

Study on the behavior of pollutants in lagoon waters and the effect of  
precipitation on the water quality of lagoon

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August, 2015

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# Abstract

Studies using stable isotopes have been important for valuable research in environmental sciences. Oxygen and hydrogen stable isotope ratios (i.e.,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) are widely used to investigate global or local hydrological cycle. Then, regular monitoring and measurement of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in lagoon waters as well as river waters and precipitations have been carried out in this work. Furthermore, in case of lagoon waters, water pollutions due to nutrients or organic materials have been observed in recent years. Therefore, regular monitoring and measurement of nutrients such as nitrogen (N) and phosphorus (P), DOC (dissolved organic carbon) or DO (dissolved oxygen) in lagoon waters as simple index of the pollutants is also significant from the viewpoint of environmental protection.

The object lagoons in this research are Sakata Lagoon (the representative lake in Niigata Prefecture, which was registered in Ramsar Convention), Toyanogata Lagoon (the largest lake in Niigata Prefecture) and Zhalong Wetland (the biggest Waterfowl Nature Reserve in China, which was registered in Ramsar Convention). Sakata is famous for the wetland registered “Ramsar Covention”, and has a water area of 43.6 ha. Sakata comprises a large (“Honkata” or “Shitakata”) and a small (“Uwakata”) freshwater lake with low bogs on the banks. This lake is situated near the major rice cropland in Japan, and was originally formed in an ancient hollow in the seaside dune. The lake has no inflow, and the water is supplied from groundwater of the dune. On the other hand, Toyanogata is the largest lake in Niigata Prefecture (lake area: 162 ha) and is located near the center of Niigata City. The lake is classified as “the first class river” (Water Systems of Shinano River), and flows into Kurinoki River.

In addition, to survey the influence of rainfall event on these lagoons and the surrounding rivers,  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , the concentration of major ions, nutrients, and heavy metals such as Cr in these water samples after rainfall were also determined as well as those in normal samples.

Consequently, the following matters have been mainly clarified: (1)  $\delta^{18}\text{O}$  values of sample waters in Zhalong Wetland are generally large probably because of the effect of evaporation, whereas those of Sakata lagoon are large which may be due to the biological process such as the activity of plankton. (2) Considering the results of nutrients concentrations, the water quality of lagoon (Sakata and Toyanogata) waters in Niigata Prefecture is better than that of Zhalong Wetland in China. (3)  $\delta\text{D}$  value of water samples in Sakata was generally larger than that in Toyanogata similarly to the case of  $\delta^{18}\text{O}$ , though remarkable large difference among samples was not found; (4) The pH

value of lagoon water samples is almost 6.5-8.5 (which is generally larger than that of river water), and pH at the spot of S1 (downstream point of Lower Lagoon (Shitakata)) is remarkably high (9.0-9.5); (5) Lagoon water has the chemical characteristics contrasting to groundwater with a focus on river water from the viewpoint of pH (acidity or alkalinity) and DO. These matters can be closely related to the biological activity such as photosynthesis due to aquatic plant and phytoplankton and the activity of *Crustacea* plankton etc. in lagoon. (6) In addition to water samples in Toyonogata,  $\delta^{18}\text{O}$  of the sample at Sakata 3 (spring water at shore of south area in Shitakata) increased after rainfall events. (7) The concentrations of  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  remarkably increased after rainfall events at Sakata 3. (8) The distribution percentage of “suspended” in most water samples remarkably increased after rainfall event. Moreover, the increase of total Cr content was also found in these samples.

# **Chapter 1**

## **General Introduction**

## **1.1 Natural Environment of lagoon**

Inland waters contain freshwater ecosystems, which reflect such features of the river systems as landscape, geology, and land use. With their rich diversity of flora and fauna and high productivity, these waters compose an important element of the natural environment. However, rivers and lakes have been the sites of human activities since prehistoric time, and the freshwater ecosystems are very susceptible to the modifications for control and utilization of water and to the influence of industrial activities.

There are many lakes in northern Japan and southern Kyushu, but very few in western Honshu and Shikoku. Lakes in Japan have many different origins, but can be grouped roughly. One group is those of volcanic origins including calderas, craters, and those dammed by ejecta. The largest caldera lake is Lake Kussharo (79.7 sq. km), and the deepest is Lake Tazawa (425 m). The second group is structural lakes, to which belongs Lake Biwa, the largest in Japan (673.8 sq. km). These are found on the Japan Sea side of Honshu and in Hokkaido. Another group has originated from biological activities including human works. Man-made lakes like reservoirs and natural ponds in peat bogs belong to this group. The surface area and volume of lakes in Japan are decreasing due to reclamation by drainage and natural filling up<sup>1)</sup>.

Here is summarized the present state of alteration by man of the natural environment of inland waters and the distribution of living organisms in them.



## **1-2 Classification of lagoon**

The majority of lakes on Earth are fresh water, and most lie in the Northern Hemisphere at higher latitudes. Most lakes have at least one natural outflow in the form of a river or stream, which maintain a lake's average level by allowing the drainage of excess water. Some lakes do not have a natural outflow and lose water solely by evaporation or underground seepage or both. They are termed endorheic lakes.

Many lakes are artificial and are constructed for hydro-electric power generation, aesthetic purposes, recreational purposes, industrial use, agricultural use or domestic water supply.

Since they progressively become filled by sediment, lakes are considered ephemeral over geological time scales, and long-living lakes imply that active processes keep forming the basins in which they form. There are a number of natural processes that can form lakes<sup>2</sup>.

Lagoons are classified into 3 main types: (1) leaky lagoons, (2) choked lagoons, and (3) restricted lagoons. Leaky lagoons have wide tidal channels, fast currents and unimpaired exchange of water with the ocean. Choked lagoons occur along high energy coastlines and have one or more long narrow channels which restrict water exchange with the ocean. Circulation within this type of lagoon is dominated by wind patterns. Restricted lagoons have multiple channels, well defined exchange with the ocean, and tend to show a net seaward transport of water<sup>3</sup>.

The object lagoons in this research are Sakata Lagoon, Toyonogata Lagoon and Zhalong Wetland. Sakata Lagoon is classified for choked lagoon, Toyonogata Lagoon is classified for restricted lagoon, and Zhalong wetland is classified for leaky lagoon.

### 1.3 Isotope Hydrology

“Isotope Hydrology” namely, the use of isotopic tools and nuclear techniques in the study of the water cycle, was born during the years just after the second world war through the merging. The one hand, of the experience gathered in environmental monitoring of radionuclide fallout (tritium in particular) and use of radioisotopes as “dating” tools in geology with, on the other hand, the theoretical knowledge gained on the fractionation of isotopic species, as exemplified by the work of H. Urey, J. Bigeleisen and their students<sup>4</sup>).

Hydrogen and oxygen have a number of isotopes, both stable and radioactive. The major isotope of hydrogen with a mass of 1, ( $^1\text{H}$ ), occurs in the hydrosphere at a mass abundance of 99.985%. It is accompanied by about 0.015% of the heavy isotope  $^2\text{H}$  whose particular name is Deuterium, designated D in the older literature. An even heavier isotope of mass 3 ( $^3\text{H}$ ), named Tritium, is unstable to  $\beta$  decay with a half-life of 12.43 years; this is the value usually accepted even though more recent measurements suggest the value of  $T_{1/2}=12.23$  years (Lucas and Unterweger, 2000). As this half-life is compatible with the holdup time in many subsurface reservoirs, Tritium is also widely used in hydrologic studies as tracer.

The most abundant oxygen isotope,  $^{16}\text{O}$ , whose mean mass abundance in the hydrosphere is given as 99.762%, is accompanied by a number of stable and radioactive isotopes. The radioactive oxygen isotopes  $^{14}\text{O}$ ,  $^{15}\text{O}$ ,  $^{19}\text{O}$ , and  $^{20}\text{O}$  all have half-lives of only seconds and are thus too short lived to be of any significance in the study of the hydrologic cycle. However, the two stable heavy isotopes of oxygen,  $^{17}\text{O}$  and  $^{18}\text{O}$ , whose average abundances are 0.0379% and 0.200%, respectively, are the powerhouses of isotope hydrology.

Given the five stable isotopes of hydrogen and oxygen, one will have nine isotopic water molecules (termed isotopologues in the recent literature) ranging from a mass of 18 for  $^1\text{H}_2^{16}\text{O}$  to mass 22 for  $^2\text{H}_2^{18}\text{O}$ . Assuming statistical distribution of the isotopic species in water, the abundances shown in Table 1-1 are proposed. It is clear that one is concerned mainly with the molecules  $^1\text{H}^2\text{H}^{16}\text{O}$ ,  $^1\text{H}_2^{17}\text{O}$ ,  $^1\text{H}_2^{18}\text{O}$  and of course,  $^1\text{H}_2^{16}\text{O}$ .

The doubly labeled molecules  $^1\text{H}^2\text{H}^{17}\text{O}$ ,  $^1\text{H}^2\text{H}^{18}\text{O}$  and  $^2\text{H}_2^{16}\text{O}$  and even more so the triply substituted molecules  $^2\text{H}_2^{18}\text{O}$ ,  $^2\text{H}_2^{17}\text{O}$ , can be disregarded at the level of natural

abundance of these isotopes<sup>5)</sup>.

Soon after the discovery of the heavy isotopes of oxygen and hydrogen in the 1920s and early 1930s, significant differences were observed in the isotopic contents of seawater, freshwater, and snow. By the early 1950s, as a result of the availability of better measurement techniques, the dependence of isotope content of rain on a variety of climatic factors such as surface air temperature, amount of rain and the altitude of precipitation, were also observed. Together with the known temperature dependence of isotope ratios, the observed relationship between isotopes and climate also provided a means to study past climates by using isotope distributions in continental and marine archives.

The foundation of applying isotopes to quantify fluxes in the hydrologic cycle were firmly established by the 1950s, albeit with a limited scope and limited records of measurements<sup>6)</sup>. Stable isotopes are chemical isotopes that are not radioactive. Stable isotopes of the same element have the same chemical characteristics and behave chemically almost identically. Mass differences, due to a difference in the number of neutrons, result in partial separation of the light from the heavy isotopes during chemical reactions. Commonly analyzed stable isotopes include oxygen, carbon, nitrogen, hydrogen and sulfur. These isotopes systems have been used in research for many years.

## 1.4 Eutrophication

Eutrophication arises from the oversupply of nutrients, which induces explosive growth of plants and algae which, when such organisms die, consume the oxygen in the body of water, thereby creating the state of hypoxia.

The source of the excess phosphate are detergents, industrial/domestic run-off, and fertilizers. With the phasing out of phosphate-containing detergents in the 1970s, industrial/domestic run-off and agriculture have emerged as the dominant contributors to eutrophication<sup>7)</sup>.

Lagoon water generally originates as oligotrophic and has only limited quantities of nutrients depending upon the mode of its formation and composition of original sediments. These nutrients are insufficient to produce any significant algal growth. At this stage the water have only autochthonous nutrients (indigenous nutrients cycling therein), which usually recycle completely in the absence of any outside supply. As the allochthonous nutrients (nutrients from outside) start to entering the lagoon, the process of eutrophication sets in<sup>8)</sup>. The principal natural sources of nutrients are the natural run-off, fall of leaves and twigs from the surrounding vegetation, periodical submergence of the nearby terrestrial vegetation, rain fall and bird droppings.

The term eutrophication has been derived from a Greek word “eutrophos”<sup>9)</sup>, meaning corpulent or rich. The first use of this term in ecology was made in connection with remnants of the extinct lakes rather than with live lakes. There was some research found that the upper layers have more nutrients in comparison to the lower layers as the original lakes received much higher nutrient. He used the terms “eutrophic” and “oligotrophic” to distinguish between these two layers.

The buildup of nutrients through this slow mode of entry gradually starts increasing the growth of algae. When the algae die and decompose, the locked nutrients are again made available to the fresh algal growth. During each cycle, the nutrients are progressively increased in the water body. With the advancement of eutrophication, the cycling of nutrients is unable to maintain the equilibrium between production and decomposition, then an ever increasing organic matter is introduced in the lagoon which ultimately gets deposited at the bottom. Slowly, the thickness of the bottom sediments increases with time, leading to the formation of swamps, bogs, marshes, and finally to

the extinction of the water body in long run.

The process of eutrophication is shown in Fig.1-1 which indicates that a lagoon passes from oligotrophic to eutrophic condition through some arbitrary intermediate stages called oligo-mesotrophic, mesotrophic and meso-eutrophic. It is also evident that with the progress of eutrophication, an increasing quantity of nutrients comes in circulation, and cycles become unable to complete. The speed of eutrophication does depend not only on the rate of nutrient supply, but also on other factors like climate and morphometric features. The tropical climate usually supports a higher rate of eutrophication as it favors higher nutrient utilization and algal growth in comparison to cold and temperate climates.

In addition, eutrophication is greatly augmented by the increased supply of nutrients through various human activities such as discharge of domestic sewage, industrial wastes, agricultural and urban run-off. Increased levels of air pollution also make the water bodies rich in nutrients through their transport with rains or by dry fallout. This increased supply of nutrients triggers the algal growth at a much faster rate, thus, increasing the speed of eutrophication, which otherwise would have been a slow natural phenomenon. The relation of the rate of eutrophication with the ageing of lagoon is shown in Fig.1-2. Though all lagoons mature in due course by eutrophication and become extinct, extinction time is considerably reduced by accelerated eutrophication. The process of eutrophication is therefore, sometimes, referred to as ageing of lagoons. It is also evident from the Fig.1-3 that the rate of eutrophication slows down with time due to reduced light penetration as a result of increased turbidity and consequent fall in primary production.

## 1.5 Chromium (Cr)

Chromium (Cr) is the seventh most abundant element on earth and is found in rocks, animals, plants, and soils. Cr is thought to exist mainly in two oxidation states, the trivalent (Cr(III)) and hexavalent (Cr(VI)) states in natural aqueous environments<sup>10) 11)</sup>. The character of Cr(III) and Cr(VI) is summarized in Table 1-2. Cr(VI) may be present in the form of  $\text{CrO}_4^{2-}$  or  $\text{HCrO}_4^-$ , and Cr(III) tends to form  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ ,  $\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2^+$ , or Cr(III) organic complexes. Cr(VI) is toxic, carcinogenic, and mutagenic, whereas Cr(III) is essential for living organisms.

## 1.6 Humic substances (HS)

Humic substances (HS) are those organic compound found in the environment, they widely exist in soils, water and sediments of the ecosphere. They are traditionally defined as humin, humic acid (HA) and fulvic acid (FA). The structures of HS (HA and FA) taken from Leenheer et al <sup>12)</sup> are shown in Fig.1-3, and the elemental analyses of HS used in this work were carried out Watanabe et al<sup>13)</sup>. It is considered that HS contain a large number of potential metal-complexing functional groups including carboxylic sites and phenolic moieties and that regulate the speciation, transport, and subsequent fractionation of heavy metals in contaminated aquatic environments. For example, the distribution of Cr in the environment is controlled by oxidation-reduction processes. The oxidation of Cr(III) occurs in the presence of MnO<sub>2</sub>. On the other hand, Cr(VI) may be reduced by organic matters such as humic substances as shown in Fig.1-4 , which have been reported to have a great effect on the reduction of Cr(VI) and on complex formation with Cr(III).<sup>14)</sup>

**Table 1-1 Isotopic water species and their relative abundance.\***

Mass	Molecule	Rel. Abundance
18	$^1\text{H}_2^{16}\text{O}$	0.99731
19	$^1\text{H}^2\text{H}^{16}\text{O}$	$3.146 \times 10^{-4}$
19	$^1\text{H}_2^{17}\text{O}$	$3.789 \times 10^{-4}$
20	$^1\text{H}^2\text{H}^{17}\text{O}$	$1.122 \times 10^{-7}$
20	$^2\text{H}_2^{16}\text{O}$	$2.245 \times 10^{-8}$
20	$^1\text{H}_2^{18}\text{O}$	$2.000 \times 10^{-3}$
21	$^2\text{H}_2^{17}\text{O}$	- negligible
21	$^1\text{H}^2\text{H}^{18}\text{O}$	$6.116 \times 10^{-7}$
22	$^2\text{H}_2^{18}\text{O}$	- negligible

(\*Assuming equilibration during disproportionation reactions)

{Note that the abundance of molecules which are singly substituted by Deuterium, e.g.  $^1\text{H}^2\text{HO}$ , is twice that of the product of the atomic abundances}. As given by Coplen et al. (2002).



**Table 1-2 Character of Chromium**

Characters	Toxicity	Environmental Standard (Japan)	Distribution	Existence form
Cr(VI)	high	<0.05ppm	At natural aqueous	$\text{CrO}_4^{2-}$ , $\text{HCrO}_4^-$
Cr(III)	low	<2ppm	At natural aqueous	$\text{Cr}(\text{H}_2\text{O})_n$ , $(\text{OH})_m(3-m)^+$

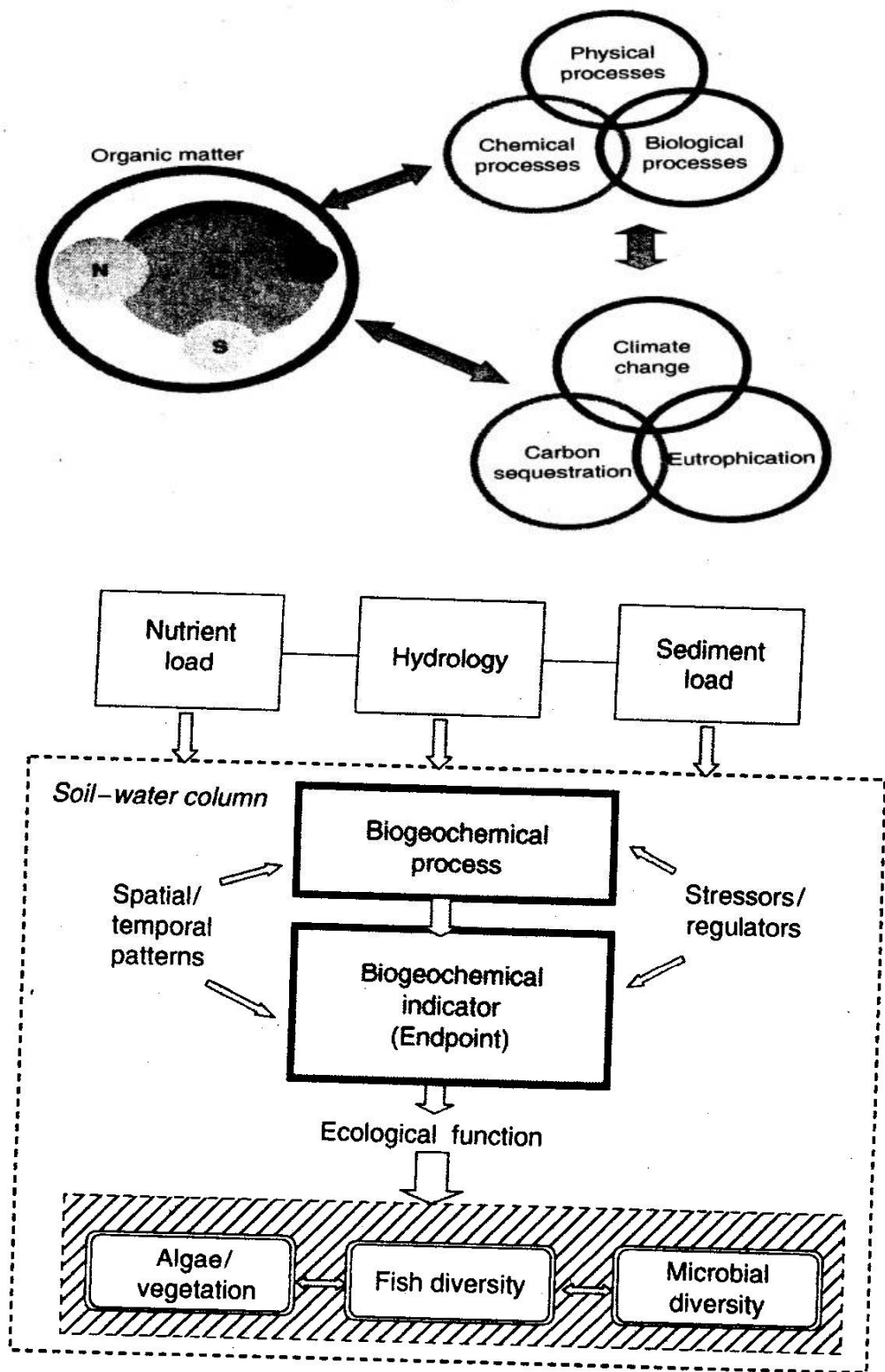


Fig.1-1 Schematic showing the effect of anthropogenic impacts on biogeochemical processes in soil and water column

