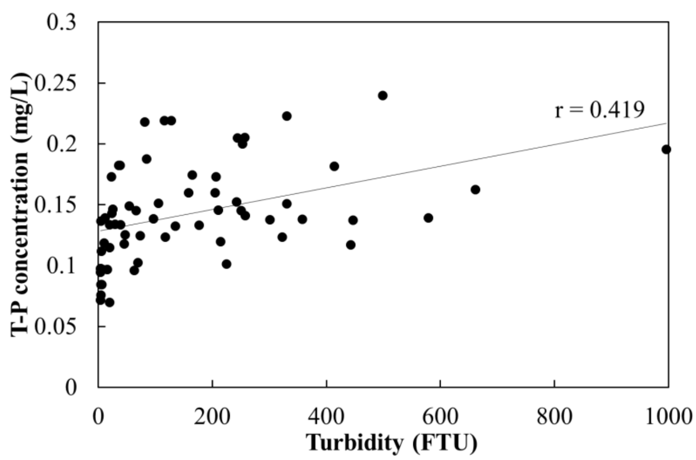
r = 0.816
Concentraiton (mg L-1)
Ratio of paddy field and agricultural land (%)

(b) T-P

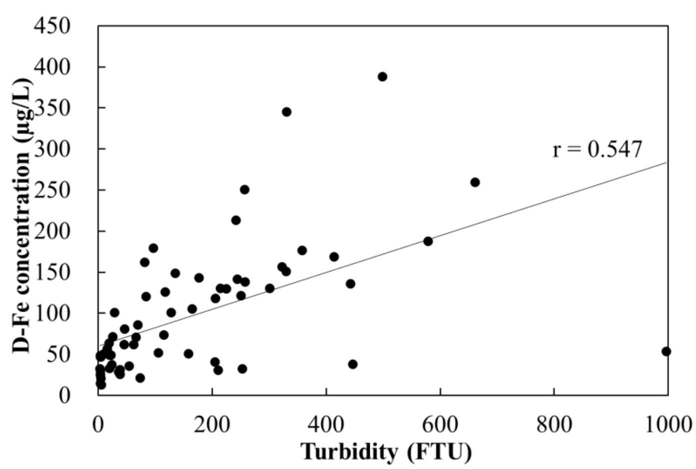
Fig. 9



(a) T-N



(b) T-P



(c) D-Fe

Fig. 10

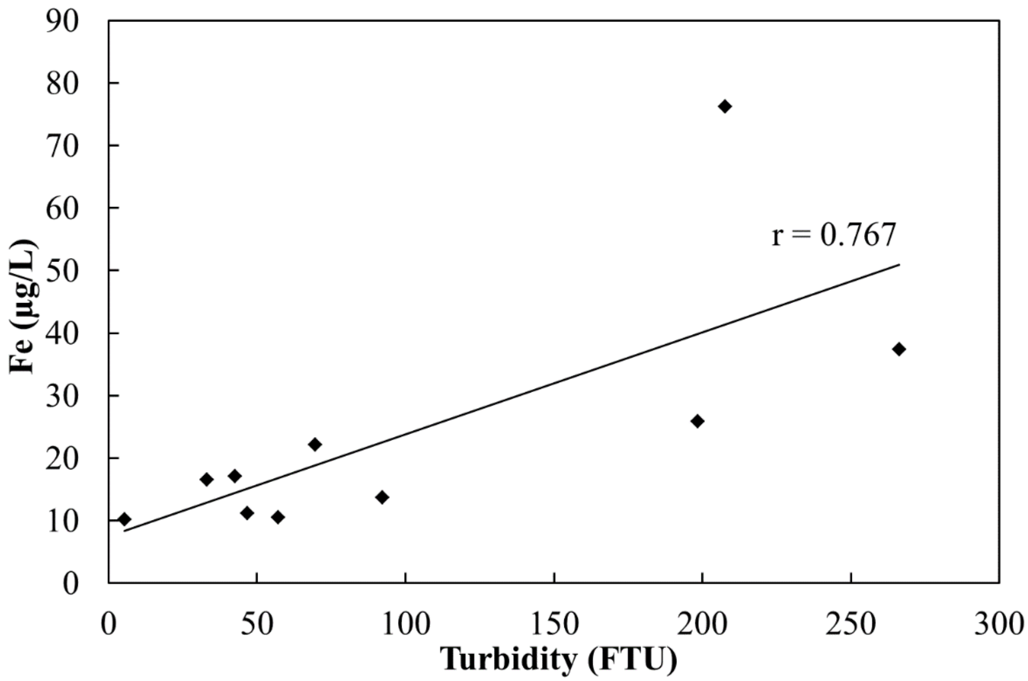

90
80
70
60
50
40
30
20
10
0
Fe (µg/L)
r = 0.767
0
50
100
150
200
250
300
Turbidity (FTU)

Fig. 11