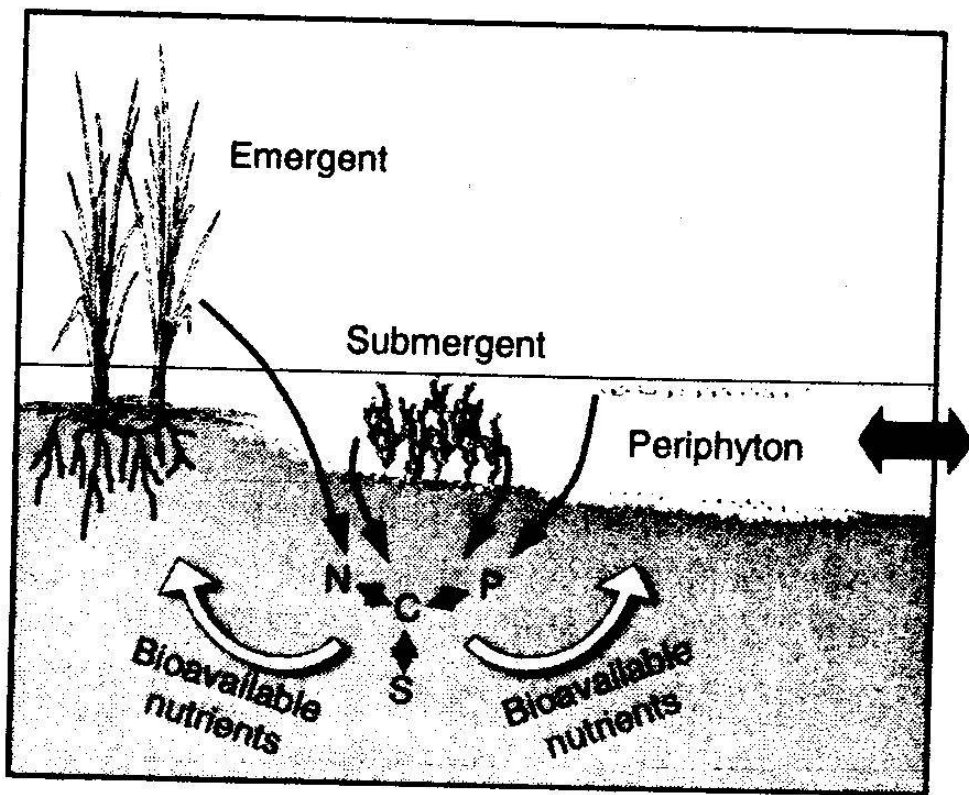
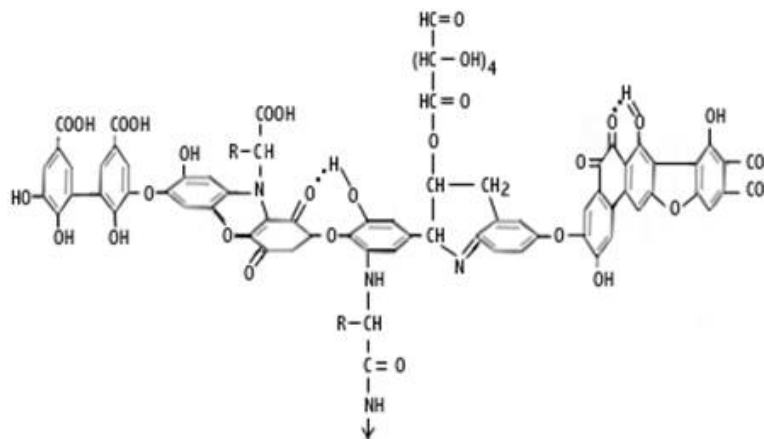


Fig.1-2 Schematic showing basic nutrient cycles in the soil-water column of wetland

(a)



(b)

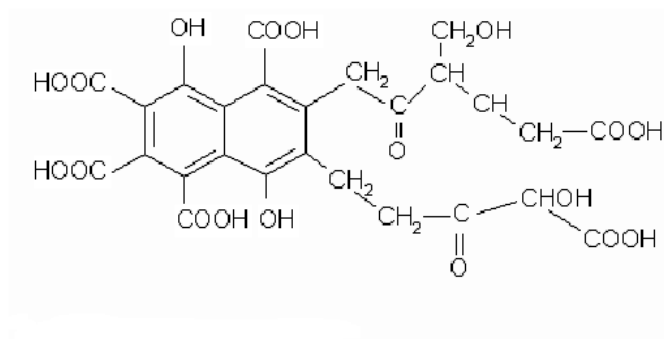


Fig.1-3 Model structures of (a) humic acid and (b) fulvic acid

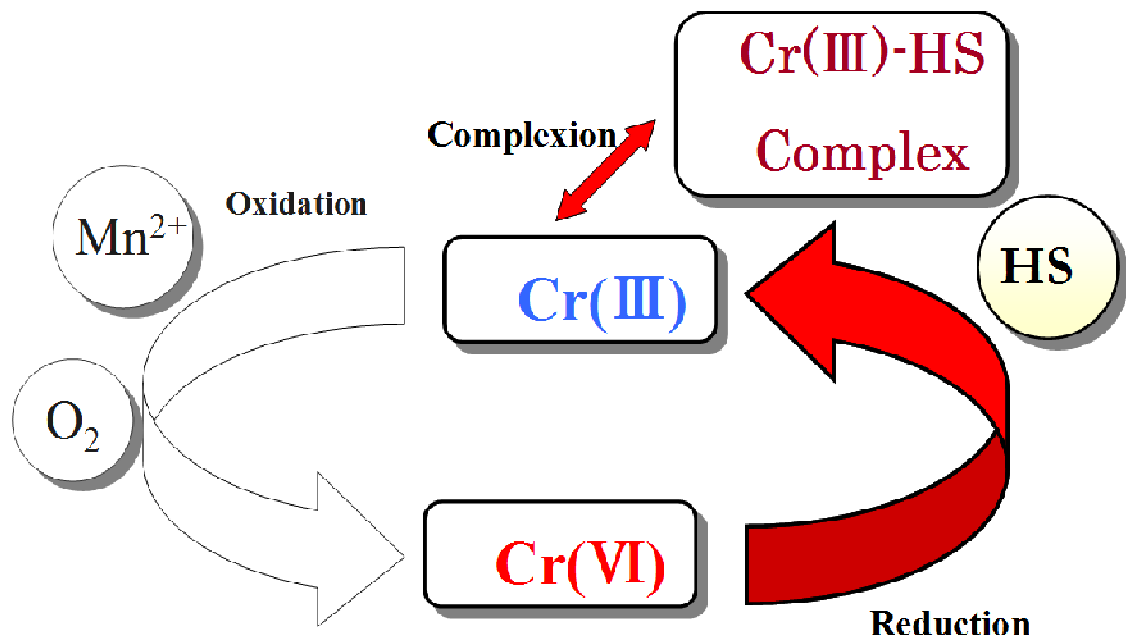


Fig.1-4 Change of chromium species in environment

## **Chapter 2**

# **Isotopic and Chemical Characteristics of Lagoon Waters in Sakata and Toyanogata and Zhalong Wetland**

## 2.1 Introduction

Oxygen and hydrogen stable isotopes (i.e.,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) serve as useful tool for characterizing the origin of local waters and local hydrological cycle. These data supply some important hydrological information such as estimating the groundwater recharge, the movement of water in soils, the origin of the atmospheric vapor or the conditions of rain formation<sup>15)16)</sup>. Hence, studies using stable isotopes are becoming an increasingly valuable component of research in environmental sciences and have been widely performed in the world<sup>15)17)</sup>.

Niigata Prefecture (Hokuriku District, Japan) is located in the geographic position where the monsoon comes from the Continent<sup>18)</sup>. Moreover, a large amount of snow falls every year in winter season. Thus, isotopic and chemical investigation of the water samples in Niigata Prefecture is significant for the understanding of hydrologic environment in this area. However, hydrological and environmental investigations using oxygen and hydrogen isotopes (i.e.,  $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) as tracers have been little reported in Niigata Prefecture.

Then the characteristics of precipitation samples in Niigata Prefecture by using  $\delta^{18}\text{O}$  and other measuring items have been investigated in our laboratory<sup>19)20)</sup>.

In this study, the main subject is focused on the environmental characteristics of lagoon waters in Niigata Prefecture. In case of lake or lagoon waters, water pollutions due to nutrients or organic materials have been observed in recent years<sup>21)22)</sup>.

Therefore, regular monitoring and measurement of Nutrients such as T and P or Cr in lagoon waters as simple index of the pollutants is also significant from the viewpoint of environmental protection.

Considering the above-mentioned, in addition to the measurement of  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , the concentrations of Eutrophication and Cr in water samples of Sakata and Toyonogata were determined in the present work to investigate the environmental characteristics of lagoon waters in Niigata Prefecture in recent years.

## 2.2 Experiment

### 2.2.1 Study area

Sakata Lagoon, the Niigata Prefecture's largest duned lake in Japan, was registered with the Ramsar Convention on Wetlands in March 1996. This lagoon and its surrounding area is designated as a special district under the Natural Parks Law, and also as the Sakata National Protection Area for Birds and Mammals. There are many forms of aquatic life inhabit Sakata lagoon, such as *Euryale ferox* and *Monochoria korsakowii*, both of which are endangered in Japan. After comprehensive considerations, we took the water samples at 3 fixed sampling spots: as shown in Fig.2-1, Sakata 1 was in the outflow of downstream, Sakata 2 was in the joint area between Kamisakata and Hongata, besides, at the south of Hongata, the Sakata 3 was placed in spring.

Toyanogata Lagoon, formed by Shinano River floods, is located in the south of Niigata Prefecture, near the coast of the Sea of Japan. As the largest part of Echigo Plain, it has a basin area of 10,000 hectare and lake area of 180 hectare. With the rapid urban construction, Toyanogata Lagoon is known as “The Land of Serenity” for its abundant aquatic, plant and bird resources. After comprehensive considerations of hydromechanics and geology, we took the water samples once a month at 4 fixed sampling spots (T1: the upstream inlet, T2: the farm drainage channel, T3: the drainage channel of residential districts, T4: the downstream outlet), as shown in Fig.2-2.

Zhalong wetland, one of the major wetlands in China, locates on Songnen Plain of Songhuab River Basin in Heilongjiang Province. In 1992, the wetland was put onto the list of Wetlands of International Importance. Zhalong Wetland is a paradise of birds and a heaven of cranes. There are more than 260 species of birds in Zhalong Natural Reserve, including 35 species of national protection birds. The Reserve is particularly renowned in the world for its large amount diversified species of cranes. In this study, the sampling point was selected at Zhalong Lake, the principal part of water system in Zhalong Wetland (Fig.2-3).



## 2.2.2 Analysis methods

For the measurement of oxygen stable isotope ratio (i.e.,  $\delta^{18}\text{O}$ ),  $\text{CO}_2\text{-H}_2\text{O}$  isotope equilibration method<sup>23)</sup> was used. The sample preparation procedure is the same as that in previous work<sup>24)25)</sup> and based on the method by Watanabe et al. as shown in Fig.2-4<sup>26)</sup>. Isotopic measurements were performed with a stable isotope ratio mass spectrometer (Micromass PRISM). The precision associated with these analyses was within  $\pm 0.2\%$ . Results of oxygen isotope ratio analysis are shown relative to SMOW (Standard Mean Ocean Water).

For the measurement of hydrogen stable isotope ratios ( $\delta\text{D}$ ),  $\text{H}_2\text{-H}_2\text{O}$  isotope equilibration method with Pt catalyst based on Coplen et al.<sup>27)</sup> was used. as shown in Fig.2-5. Isotopic measurements were performed with a stable isotope ratio mass spectrometer (Micromass PRISM).

Sample waters were immediately filtered through different size of membrane filters (i.e., the sizes are  $3.0\mu\text{m}$ ,  $0.45\mu\text{m}$ , and  $0.10\mu\text{m}$ ) one by one<sup>28)</sup>. Furthermore, unfiltered sample waters for the determination of total Cr were decomposed with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ )<sup>29)</sup>.

A schematic diagram of the procedure for the pre-concentration of Cr in environmental waters is shown in Fig.2-6. Cr content in “suspended” was estimated by subtracting that in the filtrate (obtained by  $0.45\mu\text{m}$  filter) from total Cr concentration. Cr content in “colloidal” was estimated by subtracting the concentration of the filtrate obtained by  $0.45\mu\text{m}$  filter from that obtained by  $0.10\mu\text{m}$  filter.

Each filtrate except the dissolved fraction (passed through  $0.10\mu\text{m}$  filter) for determining Cr (III) and Cr (VI) was concentrated from  $500\text{ cm}^3$  to  $50\text{ cm}^3$  by heating. The dissolved Cr was separated into Cr (III) by using Bio-rad AG50W-X8, and into Cr (VI) by using Bio-rad AG1-X8 or Eporasu K-6 chelating resin. The concentration of Cr in each fraction was determined by ICP-AES.

The detection limit of Cr (III) and Cr (VI), based on 3 times of standard deviations ( $3\sigma$ ) of the blanks by 10 replicates, was  $0.03\mu\text{g}\cdot\text{dm}^{-3}$ . Moreover, the determination limit of Cr (III) and Cr (VI), based on 10 times of standard deviations ( $10\sigma$ ) of the blanks by 10 replicates, was  $0.10\mu\text{g}\cdot\text{dm}^{-3}$ .

#### Measurement of other items

For the measurement of nutrients, i.e.  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ , total nitrogen (T-N), and total phosphorus (T-P) were determined by absorption spectrometry (HITACH, Z-5000).

Basic physical parameters such as water temperature, pH, EC (electric conductivity), ORP (oxidation-reduction potential) and DO (dissolved oxygen) in samples were measured at the sampling sites by a handy pH/COND and pH/DO Meter (HORIBA, D-24 and D-25).

## **2.3 Results and Discussion**

### **2.3.1 Physical parameters (pH,EC,ORP and DO) of lagoon waters**

Representative hydrographic data (i.e., pH, water temperature, EC, ORP, DO and ) in these lagoon waters during sampling periods are shown in Table 2-1.

### 2.3.2 Isotopic characteristics of lagoon waters

Seasonal behaviors of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of water samples at five points from two lagoons in Niigata Prefecture are shown in Fig.2-7 and Fig.2-8

From Fig. 2-7 and Fig.2-8,  $\delta\text{D}$  value of water samples in Sakata was generally larger than that in Toyanogata similarly to the case of  $\delta^{18}\text{O}$ , though remarkable large difference among samples was not found.

From the previous node in our laboratory it is found that the  $\delta^{18}\text{O}$  values of water samples in Sakata were larger than those in Toyanogata and in Shinano River as shown in Fig.2-9, and that  $\delta^{18}\text{O}$  value in one of these samples (i.e. Sakata 1) is particularly large in summer.

The cause of large  $\delta^{18}\text{O}$  in Sakata has been estimated as the following possibility: (a) the effect of evaporation; (b) the activation of biological effect such as plankton; (c) the recharge from the surrounding groundwater.

It is known that zooplankton is found both in Sakata and in Toyanogata. However, *Crustacea* plankton (i.e., zooplankton having  $\text{CaCO}_3$  on shell) exists only in Sakata according to the statistical data from Environmental Management Division in Niigata City.

From the above-mentioned matter, it is suggested that larger  $\delta^{18}\text{O}$  found in water sample of Sakata particularly in summer is closely related to the activity of *Crustacea* plankton. That is to say, it is considered that the O (oxygen) of this sample is enriched in  $^{18}\text{O}$  due to the following exchange reaction with the O of  $\text{CaCO}_3$  included in *Crustacea* plankton.



Moreover, the effect of the recharge from the surrounding groundwater is also considered for explaining high  $\delta^{18}\text{O}$  values of waters in Sakata.

From the results of isotopic analyses of  $\delta\text{D}$  (in addition to  $\delta^{18}\text{O}$ ) in this work, the biological effect based on Eq. (1) may be active in case of Sakata because  $\delta\text{D}$  value in summer was not larger than that in other season compared to  $\delta^{18}\text{O}$  values.

Then the sample water of Sakata is strongly affected by the activity of crustacean plankton. Seasonal variation of  $\delta^{18}\text{O}$  is found clearly in Sakata lagoon water (particularly in Sakata 1) as shown in Fig.2-7.

Hourly variation of  $\delta^{18}\text{O}$  is also expected. Then, we collected water samples with every 2 hours in the whole day at Sakata 1 and Sakata 2 to investigate hourly variation of  $\delta^{18}\text{O}$  and pH in Sakata.

The investigation was carried out twice in summer and winter, and the result is shown

in Fig.2-10 From this figure, “s1” and “s2” denote the samples taken in summertime on Sakata 1 and Sakata 2, and similarly “w1” and “w2” denote the samples in wintertime on Sakata 1 and Sakata 2. On the contrary to our expectation, no remarkable hourly variation of  $\delta^{18}\text{O}$  (i.e., the difference on “day” and “night”) was found (Fig.2-10).

The mean value of each  $\delta^{18}\text{O}$  is shown as follows:  $\delta^{18}\text{Os1} = -5.84\text{‰}$ ,  $\delta^{18}\text{Os2} = -7.76\text{‰}$ ,  $\delta^{18}\text{Ow1} = -7.45\text{‰}$ ,  $\delta^{18}\text{Ow2} = -8.10\text{‰}$ . The difference of  $\delta^{18}\text{O}$  values between Sakata 1 (downstream) and Sakata 2 (upstream) are 1.92‰ in summertime, and 0.65‰ in wintertime. Large differences of  $\delta^{18}\text{O}$  between 2 points in summertime may be attributable to the biological process in the lagoon such as the activity of above-mentioned *Crustacea* plankton in addition to the effect of evaporation process. It is noteworthy that even in wintertime, the differences of  $\delta^{18}\text{O}$  between 2 points are found to some extent. In wintertime, there is a possibility that isotope-exchange reaction between dead shell remains of *Crustacea* plankton and water occurred.

The investigation was carried out twice in summer and winter, and the result is shown in Fig.2-11 From this figure, time course of the pH, summer is high but no trend in winter.

Annual variation of  $\delta^{18}\text{O}$  in the depth distribution (Toyanogata) is shown in Table 2-2 On the other hand, monthly variation of  $\delta\text{D}$  (June~October) is also shown in Table2-3. Clear difference was not observed among the depth.

### **2.3.3 Nutrient concentrations in lagoon waters**

For the observation of eutrophication situation, the amount of nitrogen referred to TN (total nitrogen), ammonia nitrogen ( $\text{NH}_4^+\text{-N}$ ) and nitric nitrogen ( $\text{NO}_3^-\text{-N}$ ), similarly the phosphorus determination including TP (total phosphorus) and  $\text{PO}_4^{3-}\text{-P}$  (phosphate phosphorus). It was found that Sakata3 had the larger TN concentration in Fig.2-12, the annual minimum was 4.26mg/L, and the annual maximum was 71.29mg/L. The maximum of Zhalong Lake was the biggest one, 18.00mg/L.

The data of Zhalong Wetland exceeded Sakata Lagoon several times (Fig.2-13) demonstrated that its annual TP concentration maximum reached 0.400mg/L, even though the annual minimum was still 0.011mg/L, more than surface water standard value (0.02mg/L). The second precedent individual was Sakata 2, annual minimum was 0.019mg/L and the maximum came up to 0.23mg/L. The last one was Sakata 3, annual minimum and maximum attained to 0.014mg/L and 0.042mg/L respectively.

Based on the TP concentration, Trophic State Index (TSI) is calculated, and shown in table 2-5.

### **2.3.4 Chromium concentrations in lagoon waters**

The distribution percentage of Cr (III) and Cr (VI) in each lagoon water sample is shown in Fig.2-14 along with the ratio of Cr (III) to Cr (VI) (i.e., Cr(III)/Cr(VI)).

The ratio of Cr (III) to Cr (VI) is 1.5-2.4, suggesting that the concentration of Cr (III) is larger than that of Cr (VI) at all sampling points. The ratio of Cr (III) to Cr (VI) may be a tracer for representing the oxidation-reduction state.

The distribution percentage of Cr (III) and Cr (VI) at depth distribution in lagoon water (Toyanogata) is shown in Fig.2-15 along with Cr(III)/Cr(VI). The ratio of Cr (III) to Cr (VI) is 2.0-2.8, and Cr(III)/Cr(VI) tend to increase with the increasing the depth. This may be related to the humic substances because the concentration of humic substances also increase with the increasing the depth.

## 2.4 Conclusions

### (i) Stable Isotope

$\delta^{18}\text{O}$  values of sample waters in Zhalong Wetland are generally large probably because of the effect of evaporation, whereas those of Sakata lagoon are large which may be due to the biological process such as the activity of plankton.  $\delta\text{D}$  value of water samples in Sakata was generally larger than that in Toyonogata similarly to the case of  $\delta^{18}\text{O}$ , though remarkable large difference among samples was not found. It was suggested that the biological process such as the activity of *Crustacea* plankton as well as the recharge from surrounding groundwater is active in Sakata.

### (ii) Nutrients

It is quantitatively revealed that the water quality of lagoon (Sakata and Toyonogata) waters in Niigata Prefecture is better than that of Zhalong Wetland in China. Particularly, self-purification is active because of the biological process in Sakata.

### (iii) Chromium

For all of the investigated water samples, the concentration of Cr (III) species is higher than that of Cr (VI) species. The ratio of Cr (III) to Cr (VI) is generally larger with increasing the depth, although significant differences cannot be detected. The ratio of Cr (III) to Cr (VI) can be a good indicator for represent the oxidation-reduction state at the spot.



Table 2-1 Representative hydrographic data of sample waters in Sakata and Toyanogata lagoon

pH					
Month	Sakata1	Sakata2	Sakata3	Toyano1	Toyano2
Jan	8.5	8.3	7.6	7.3	7.3
Feb	6.9	6.9	7.2	6.9	6.9
Mar	8.5	6.9	8.6	7.1	6.9
Apr	8.9	8.0	7.1	8.4	6.9
May	6.9	9.2	6.8	6.9	6.3
Jun	10.6	8.0	7.7	8.6	7.3
Jul	9.9	7.8	7.1	7.4	6.9
Aug	10.4	7.3	7.6	8.3	7.1
Sep	10.4	7.7	7.8	7.7	7.3
Oct	9.9	6.8	7.5	7.6	7.1
Nov	9.4	7.5	7.2	7.3	7.0
Dec	9.6	8.0	7.4	7.5	7.2

EC( $\mu$ S/cm)					
Month	Sakata1	Sakata2	Sakata3	Toyano1	Toyano2
Jan	297	319	366	426	465
Feb	302	393	267	248	305
Mar	133	279	236	244	484
Apr	291	304	348	385	258
May	319	285	353	164	116
Jun	276	307	375	289	309
Jul	231	334	382	301	325
Aug	296	352	353	346	619
Sep	22	285	322	511	133
Oct	145	316	213	61	98
Nov	283	293	379	79	65
Dec	288	156	387	382	278

ORP(mV)					
Month	Sakata1	Sakata2	Sakata3	Toyano1	Toyano2
Jan	289	302	339	284	279
Feb	288	206	270	331	116
Mar	281	239	208	244	90
Apr	207	206	246	198	104
May	233	150	199	189	178
Jun	122	211	202	169	214
Jul	113	162	213	204	183
Aug	45	174	202	151	178
Sep	108	190	193	186	193
Oct	135	118	177	195	83
Nov	182	199	125	189	77
Dec	208	240	259	259	25

DO( mg/L)					
Month	Sakata1	Sakata2	Sakata3	Toyano1	Toyano2
Jan	15.6	11.4	12.3	11.4	10.4
Feb	9.5	8.2	12.3	11.4	10.7
Mar	13.8	11.0	12.9	10.9	9.1
Apr	11.4	13.0	10.4	12.0	9.2
May	10.5	10.8	12.7	10.5	8.4
Jun	8.8	18.8	10.6	11.3	7.5
Jul	19.9	8.7	7.8	7.4	5.1
Aug	-	4.8	12.4	10.7	5.6
Sep	19.1	8.6	11.3	9.6	5.3
Oct	15.1	3.9	9.8	8.3	7.2
Nov	13.6	9.0	8.3	9.0	8.1
Dec	16.3	10.6	8.8	8.7	8.8

Table 2-2 Annual variation of  $\delta^{18}\text{O}$  in the depth distribution (Toyanogata)

	Jun	Jul	Aug	Sep	Oct	Nov
0cm	-9.91	-12.0	-13.6	-8.65	-10.2	-9.74
25cm	-9.96	-11.6	-13.4	-9.20	-10.1	-9.75
50cm	-9.44	-11.2	-13.5	-9.04	-10.5	-9.71
75cm	-10.2	-11.0	-13.3	-9.08	-10.3	-9.58
100cm	-9.50	-11.2	-13.4	-9.07	-10.0	-9.17
	Dec	Jan	Feb	Mar	Apr	May
0cm	-9.39	-6.83	-8.88	-10.2	-10.3	-10.6
25cm	-9.28	-8.32	-8.63	-10.3	-10.3	-9.94
50cm	-9.65	-8.52	-8.30	-10.3	-10.3	-8.77
75cm	-9.19	-10.4	-8.72	-9.85	-10.3	-9.55
100cm	-8.92	-10.7	-9.05	-10.4	-10.4	-10.8

Table 2-3 Annual variation of  $\delta\text{D}$  in the depth distribution (Toyanogata)

	Jun	Jul	Aug	Sep	Oct
0cm	-62	-----	-60.1	-52.9	-59.3
25cm	-65.7	-69.6	-65.7	-56	-55.3
50cm	-64.6	-69.6	-63.2	-55.3	-58.7
75cm	-64.4	-68.5	-65.1	-54.6	-58.6
100cm	-64	-70.2	-64.9	-53.7	-56.3

Table 2-4-a Physical parameters of depth distribution of Toyano Lagoon .

pH	0cm	25cm	50cm	75cm	100cm
Mid, s	7.17	6.98	6.91	6.8	6.84
DO [mg/L]	0cm	25cm	50cm	75cm	100cm
Mid, s	7.03	6.85	7.22	7.26	7.69
EC[ $\mu$ S/cm]	0cm	25cm	50cm	75cm	100cm
Mid, s	326	309	165.5	160.3	167.6
ORP[mV]	0cm	25cm	50cm	75cm	100cm
Mid, s	154	169	180	191	199
w.t.[ $^{\circ}$ C]	0cm	25cm	50cm	75cm	100cm
Mid, s	11.4	11	11.3	11.1	11.1

Table 2-4-b Chlorophyl-a and Humic substance of depth distribution of Toyano Lagoon .

Chl-a [ppm]	0cm	25cm	50cm	75cm	100cm
Mid, s	0.00161	0.00197	0.00162	0.00156	0.00182
Hum. [ppm]	0cm	25cm	50cm	75cm	100cm
Mid, s	11.4	11.9	12.2	14.1	14.7

Table 2-4-c  $\text{NO}_2^-$ -N and  $\text{NO}_3^-$ -N and T-N of depth distribution of Toyano Lagoon .

$\text{NO}_2^-$ -N [mg/L]	0cm	25cm	50cm	75cm	100cm
Mid, s	0.00686	0.00686	0.00696	0.0104	0.0128
$\text{NO}_3^-$ - N [mg/L]	0cm	25cm	50cm	75cm	100cm
Mid, s	3.83	4.86	3.68	8.33	4.27

T-N[mg/L]	0cm	25cm	50cm	75cm	100cm
Mid, s	1.527	1.517	1.363	1.512	1.437

Table 2-4-d PO<sub>4</sub><sup>3-</sup>-P and T-P of depth distribution of Toyano Lagoon.

PO <sub>4</sub> <sup>3-</sup> -P[mg/L]	0cm	25cm	50cm	75cm	100cm
Mid, s	0.00599	0.00450	0.00450	0.00450	0.00599

T-P[mg/L]	0cm	25cm	50cm	75cm	100cm
Mid, s	0.017	0.017	0.017	0.017	0.017

Table 2-4-e Major anions and cations of depth distribution of Toyano Lagoon.

Cl <sup>-</sup> [ppm]	0cm	25cm	50cm	75cm	100cm
Mid, s	41.68	41.84	43.44	47.13	41.46

SO <sub>4</sub> <sup>2-</sup> [ppm]	0cm	25cm	50cm	75cm	100cm
Mid, s	25.57	16.55	16.14	23.71	16.91

Na <sup>+</sup> [ppm]	0cm	25cm	50cm	75cm	100cm
Mid, s	27.47	40.66	45.15	45.61	39.01

K <sup>+</sup> [ppm]	0cm	25cm	50cm	75cm	100cm
Mid, s	0.7969	0.9163	1.559	1.193	0.9477

Mg <sup>2+</sup> [ppm]	0cm	25cm	50cm	75cm	100cm
Mid, s	8.366	6.209	5.251	7.524	6.564

Ca <sup>2+</sup> [ppm]	0cm	25cm	50cm	75cm	100cm
Mid, s	24.11	20.15	17.08	20.33	18.82

Table 2-5 Trophic State Index (TSI) of each point in several lagoons

Points	TSI (min)	TSI (max)	Status
Sakata1	49.9	70.0	Eutrophication
Sakata2	41.2	79.6	Mesotrophication-Eutrophication
Sakata3	37.2	53.8	Mesotrophication
Toyanogata1	46.7	74.6	Mesotrophication-Eutrophication
Toyanogata2	40.0	60.2	Mesotrophication-Eutrophication
Zhalong	63.5	86.3	Eutrophication

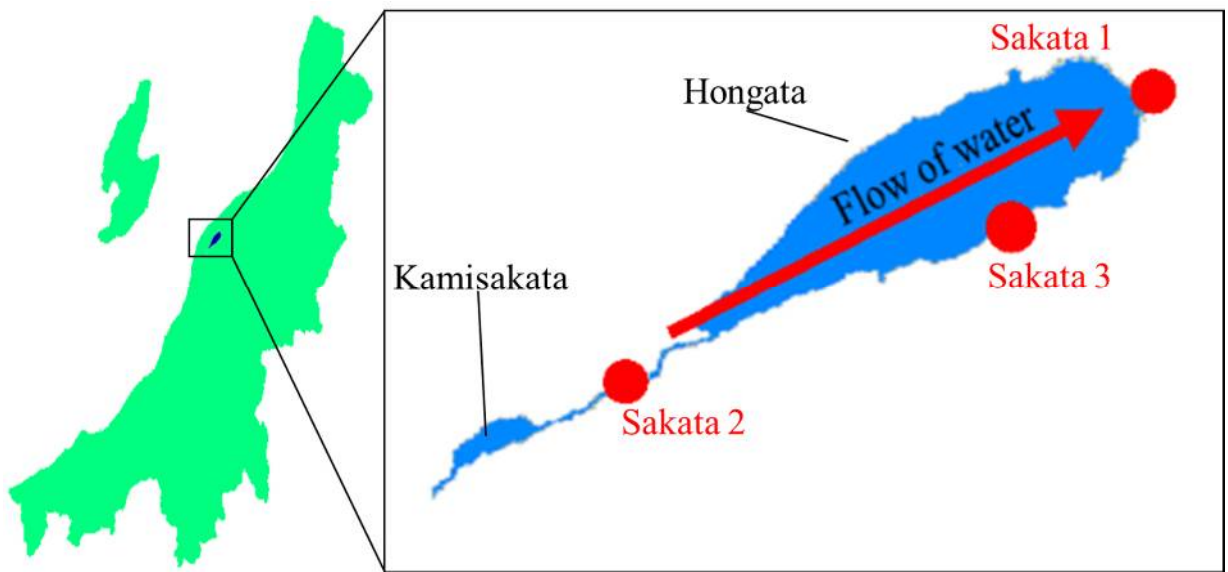


Fig.2-1 Sampling spots of Sakata Lagoon

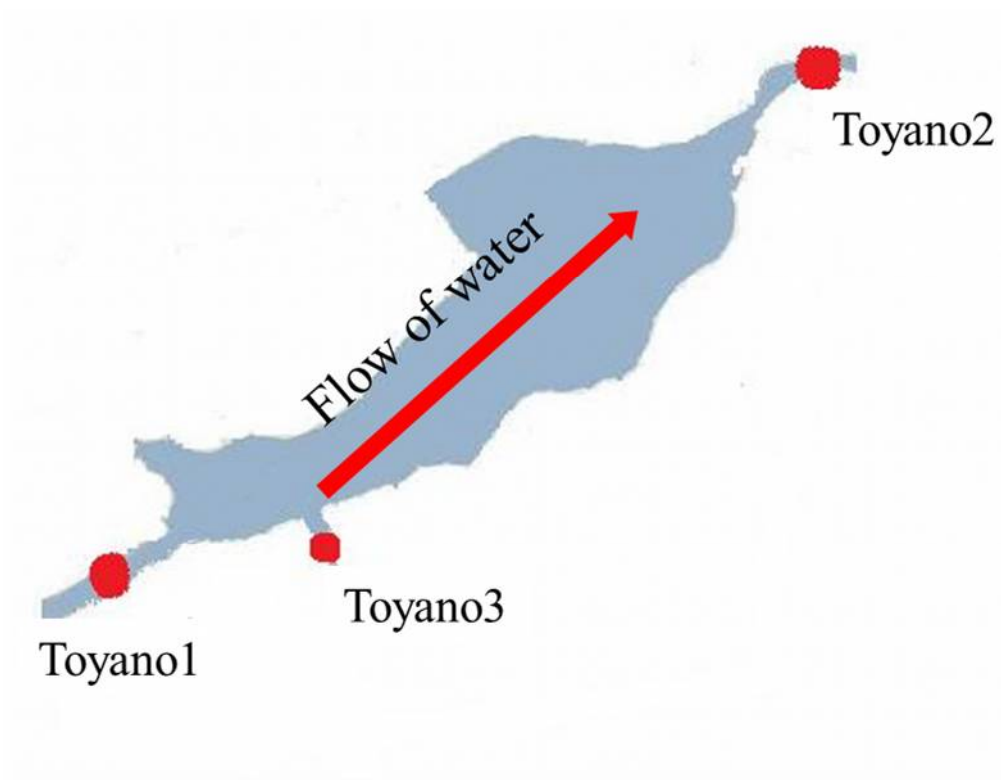
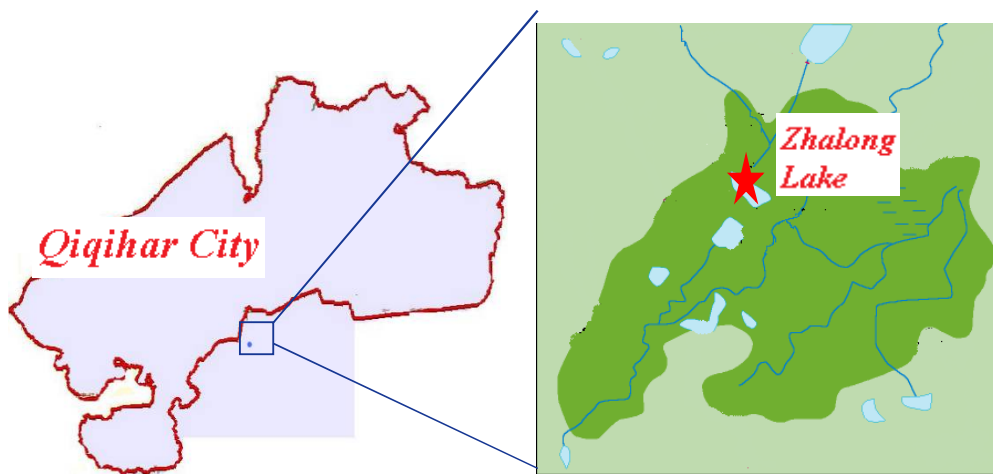
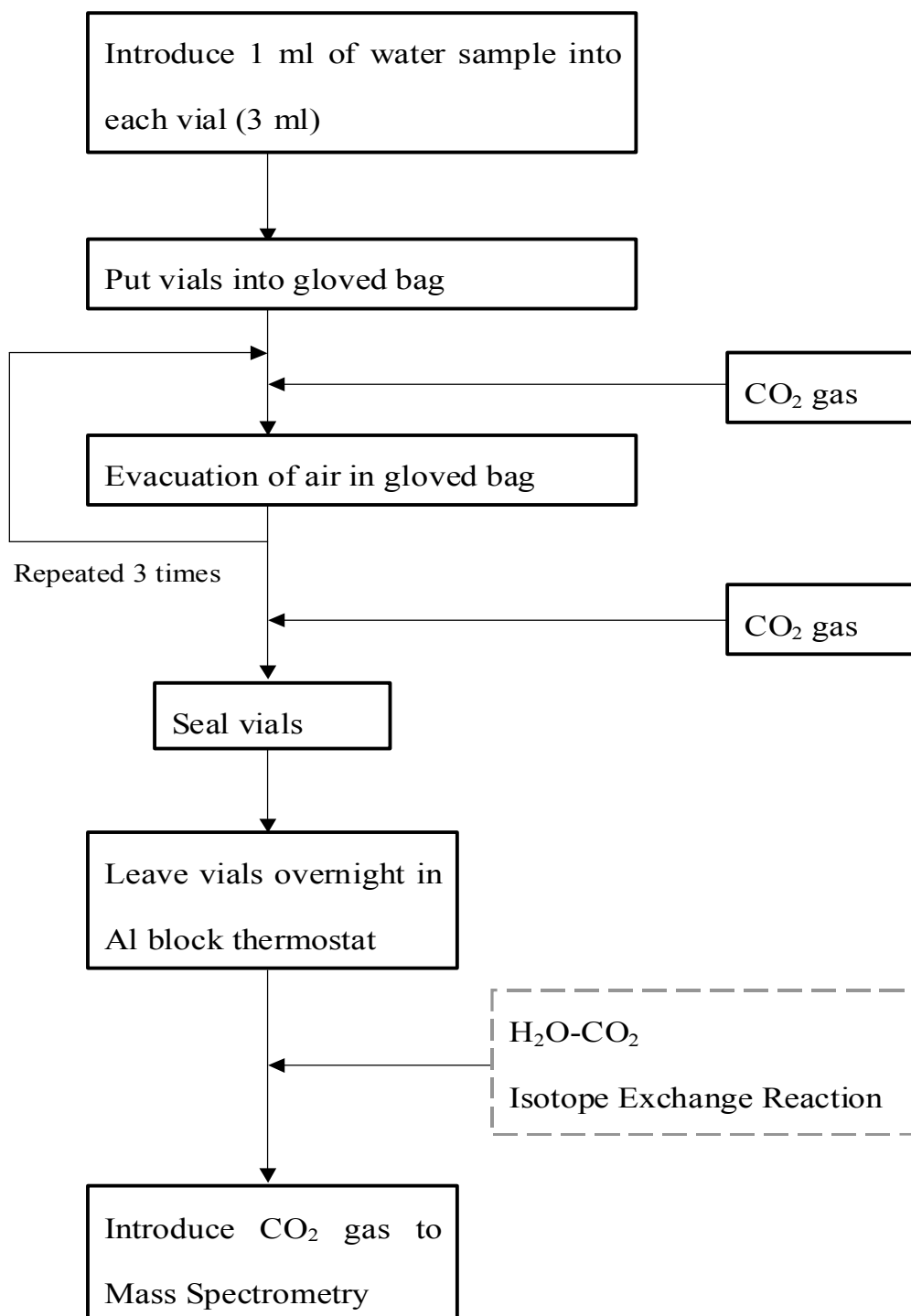


Fig.2-2 Sampling spots of Toyano Lagoon

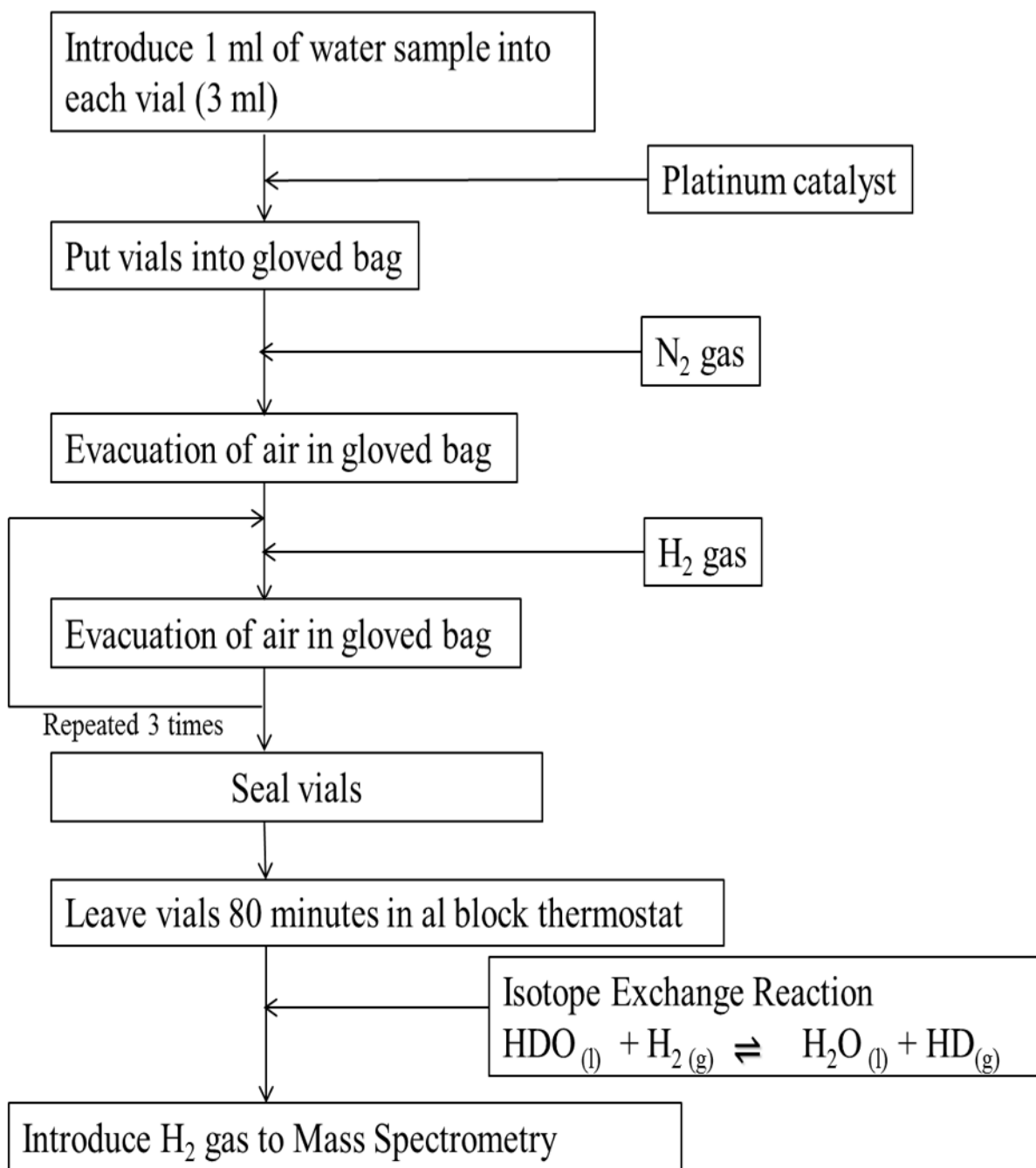


**Fig.2-3 Sampling spots of Zhalong Wetland**

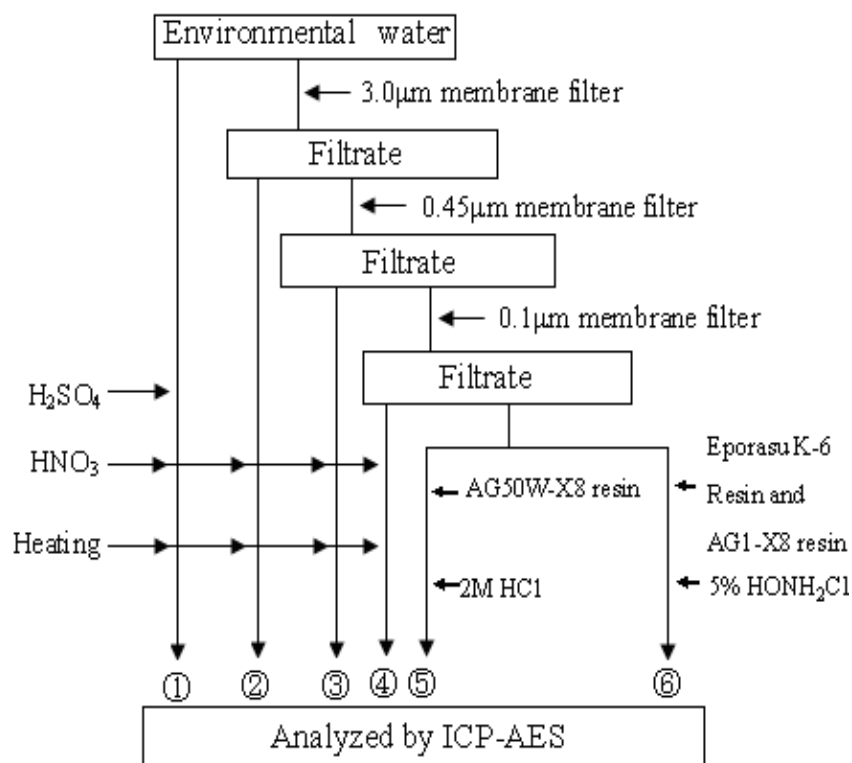




**Fig.2-4 Scheme of sample preparation procedure for oxygen isotopic analysis.**



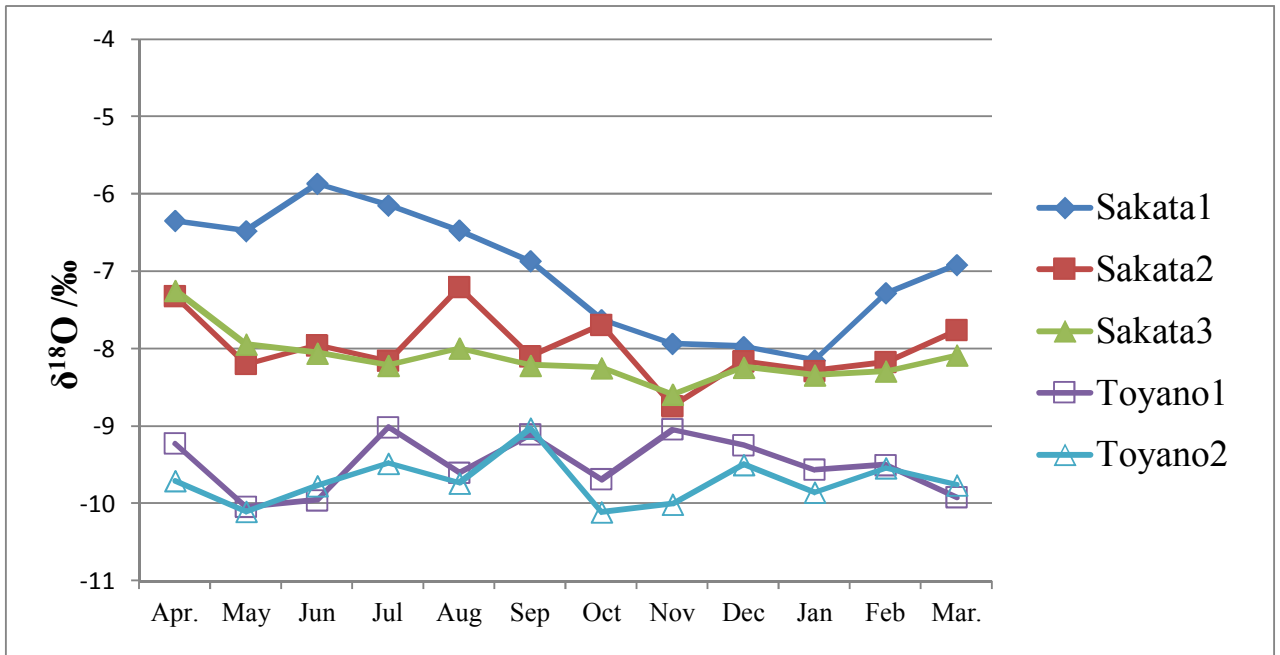
**Fig.2-5 Scheme of sample preparation procedure for hydrogen isotopic analysis**



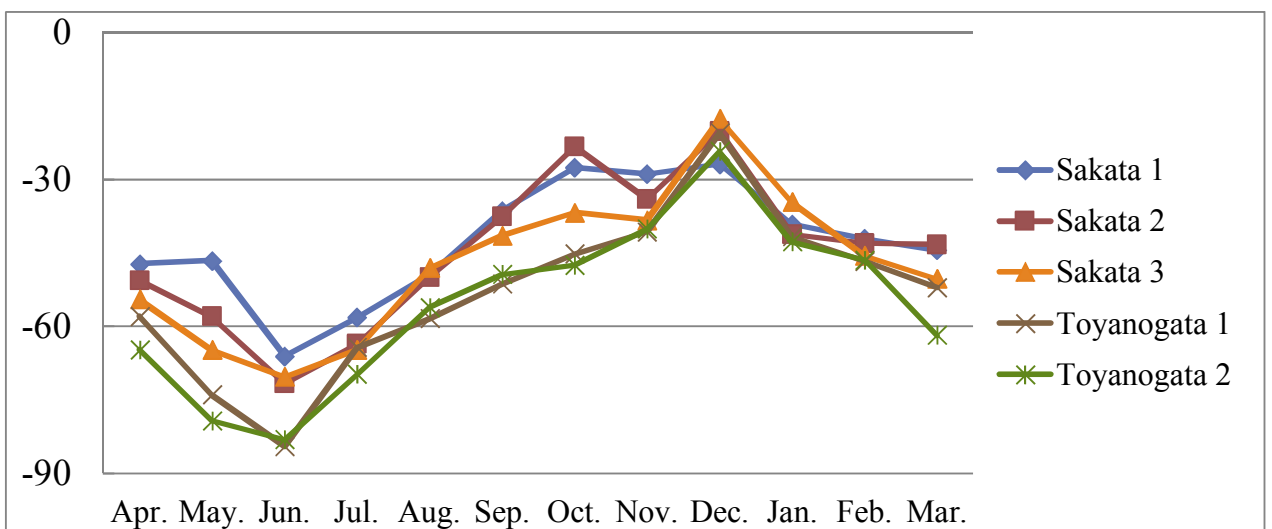
**Total Cr:** ①, **Suspended:** ①-③ (①-②:coarse suspended, ②-③: fine suspended), **Colloidal:**

③-④, **Dissolved:** ④ (Dissolved Cr(III):⑤, Dissolved Cr(VI):⑥)

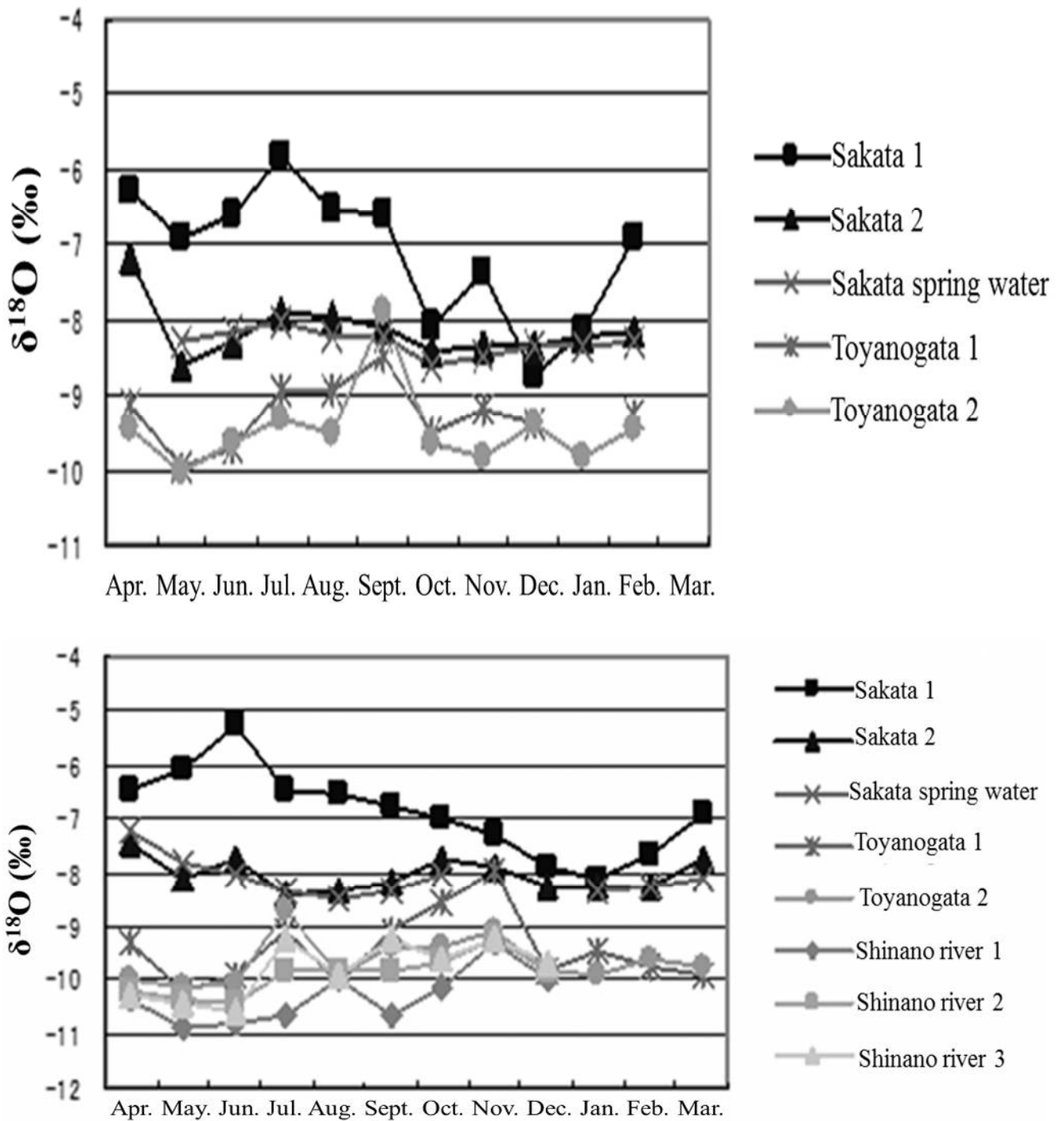
**Fig.2-6 Pre-concentration and speciation procedure for chromium in environmental water**



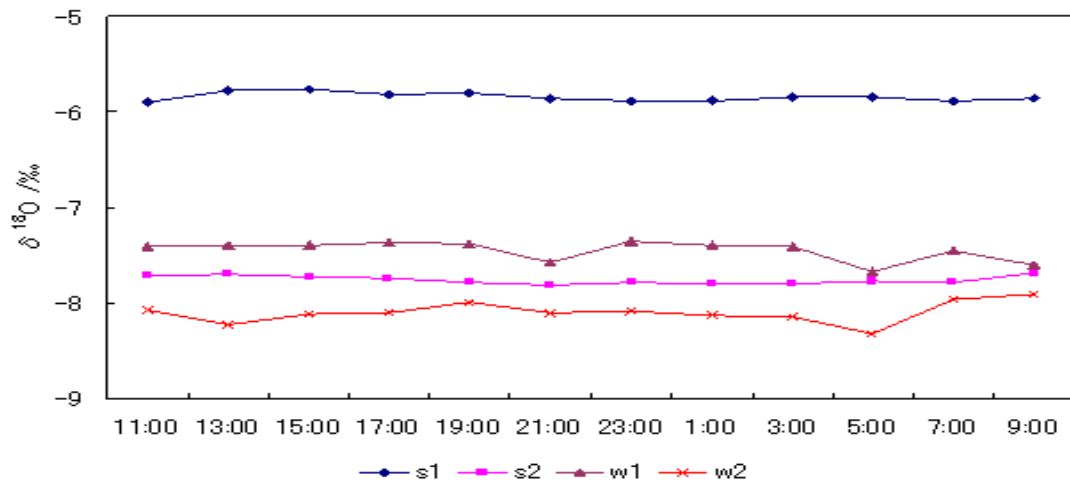
**Fig.2-7** monthly variation of  $\delta^{18}\text{O}$  in sample waters of lagoon



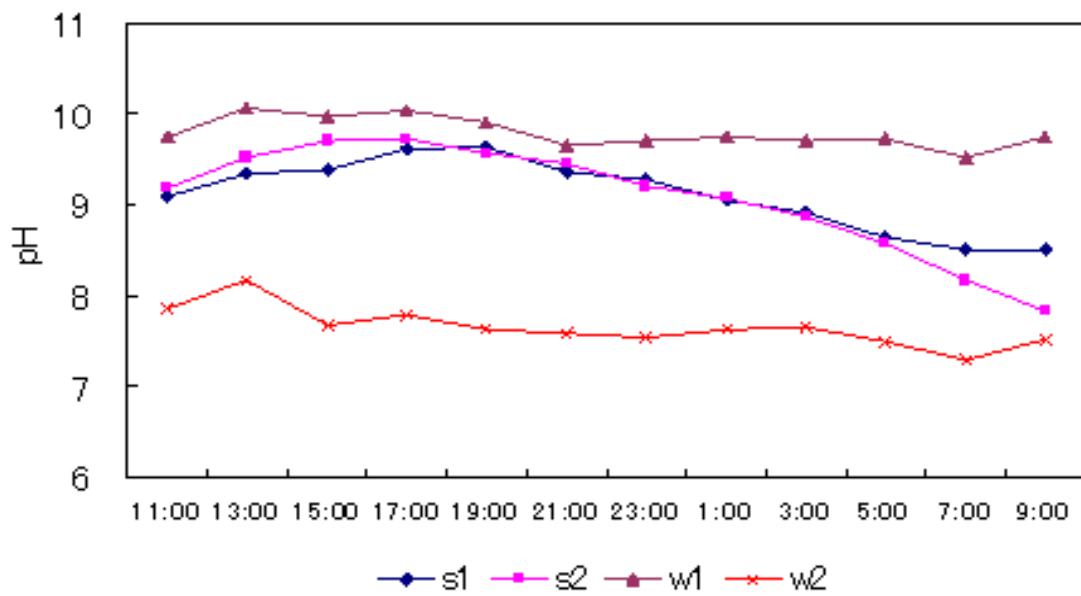
**Fig.2-8** monthly variation of  $\delta\text{D}$  in sample waters of lagoon



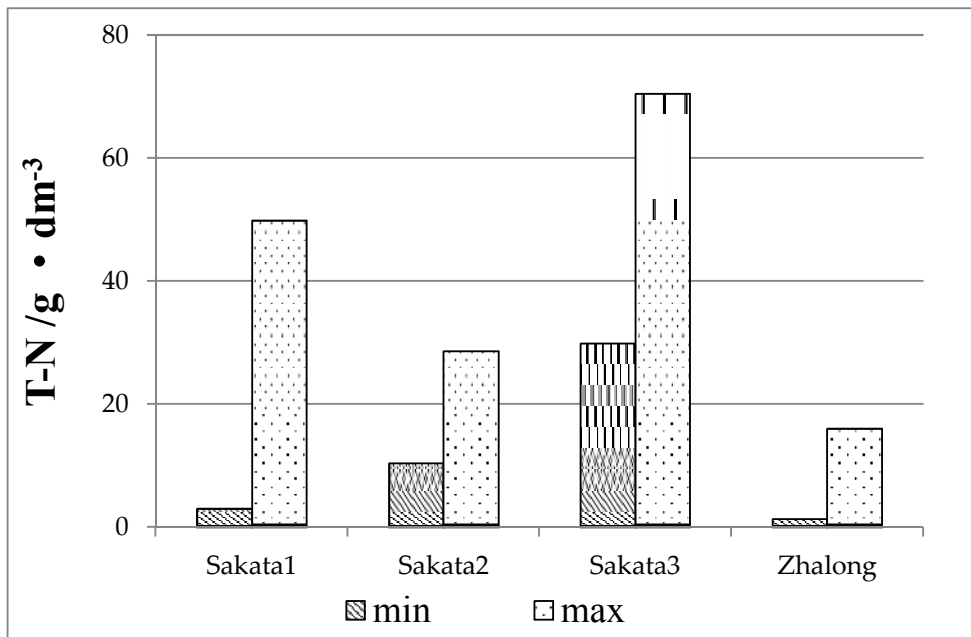
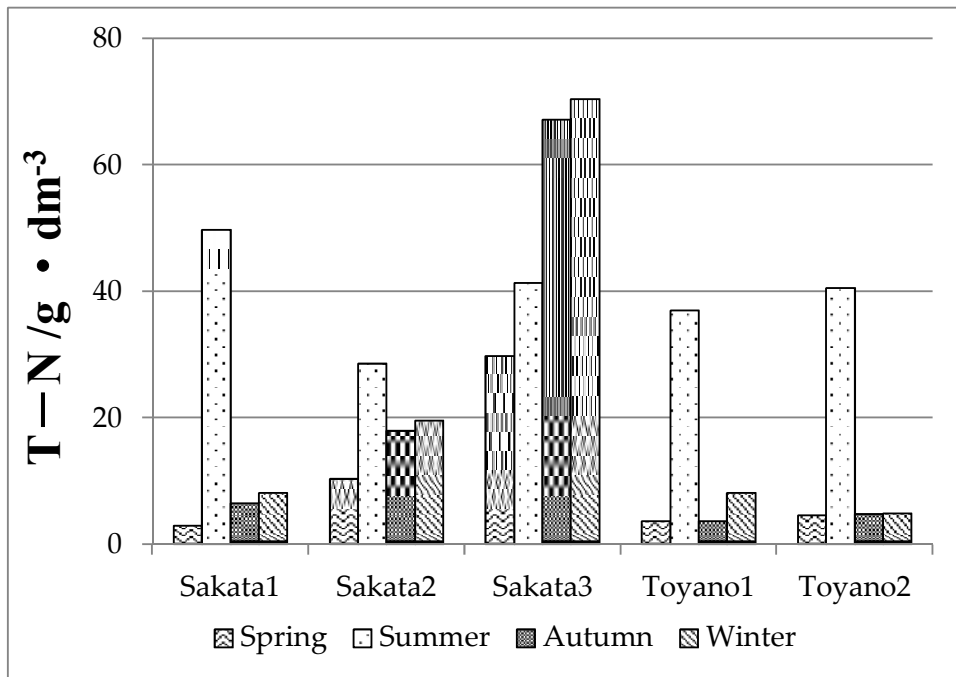
**Fig.2-9 Monthly variation of  $\delta^{18}\text{O}$  in Sakata and Toyanogata ( $\delta^{18}\text{O}$  of samples at three points in Shinano River in are also shown).**



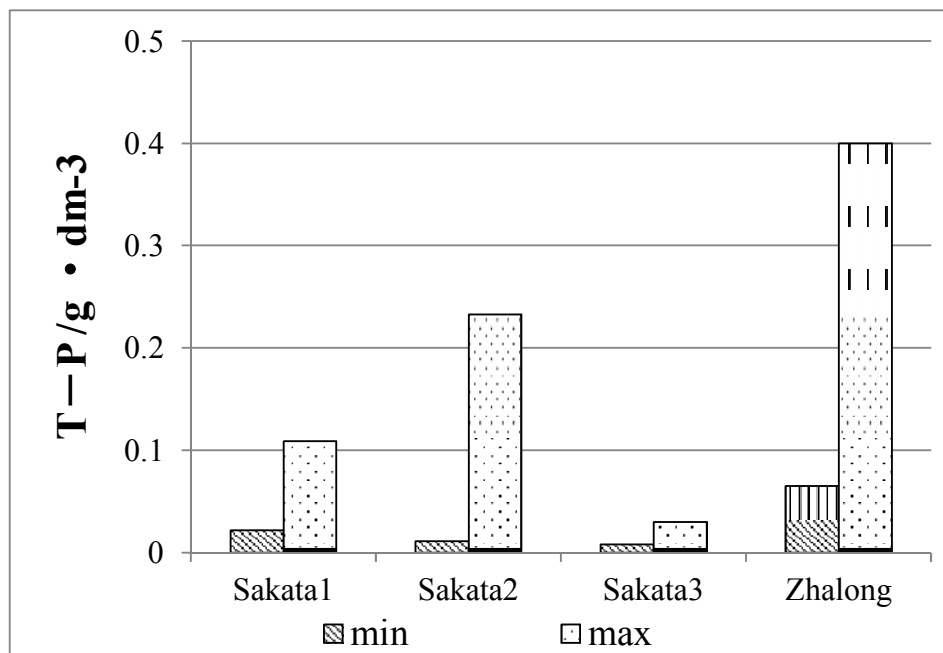
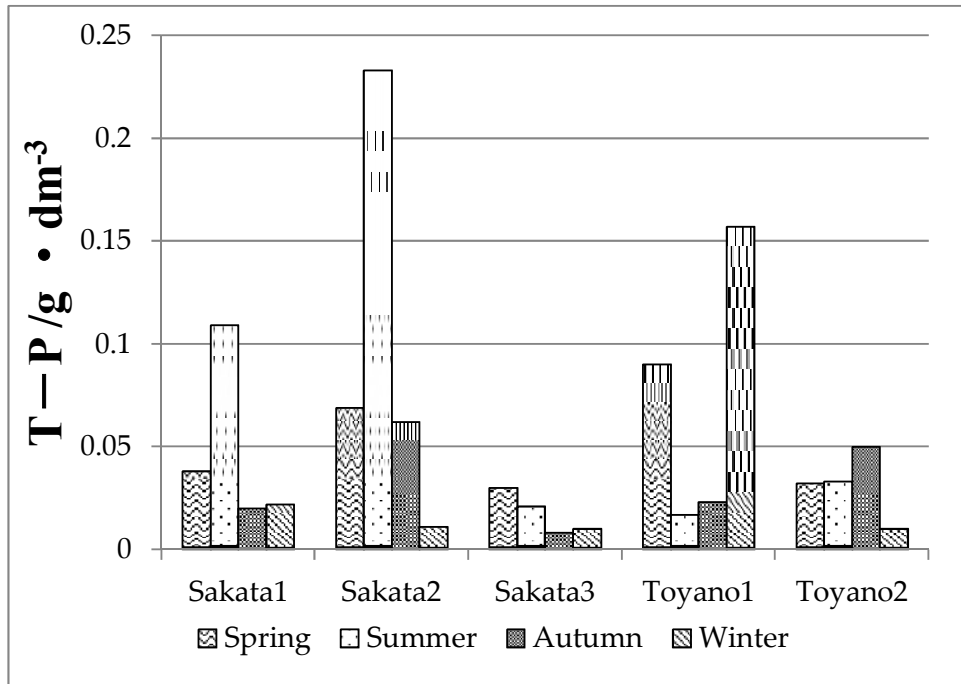
**Fig.2-10** Every 2 hours variation of  $\delta^{18}\text{O}$  in Sakata lagoon waters in summer and winter.



**Fig.2-11** Every 2 hours variation of pH in Sakata lagoon waters in summer and winter.

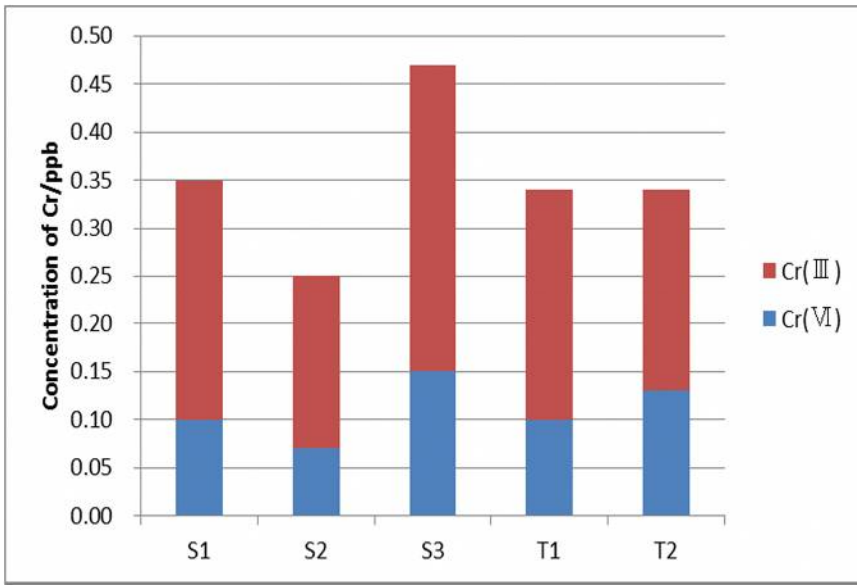


**Fig.2-12 Season variations and Comparison of T-N Concentrations between Sakata Lagoon and Zhalong Wetland**



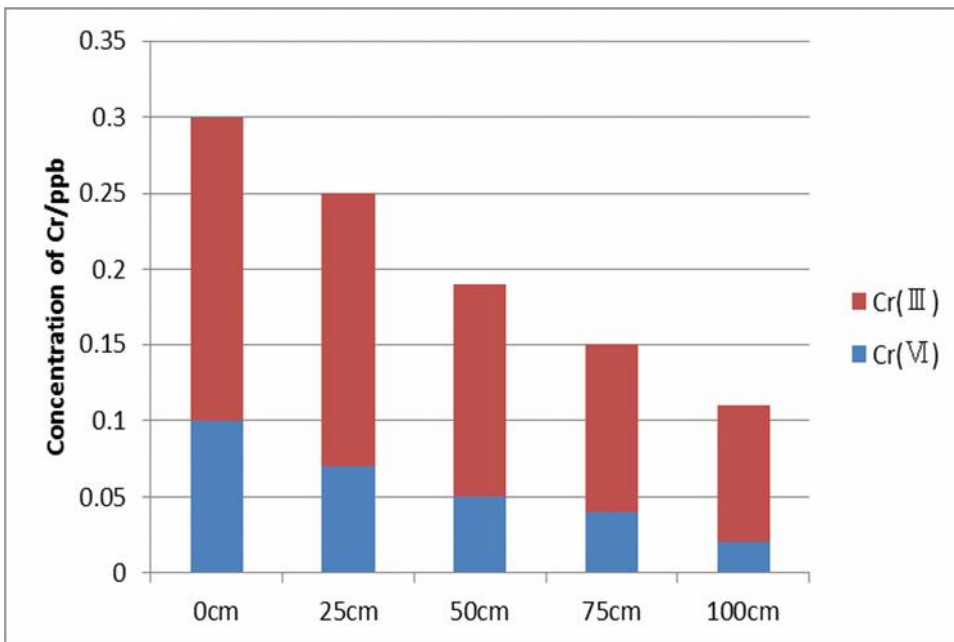
**Fig.2-13 Season variations and Comparison of T-P Concentrations between Sakata Lagoon and Zhalong Wetland**





S1	S2	S3	T1	T2
1.9	2.3	2.1	2.4	1.5

**Fig.2-14 Percentage of Cr species in environmental water in fine condition**



0cm	25cm	50cm	75cm	100cm
2.0	2.2	2.6	2.5	2.8

**Fig.2-15 Influence of the depth of water given to percentage of Cr species**

## **Chapter 3**

**Behavior of pollutants in lagoon waters  
and the effect of precipitation on the  
water quality of lagoon**

### 3.1 Introduction

Studies using stable isotopes have been important for valuable research in environmental sciences. Oxygen and hydrogen stable isotope ratios (i.e.,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) are widely used to investigate global or local hydrological cycle. These data supply some important hydrological information such as the groundwater recharge, the origin of the atmospheric vapor, and the movement of water in soils etc.

Hence, isotopic analyses of oxygen and hydrogen in environmental waters have been widely performed in the world.

Niigata Prefecture is located in the geographic position where the monsoon comes from the Continent. Moreover, a large amount of snow falls every year in winter season. Thus, isotopic and chemical investigation of the natural water samples in this area is very important for the understanding of hydrologic environment.

Therefore, we have investigated the characteristics of environmental water samples in Niigata Prefecture by using mainly  $\delta^{18}\text{O}$  as well as the concentration of major ions or trace metallic elements<sup>1)</sup>. In this study, the main subject is focused on the influence of rainfall event on the quality and characteristics of lagoon waters in Niigata Prefecture.

Then,  $\delta^{18}\text{O}$  and the concentration of major ions, the nutrients such as nitrogen (N) and phosphorus (P), heavy metals such as Cr in water samples after rainfall were determined as well as those in normal samples. The speciation analysis of chromium (Cr) in lagoon waters in Niigata Prefecture was also performed by applying ion-exchange methods in the present work.

The objective of this chapter is particularly to investigate the behavior of pollutants, and to estimate the source and/or supply route of the pollutants.

Then, in addition to the determination of COD (Chemical oxygen demand) and TOC (Total organic carbon) or DOC (Dissolved organic carbon), chlorophyll a was also determined. Furthermore, organic-origin nutrients (i.e., organic-N and organic-P) was calculated by subtracting inorganic-N (i.e.,  $\text{NH}_4^+\text{-N} + \text{NO}_2^-\text{-N} + \text{NO}_3^-\text{-N}$ ) from Total-N or inorganic-P (i.e.,  $\text{PO}_4^{3-}\text{-P}$ ) from Total-P.

In addition, to estimate the effect of surrounding environment, the sampling of surrounding river and drainage channel around Toyanogata was conducted. The ambient well water samples around Sakata was taken likewise.

Moreover, to survey the influence of precipitations on these lagoons,  $\delta^{18}\text{O}$  and the concentration of major ions and Cr in these samples after rainfall event were also determined as well as those in normal samples.

## **3.2 Experimental**

### **3.2.1 Study area (surrounding area of lagoon)**

The location of 5 ambient well water samples around Sakata is shown in Fig 3-1. In case of Toyanogata, the surrounding river and drainage channel around Toyanogata was researched. The sampling maps are shown in Fig. 3-2.

### 3.2.2 Analytical method

A stable isotope ratio mass spectrometer (Micromass PRISM) was used for measuring  $\delta^{18}\text{O}$ . For the measurement of  $\delta^{18}\text{O}$ ,  $\text{CO}_2\text{-H}_2\text{O}$  isotope equilibration method (Epstein & Mayeda 1953) was used. An ICP-AES instrument (Seiko Instruments, Inc., SPS1500) was used to determine the Cr concentration.

The concentrations of major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) were determined by ion chromatography (DIONEX, DX-100). Nutrients such as  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{PO}_4^{3-}$  and TN, TP were determined by Absorption Spectrophotometer (Hitachi-U5100).

The basic water quality data, such as temperature, pH, EC (electric conductivity), ORP (oxidation- reduction potential) and DO (dissolved oxygen) for samples were measured at each sampling point by a handy pH/COND and pH/DO Meter (HORIBA, D-24 and D-25).

The concentration of total organic carbon (TOC) was measured by TOC Meter (SHIMAZU, 5050A). Chemical oxygen demand (COD) was determined by titration with Potassium Permanganate ( $\text{KMnO}_4$ ). The content of Chlorophyll-a and humic substances were analyzed by fluorescence spectrometer (SHIMADZU, RF5300-PC).

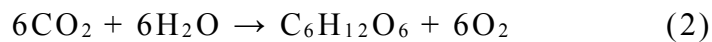
### 3.3 Results and Discussion

#### 3.3.1 DO and DOC of lagoon waters

Representative seasonal variations of pH of water samples at five points from Sakata and Toyanogata in Niigata Prefecture are shown in Fig.3-3

From Fig.3-3, it is found that pH of lagoon water samples is 6.5-8.5 (which is generally larger than that of river water), and that pH at the spot of Sakata1 (downstream point of Lower Lagoon (Shitakata)) is remarkably high (9.0-10.5). It might be attributable to photosynthesis due to aquatic plant and phytoplankton.

When these plants perform photosynthesis as following Eq. (2), CO<sub>2</sub> are consumed in lagoon waters.



Furthermore, it is considered that consumed CO<sub>2</sub> can be supplied from HCO<sub>3</sub><sup>-</sup> (hydrogen carbonate ion), and OH<sup>-</sup> (hydroxide ion) are given off as following Eq. (3).



Then pH of the lagoon water shows basic by the release of OH<sup>-</sup>.

Seasonal variations of DO and DOC in the representative lagoon water samples from Sakata and Toyanogata in Niigata Prefecture are shown in Fig.3-4, respectively. From Fig.3-5, it is noting that the value of DO in Sakata is relatively large in summer (particularly in July) in spite of large value of DOC in summer. It is suggested that the self-purification effect is existed in waters of Sakata because the dissolved oxygen is large in spite of large amount of organic materials. It may be related to photosynthesis of aquatic plants such as phytoplankton, considering it in conjunction with the results of above-mentioned pH. On the other hand, remarkable seasonal behavior of DOC or DO is not found in water samples of Toyanogata.

### **3.3.2 Organic components of lagoon waters**

The organic matter components at the fixed 5 points in Sakata and Toyanogata are shown in Table 3-1. It is noteworthy that the value of Chlorophyll-a is remarkably high in Sakata 1 as well as large values of DOC at spring and summer as mentioned in 3.3.1. It is suggested that the phytoplankton growth is active in Sakata 1.



### **3.3.3 Relationship between TOC and COD in lagoon waters**

The relationships between TOC and COD at Sakata and Toyanogata are shown in Fig 3-6(a) and (b). For a comparison, the relationships at Nishi River and Shinano River are shown in Fig 3-6(c) and(d).

From these figures, it is found that TOC vs. COD is generally good relationship, although the relationship at Shinano River is not good. In Shinano River, it is suggested that several species of organic materials was flowed in this river because there are some kinds of rivers in this water-system.

The relationships between TOC and COD may serve as a useful tool for estimating the effect of mixing from other kinds of water systems or from inflow of some organic materials.

### **3.3.4 $\delta^{18}\text{O}$ values of surrounding river and groundwaters near Toyanogata**

Seasonal behaviors of  $\delta^{18}\text{O}$  in surrounding river and groundwaters near Toyanogata are shown in Fig 3-7. It indicates that  $\delta^{18}\text{O}$  values of water samples in Shinano River is similar to that in Toyanogata throughout the year, and  $\delta^{18}\text{O}$  values of representative river waters such as Shinano River are almost from  $-11\text{‰}$  to  $-10\text{‰}$  throughout the year. On the other hand, the mean  $\delta^{18}\text{O}$  values of the representative groundwater samples in Niigata Prefecture are larger than that of river samples, and the values are about  $-9\text{‰}$  ( $-9.5\text{‰}$  to  $-8.5\text{‰}$ ) throughout the year.

### **3.3.5 $\delta^{18}\text{O}$ values of surrounding groundwaters near Sakata**

To confirm the effect of the recharge from the surrounding groundwater on Sakata lagoon waters,  $\delta^{18}\text{O}$  values of 5 ambient well water samples around Sakata (The location of these well water samples is (a), (b), (c), (d) and (e) in Table 3-2) were determined recently. These values are as follows:  $-8.28\text{‰}$  for (a),  $-8.22\text{‰}$  for (b),  $-8.32\text{‰}$  for (c),  $-8.53\text{‰}$  for (d) and  $-8.52\text{‰}$  for (e); and larger than those of other groundwater samples ( $-9.5\text{‰}$  to  $-8.5\text{‰}$ )<sup>17)</sup> near rivers in Niigata Prefecture.

From these results, it may be suggested that the recharge from the surrounding groundwater is one of important factors for the cause of large  $\delta^{18}\text{O}$  values in Sakata lagoon waters.

### **3.3.6 Relationship between DO and water temperature in environmental waters in Niigata Prefecture**

Relationship between DO and water temperature in lagoon waters is shown in Fig 3-8. The data in river waters are mostly distributed around a certain curve (i.e., the solubility curve), which might be related to the fact that the solubility of gas is inversely proportional to water temperature.

In case of lagoon waters, the data are mostly distributed over the upper part of the curve, whereas the data in groundwater are mostly distributed over the bottom of the curve.

As mentioned above, in lagoon, the photosynthesis due to aquatic plant and phytoplankton may perform, which leads to the production of a large amount of oxygen, and generally attain to supersaturation state of oxygen. On the other hand, oxygen is considered to be consumed by the active activity of microbes in groundwater because it is generally in contact with soil or rock. Then oxygen is mainly in unsaturated state in groundwater, and pH of the water shows acidic by the release of CO<sub>2</sub>. That is to say, it is suggested that lagoon water has the chemical characteristics contrasting to groundwater with a focus on river water from the viewpoint of pH (acidity or alkalinity) and DO.

### **3.3.7 The effect of precipitations on the variation of $\delta^{18}\text{O}$ in lagoon waters**

The  $\delta^{18}\text{O}$  values before and after rainfall events are compared in Fig 3-9. The sample collected after rainy weather is denoted as the symbol “\*” after each sample (e.g., LS1\*). For reference,  $\delta^{18}\text{O}$  variations of water samples at 3 points in Shinano River are also shown.

From Fig 3-9, it is found that  $\delta^{18}\text{O}$  in Sakata water samples after rainfall events is smaller than that in fine day (before rainfall). On the contrary to the samples in Sakata, reversal tendency was found for Toyanogata.

The following factors can be considered to alter  $\delta^{18}\text{O}$  values in lagoon waters after rainfall events:

- (1) dilution by the direct inflow of precipitation
- (2) supply from surrounding soil (rock) or groundwater
- (3) the reduction of “evaporation effect” relative to fine day

An enrichment of  $^{18}\text{O}$  after rainfall events may be caused by the factor (2) because  $\delta^{18}\text{O}$  in rock or groundwater is larger than that in lagoon or river waters; whereas the opposite change (i.e., depletion of  $^{18}\text{O}$ ) may be caused by the factor (3) because the concentration of heavy isotope (i.e.,  $^{18}\text{O}$ ) due to evaporation effect is larger in fine day than in rainy day. It can not be presumed whether factor (1) enriches or depletes  $\delta^{18}\text{O}$  of lagoon waters depending on  $\delta^{18}\text{O}$  of precipitation at each rainfall events.

Accordingly, it may be considered that in the case of sample waters in Sakata, factor (3) is dominant, which may be attributed to the fact that Sakata lagoon is relatively small lagoon. On the other hand, factor (2) may dominate in the case of Toyanogata.

### **3.3.8 The effect of precipitations on the variation of Cr in lagoon waters**

Furthermore, the speciation analysis of Cr in river waters after rainfall event was also shown in Fig.3-10. It is found that the distribution percentage of “suspended” remarkably increased for each sample taken on the day after rain fall event. Moreover, the increase of total Cr content was also found in all samples. Generally, the concentration of Cr in rainfall is lower than environmental water (river water or lagoon water) and the average is  $0.19 \mu\text{g}\cdot\text{dm}^{-3}$  <sup>28)</sup>. <sup>29)</sup>. On the other hand, the concentration of Cr in soil is much higher than environmental water and is about  $50 \text{mg}\cdot\text{dm}^{-3}$ . <sup>28)</sup> It is considered that the increase of total Cr (and the “suspended”) is caused by the supply from surrounding soil (or rock) due to the rainfall event instead of the direct inflow of precipitation.

### **3.3.9 The effect of precipitations on the variation of major ions in lagoon waters**

Compared with Sakata 1 and 2, specific variation of major ions was found in Sakata spring water (Table3-3). In particular, the concentrations of  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  increase after rainfall events. suggested that the weathering of calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and amphibole ( $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ) generally accounts for the concentration of  $\text{Ca}^{2+}$  in river and groundwater. In addition, Bischoff et al.30) described that the composition of the springs is entirely consistent with the chemical weathering of basaltic rock by carbonic acid solutions. Compared with lagoon waters, spring water is more affected by groundwater. Hence, increase of the concentration of  $\text{Ca}^{2+}$  after rainfall events in Sakata spring water indicates the possibility of geochemical weathering by the interaction with surrounding soil (rock). Moreover, it is well known that there are many paddy and upland fields around the sampling spots of Sakata spring water, consequently the fertilizer used in these fields may result in the increase of  $\text{NO}_3^-$  concentration after rainfall events.

On the contrary to the samples in Sakata, the concentrations of most major ions in Toyanogata increased after rainfall events. Enormous increase of the concentration of  $\text{Na}^+$ ,  $\text{Cl}^-$  was found in Toyanogata 2. In addition, higher concentration of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  after rainfall events is characteristic of Toyanogata, which may be attributed to the interaction of precipitation with calcium carbonate ( $\text{CaCO}_3$ ) in nearby soil of this lagoon. In other words, factor (2) may be dominant in Toyanogata as expected from analytical results of  $\delta^{18}\text{O}$ .

From the above-mentioned, one should note that the effect of rainfall event on lagoons was obviously different between Sakata and Toyanogata from analytical results of both  $\delta^{18}\text{O}$  and the concentrations of major ions.

### **3.3.10 Annual variations on the physical parameters in lagoon waters**

The data of physical parameters for lagoon water samples at the fixed 3 points in Sakata 2005 and 20014 are shown in Table3-4.

Among these data in Table3-4, it is found that the variations of physical parameters for lagoon water samples are generally small throughout the year. It may reflect that the pollution was not proceed so much.

Particularly, self-purification is active because of the biological process in Sakata.



## 3.4 Conclusions

(i) The value of DO in Sakata is relatively large in summer in spite of large value of DOC in summer. Moreover, the eutrophication is not relatively large in spite of high concentrations of chlorophyll a. Self-purification is active because of the biological process in Sakata.

(ii) Lagoon water has the chemical characteristics contrasting to groundwater with a focus on river water from the viewpoint of pH (acidity or alkalinity) and DO. These matters can be closely related to the biological activity such as photosynthesis due to aquatic plant and phytoplankton and the activity of *Crustacea* plankton etc. in lagoon.

(iii) After rainfall events, the following matters were considered.

1.  $\delta^{18}\text{O}$  of sample at S3 increased after rainfall events as well as those of samples in Toyonogata.
2. The concentrations of  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  increased after rainfall events at S3.
3. The concentration of total Cr and the percentage of “suspended” remarkably increased after rainfall event. The concentration of Cr(III) is larger than that of Cr(VI) species in our samples.

It is suggested that the increase of dissolved components may be caused by the supply from surrounding soil (or rock) due to the rainfall event instead of the direct inflow of precipitation.

**Table 3-1 The organic matter components in Sakata and Toyanogata**

Sampling Points		Measurement items				
		DOC (mg/l)	COD(mg/l)	DON (mg/l)	DOP (mg/l)	Chl-a (mg/l)
Sakata Lagoon 1	Spring	9.3	---	0.9	0.05	---
	Summer	10.8	26.9	0.8	0.06	0.28
	Autumn	3.3	24.1	0.3	0.01	0.25
	Winter	1.7	26.8	2.6	0.01	0.41
Sakata Lagoon 2	Spring	3.6	---	2.2	0.04	---
	Summer	8.1	4.8	1.3	0.07	0.03
	Autumn	1.4	5.4	3.0	0.03	0.02
	Winter	1.7	3.7	5.2	0.03	0.02
Sakata Lagoon 3	Spring	2.8	---	6.6	0.01	---
	Summer	4.5	1.9	6.7	0.01	0.02
	Autumn	0.9	2.3	13.5	0.003	0.03
	Winter	0.9	1.2	12.2	0.004	0.01
Toyano Lagoon ①	Spring	3.1	---	0.5	0.01	---
	Summer	3.5	5.1	0.3	0.01	0.1
	Autumn	3.1	4.2	0.9	0.01	0.006
	Winter	2.1	2.7	1.1	0.01	0.002
Toyano Lagoon ②	Spring	3.4	---	1.3	0.02	---
	Summer	3.4	2.9	0.6	0.01	0.001
	Autumn	1.9	2.6	1.0	0.01	0.001
	Winter	2.5	2.4	1.2	0.01	0.01

Table 3-2  $\delta^{18}\text{O}$  average values of well water and lagoon water

Sampling point	$\delta^{18}\text{O} / \text{‰}$
a	-8.28
b	-8.22
c	-8.32
d	-8.53
e	-8.52
S1	-7.10
S2	-8.28
S3	-8.24

**Table3-3 Concentration (ppm) of major ions in S3 before and after rainfall events**

	Before rainfall	After rainfall
Na <sup>+</sup>	23.9	23.9
K <sup>+</sup>	3.30	4.34
Ca <sup>2+</sup>	29.1	43.7
Mg <sup>2+</sup>	14.8	13.7
Cl <sup>-</sup>	20.2	18.2
NO <sub>3</sub> <sup>-</sup>	56.2	81.8
SO <sub>4</sub> <sup>2-</sup>	88.8	72.5

**Table3-4 The data of physical parameters for lagoon water samples at the fixed 3 points in Sakata 2005 and 20014**

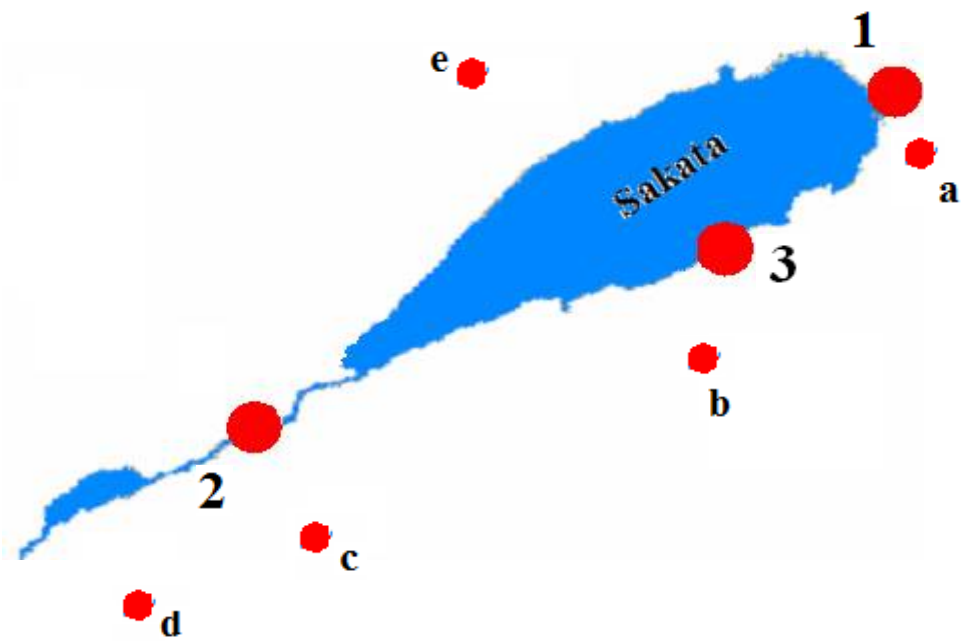
	pH	Apr	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
2005	Sakata 1	9.5	9.6	9.5	9.4	9.2	8.5	9.6	8.6	8.9
	Sakata 2	8.5	8.4	7.3	6.9	6.8	6.8	7.4	7.4	8.2
	Sakata 3	7.0	7.2	7.0	7.0	7.0	7.3	7.7	7.2	7.9
2010	Sakata 1	9.4	8.6	9.2	6.9	6.9	6.9	7.3	9.4	8.8
	Sakata 2	7.1	9.1	7.7	6.6	6.5	6.8	7.0	6.9	7.5
	Sakata 3	7.5	7.1	7.5	7.0	6.9	6.8	6.8	6.9	7.2
2014	Sakata 1	8.9	6.9	10.6	9.9	10.4	10.4	9.9	9.4	9.6
	Sakata 2	8.0	9.2	8.0	7.8	7.3	7.7	6.8	7.5	8.0
	Sakata 3	7.1	6.8	7.7	7.1	7.6	7.8	7.5	7.2	7.4

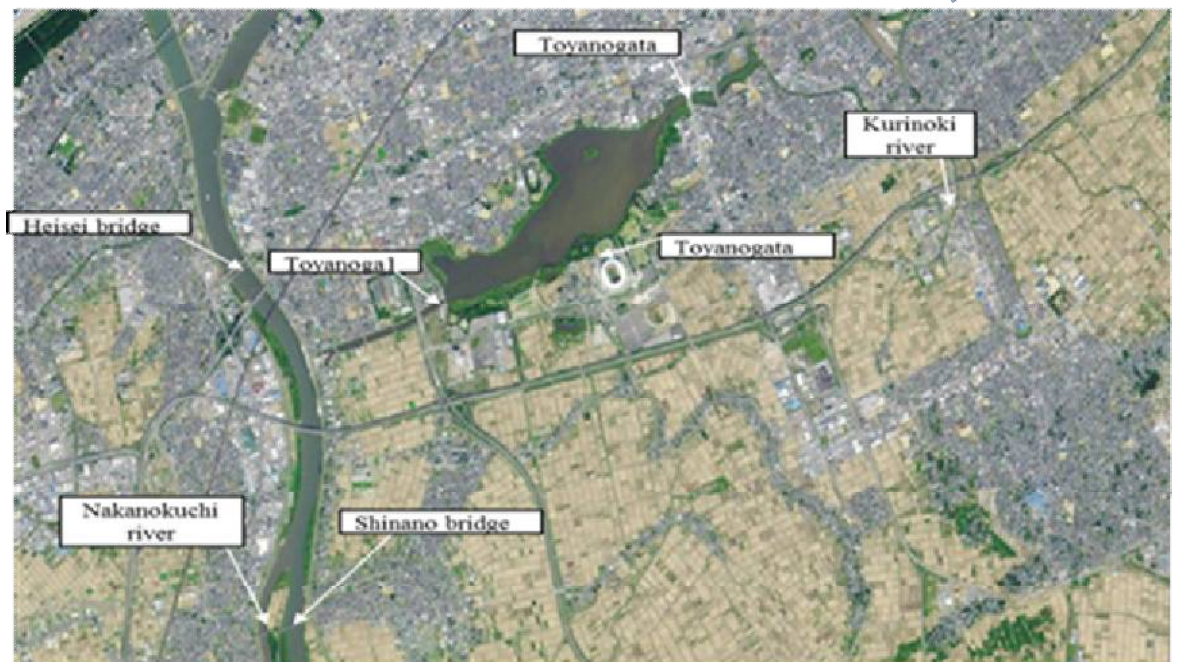
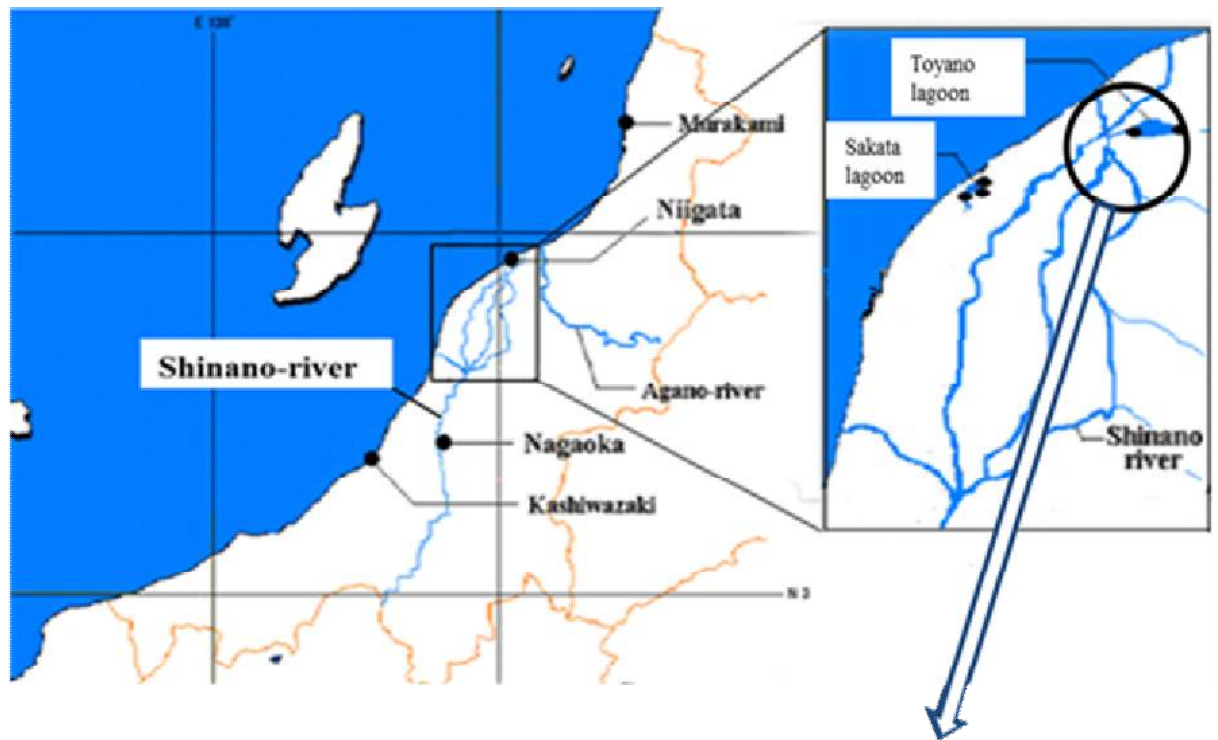
	EC(S/cm)	Apr	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
2005	Sakata 1	28.6	26.8	23.8	23.3	28.3	30.1	27.8	29.1	28.9
	Sakata 2	27.4	28.6	31.2	31.8	33.8	31.4	30.7	32.6	29.3
	Sakata 3	39.6	37.5	35.4	37.2	59.7	39.0	36.5	33.5	37.4
2010	Sakata 1	14.7	27.0	26.3	28.0	27.7	26.1	35.3	29.5	26.3
	Sakata 2	14.9	29.2	29.4	32.1	28.1	30.3	32.6	33.5	30.2
	Sakata 3	35.5	38.2	40.5	40.7	37.8	38.3	40.4	40.8	40.3
2014	Sakata 1	29.1	31.9	27.6	23.2	29.6	22.0	14.6	28.3	28.8
	Sakata 2	30.4	28.5	30.7	33.4	35.2	28.5	31.6	29.3	15.7
	Sakata 3	34.8	35.3	37.5	38.2	35.3	32.2	21.3	37.9	38.7

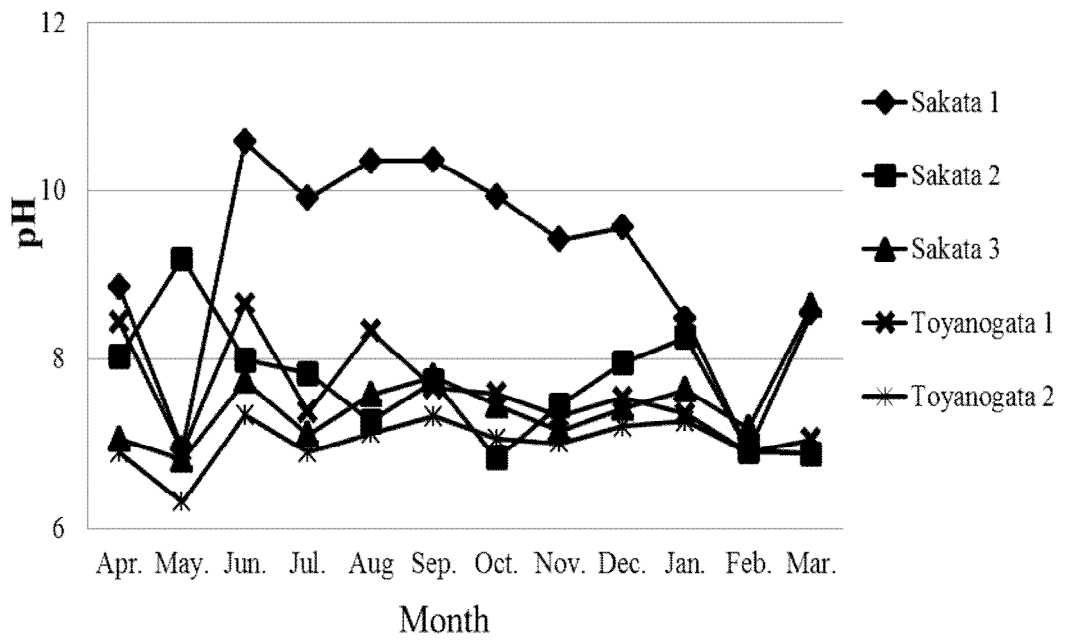
	DO(mg/l)	Apr	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
2005	Sakata 1	6.6	7.0	12.6	10.8	5.9	9.4	11.2	11.3	12.9
	Sakata 2	7.6	7.6	5.2	2.1	5.0	3.8	6.1	6.3	8.9
	Sakata 3	7.3	7.4	6.7	7.3	7.1	8.3	7.0	7.3	6.9
2010	Sakata 1	12.3	11.8	14.6	4.3	2.5	3.3	4.6	14.3	15.5
	Sakata 2	9.7	16.1	8.4	3.1	1.6	2.5	5.0	3.5	6.3
	Sakata 3	9.4	10.3	11.5	10.5	7.7	8.8	9.8	11.6	12.6
2014	Sakata 1	11.4	10.5	8.8	19.9	-	19.1	15.1	13.6	16.3
	Sakata 2	13.0	10.8	18.8	8.7	4.8	8.6	3.9	9.0	10.6
	Sakata 3	10.4	12.7	10.6	7.8	12.4	11.3	9.8	8.3	8.8



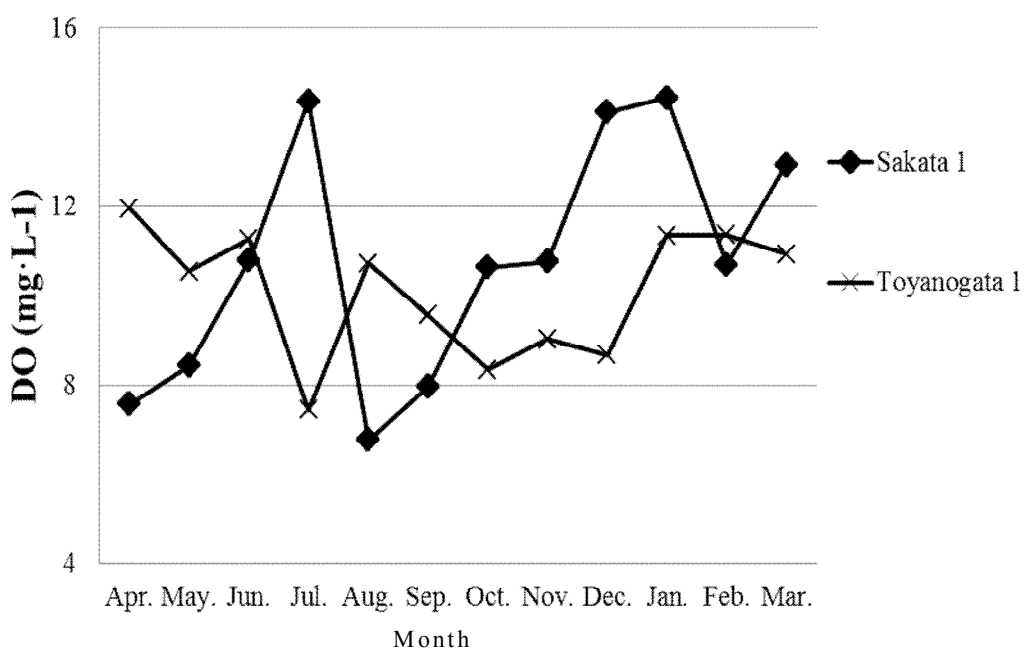
**Fig.3-1 The location of ambient well water samples around Sakata**



**Fig.3-2 The location of ambient samples around Toyanogata**

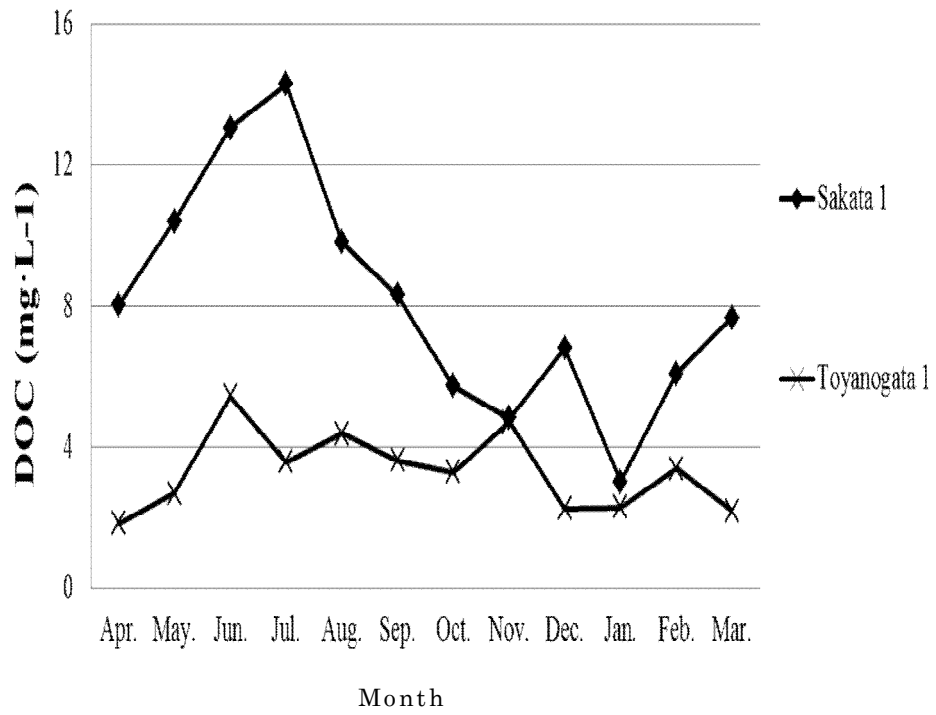


**Fig.3-3 Monthly variation of pH in Sakata and Toyanogata.**

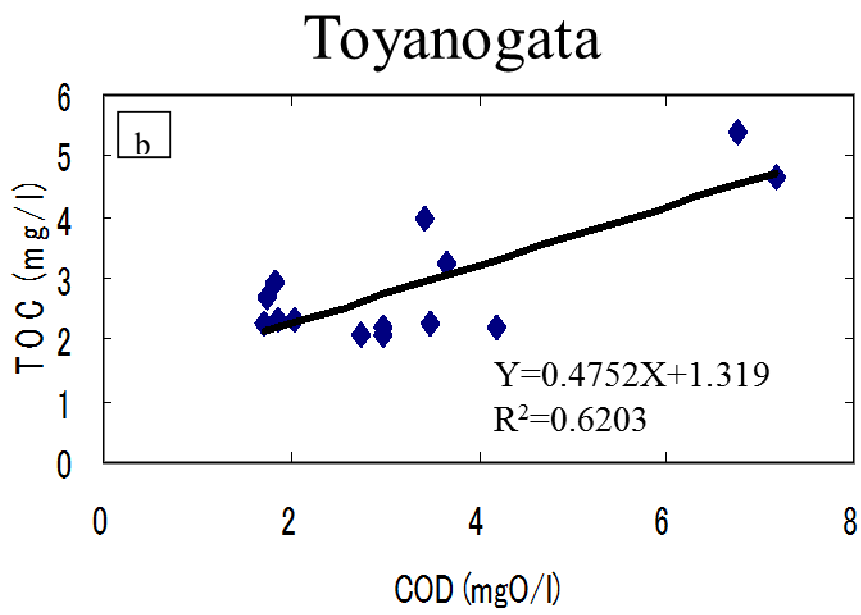
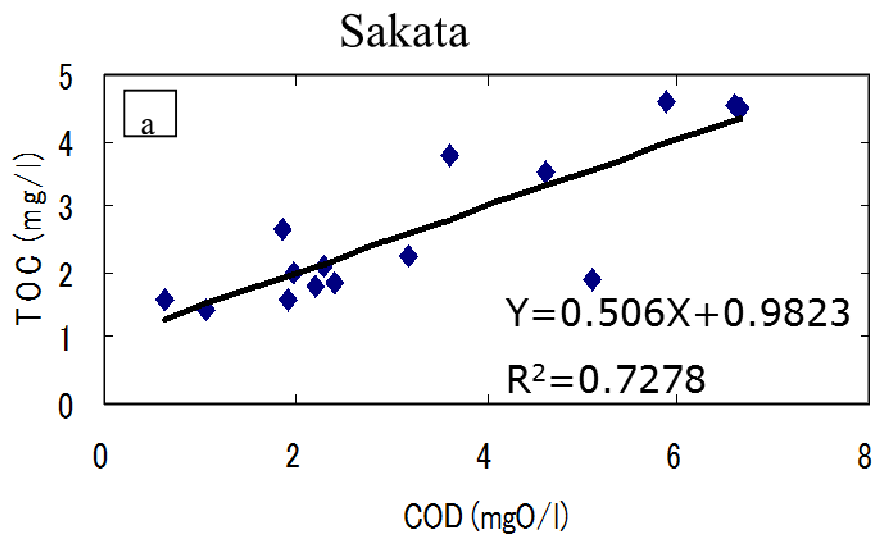


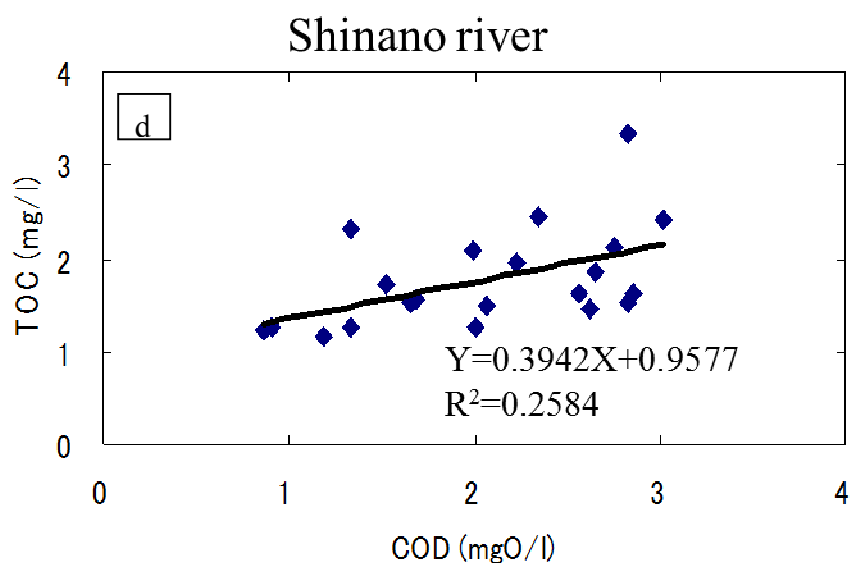
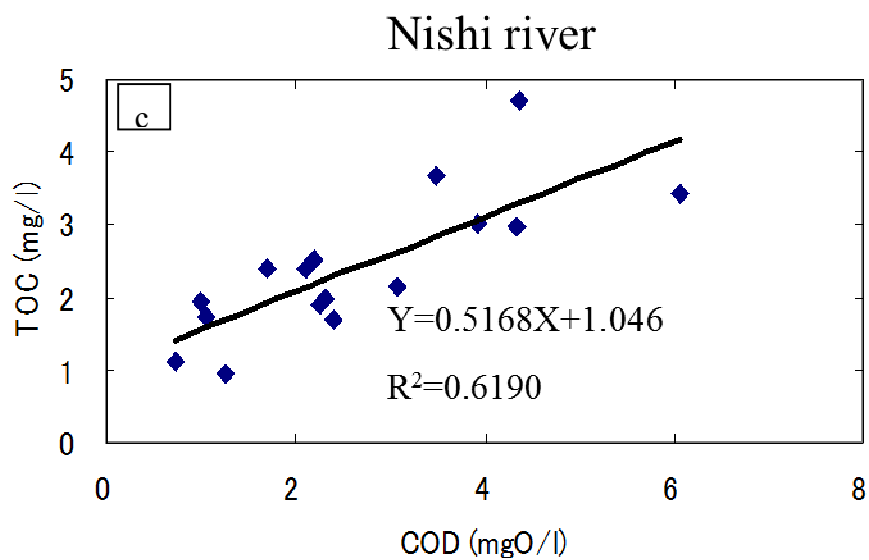
**Fig.3-4 Monthly variation of DO in Sakata and Toyanogata.**





**Fig.3-5 Monthly variation of DOC in Sakata and Toyanogata.**





**Fig.3-6 The relationships between TOC and COD**

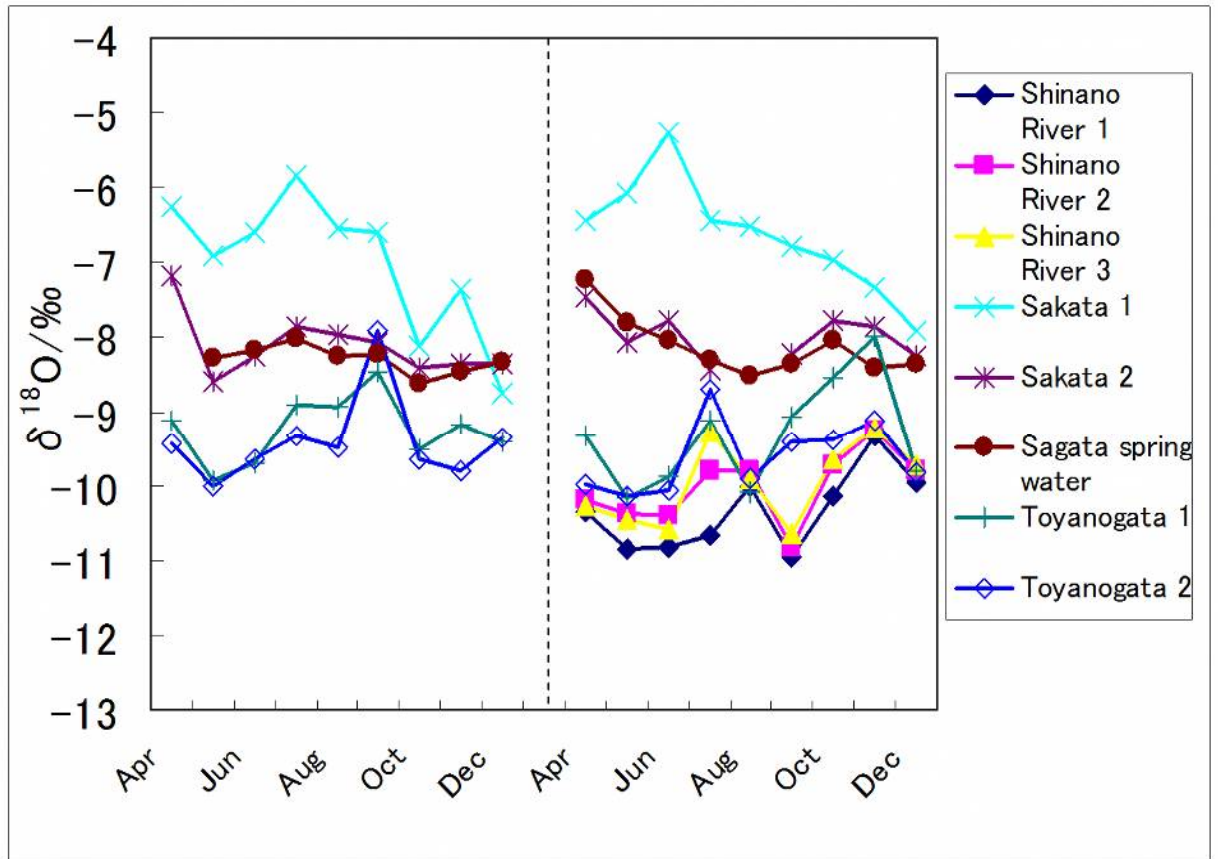
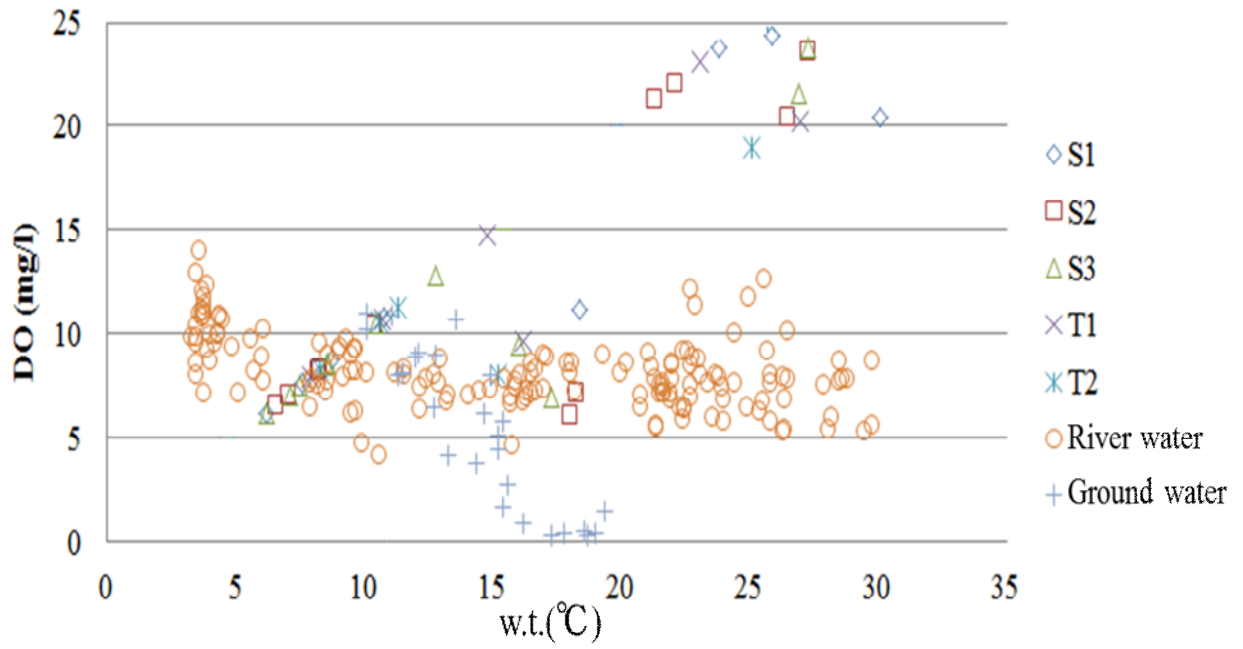
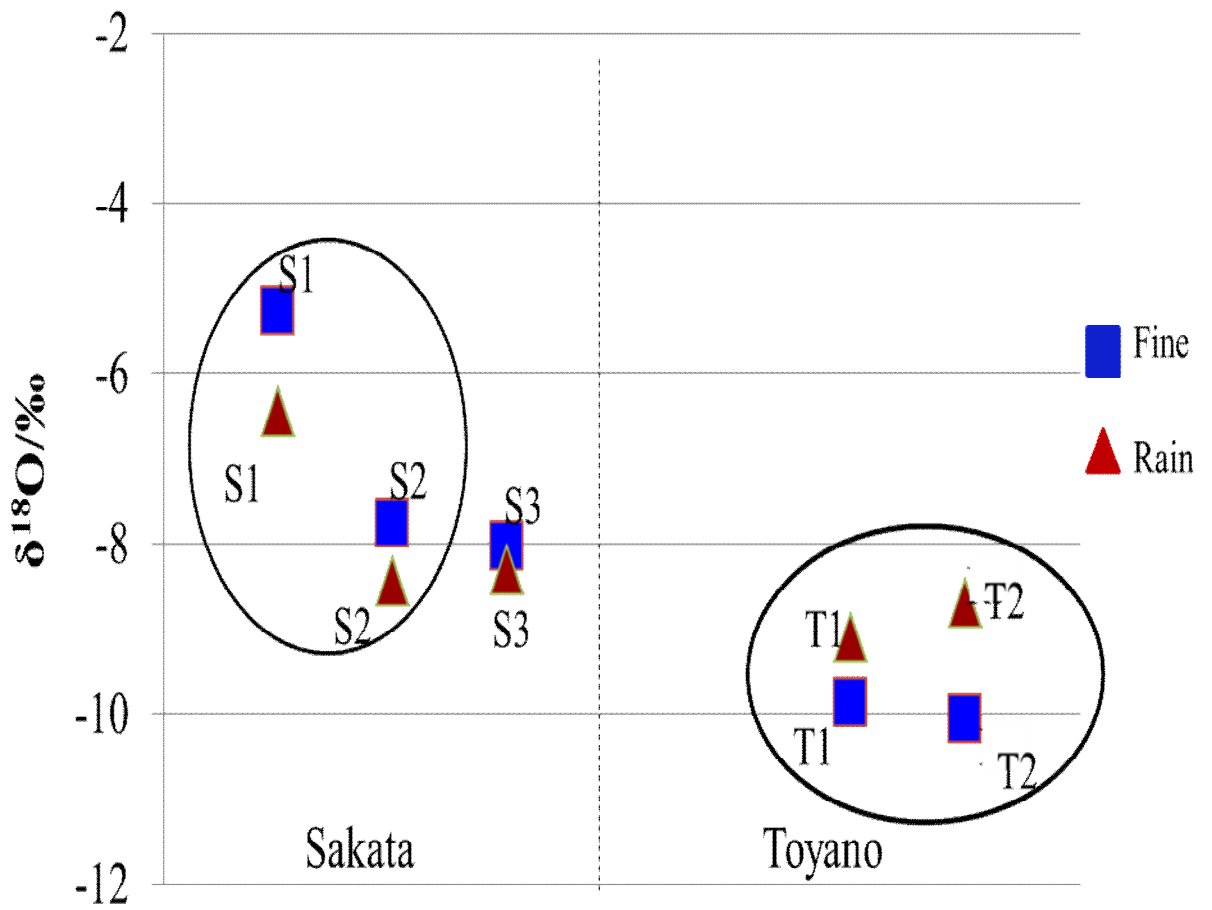


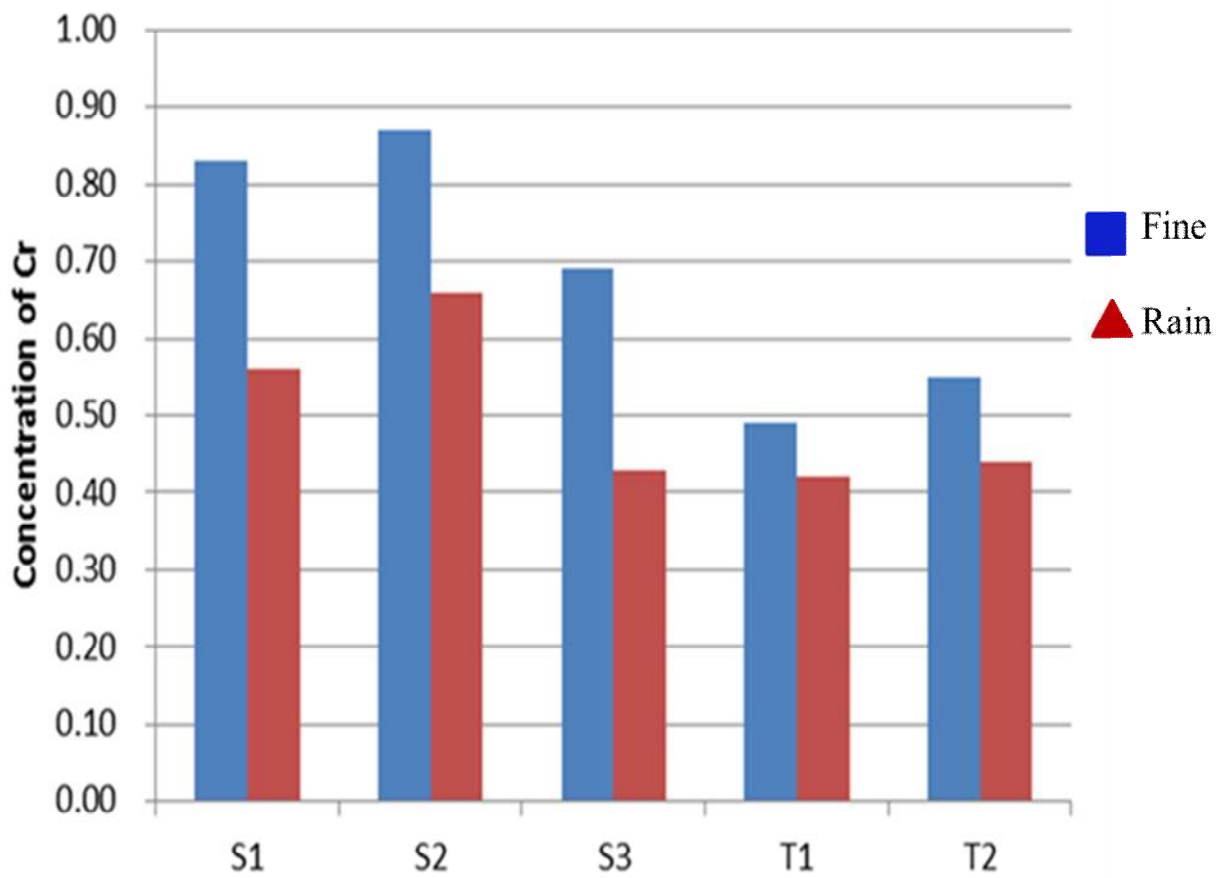
Fig.3-7 Monthly variation of  $\delta^{18}\text{O}$  in environmental waters



**Fig.3-8 Relationship between DO and water temperature in lagoon waters**



**Fig.3-9 Comparing the  $\delta^{18}\text{O}$  in “ normal weather condition ” and “ after rainfall event ”.**



**Fig.3-10 Percentage of Cr species in environmental water after rainfall event**

# **Chapter 4**

## **Oxygen stable isotopic ratio in precipitations in Niigata Prefecture, Japan**



## 4.1 Introduction

Oxygen and hydrogen stable isotope ratios (i.e.,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) have already been extensively used to investigate global or local hydrological cycle and to trace the origin and evolution of water<sup>31)33)</sup>.

Oxygen and hydrogen isotope play an important role to survey isotope distribution of precipitation.

The stable isotopic compositions of precipitations vary with physical-chemical conditions such as evaporation and condensation in hydrological cycle<sup>32)33)</sup>. In addition, researches on precipitation chemistry in different areas have received some attention in recent years<sup>34)35)36)</sup>. It is considered that  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of precipitation reflect the origin of the atmospheric vapor and the conditions of precipitation formation above the sampling site<sup>37)</sup>. Thus, the isotopic variations of individual precipitation allow us to assess gradual or abrupt changes in the meteorological conditions governing the precipitation formation<sup>38)</sup>.

Furthermore, the  $\delta^{18}\text{O}$  value of the precipitation is considered to be correlated with the air temperature of the place where the precipitation is formed<sup>37)39)40)</sup>. Hence, estimating time-course of  $\delta^{18}\text{O}$  in individual precipitation for a short period is important for the standpoint of the meteorology as well as investigating annual or seasonal behavior of  $\delta^{18}\text{O}$ .

Niigata Prefecture is located in the center of Honshu Island in Japan, and acts as a receptor for the huge natural and anthropogenic emissions from adjacent continent, and also has long range transport with the influence of monsoon<sup>41)</sup> Moreover, a large amount of snow falls every year in winter season. Thus, isotopic and chemical investigation of the precipitation samples in Niigata Prefecture is significant for the understanding of hydrologic environment in this area.

Considering the above-mentioned, the characteristics of precipitation samples in Niigata Prefecture by using  $\delta^{18}\text{O}$  and other measuring items have been investigated in previous work<sup>42)</sup>.

In this paper, to investigate the characteristics and sources of precipitations in Niigata Prefecture in more detail, in addition to regularly sampling conducted every one or two weeks as described in previous paper<sup>42)</sup>, sequential rainfalls sampling for a short period was preliminarily carried out for five precipitations in any seasons including during the passage of typhoon. For these samples, time-course of  $\delta^{18}\text{O}$  was examined during rainfalls; and backward trajectories analyses have been also conducted to estimate the passing route of air mass which bring about the precipitation.

## **4.2. Experimental**

### **4.2.1 Samples**

Precipitation samples have been weekly collected with a filtrating bulk sampler (Fig. 4-1) at the rooftop of Niigata University, Niigata City of Japan (139°02' E, 37°55' N). Furthermore, precipitations from several sampling points in Niigata Prefecture have been supplied as occasional demands by Niigata Prefectural Research Institute of Public Health and Environmental Sciences. In this work, samples in four points in Niigata Prefecture (Fig. 4-2) taken in 2005-2006 were examined.

In addition to above samples, some precipitations were taken sequentially for a short period from July 2009 to March 2010. Sequentially taken rainfalls are listed in Table 4-1. Among these samples, the second precipitations were taken during passage of the No. 18 Typhoon in 2009<sup>43)</sup>.

### **4.2.2 Analytical Method**

For the measurement of oxygen stable isotope ratios ( $\delta^{18}\text{O}$ ),  $\text{CO}_2\text{-H}_2\text{O}$  isotope equilibration method<sup>44)</sup> was performed. The sample preparation procedure was the same as described in previous work<sup>42)</sup>. Isotopic measurements were performed with a stable isotope ratio mass spectrometer (Micromass Prism).

### **4.2.3 Backward Trajectories Analyses**

Backward trajectories analyses have been conducted for sequentially taken rainfalls based on METEX (Meteorological Data Explorer)<sup>45)</sup> by Center for Global Environmental Research, National Institute for Environmental Studies.

## 4. 3. Results and Discussion

### 4.3.1 Seasonal Variation of $\delta^{18}\text{O}$ Values in the Precipitation

The basic data such as pH, EC (electric conductivity), temperature and amount of precipitation for samples weekly taken at the rooftop of Niigata University in 2010 are shown in Table4-2. Monthly variation of  $\delta^{18}\text{O}$  for these precipitation samples is shown in Fig.4-3 along with the amount of precipitation.

The  $\delta^{18}\text{O}$  values of the precipitation samples at four points in Niigata Prefecture from April 2005 to March 2006 are shown in Table4-3. It is found that the mean value of  $\delta^{18}\text{O}$  at seaside spots (i.e., Niigata City) is larger than that of inland spots (Nagaoka or Sanjyo City). Particularly, it is notable that the mean value of  $\delta^{18}\text{O}$  in Sanjyo (-8.68‰) is remarkably small compared to that of other points.

From Fig.4-4, which was displayed based on the data in Table4-3, it is found that  $\delta^{18}\text{O}$  values in Sanjyo City are generally small throughout the year, although  $\delta^{18}\text{O}$  value in Jouetsu is low depending on season. It may reflect that the precipitations in Niigata Prefecture are dominantly affected by “continental effect” [1].

From Figs.4-3 and 4- 4, the following features have been generally presented in the precipitation in Niigata Prefecture: (1) In rainy season or autumn (particularly typhoon season),  $\delta^{18}\text{O}$  values of precipitation are relatively small, whereas  $\delta^{18}\text{O}$  values of precipitation are relatively large in summer; (2) The variation of  $\delta^{18}\text{O}$  value in precipitation is generally smaller in winter than in summer at each area in Niigata Prefecture. In rainy season, when the development of the seasonal rain front over Japan is large, the air mass (which origin is generally Pacific Ocean or East China Sea) based on the seasonal rain front bring rain slowly from south, and decrease  $^{18}\text{O}$  with the movement to northward. Thus low  $\delta^{18}\text{O}$  value observed in high latitude (such as Niigata City) can be attributed to the effect of “latitude effect” [1] as well as “amount effect” [1]. Higher  $\delta^{18}\text{O}$  values observed in summer may be related to the development of Pacific high pressure because the Pacific high pressure is dominant in summer in Japan. This may be predominantly affected by “temperature effect” [1]. Liu et al. <sup>43)</sup> mentioned that  $\delta^{18}\text{O}$  of summer monsoon precipitation in East Asia is relatively larger than that of winter precipitation, and is in good agreement with this work<sup>43)</sup>. In winter, the Siberian air mass crosses northern Japan including Niigata Prefecture and the supply route of precipitation is relatively uniform. It can be one of the causes that the variation of  $\delta^{18}\text{O}$  in precipitation is generally small in winter.

From the above-mentioned, it is considered that the variation of  $\delta^{18}\text{O}$  values is closely related to the dominance or stability of the air mass in each season.

### 4.3.2 Time-Course of $\delta^{18}\text{O}$ Values in the Precipitation

Time-course of  $\delta^{18}\text{O}$  for sequentially sampled precipitations on July 27, 2009 is presented in Fig.4-5 along with the amount of precipitation. From Fig.4-5, it is found that  $\delta^{18}\text{O}$  decreased with time during 10:00-14:00, although slightly increased at first and final stage. Taking time-course of  $\delta^{18}\text{O}$  (during 10:00-14:00) into consideration with the backward trajectories analyses (Fig.4-5)<sup>45)</sup>, it is suggested that the precipitations might be brought about by the same air mass (i.e., the source is near East China Sea and the passing route is almost constant) during precipitations. It may reflect the feature as predicted by “Rayleigh model of atmospheric vapor condensation<sup>28)34)35)</sup>”. On the other hand,  $\delta^{18}\text{O}$  increased at 10:00 and at 16:00, which may be related to “amount effect” [1] (because the amount of precipitation is small at 10:00 and at 16:00). Alternatively, the inflow of air having different origin (with relatively large  $\delta^{18}\text{O}$  value) can be considered.

Time-course of  $\delta^{18}\text{O}$  for sequentially sampled precipitations on October 8, 2009 is presented in Fig.4-6 along with the amount of precipitation. From Fig.6 it is found that  $\delta^{18}\text{O}$  decreased with time until the final stage, as predicted by “Rayleigh model of atmospheric vapor condensation”. Taking time-course of  $\delta^{18}\text{O}$  into consideration with the backward trajectories analyses (Fig.4-6)<sup>45)</sup>, it is suggested that the series of precipitations might be brought about by the same air mass (i.e., the source is near Pacific Ocean and the passing route is almost constant) during precipitations. Furthermore, the amount of precipitations decreased with time until the final stage, suggesting that the new inflow of air cannot be found during the series of precipitations.

Time-course of  $\delta^{18}\text{O}$  of the sequentially precipitations taken from November 11, 2009 is shown in Fig.4-7 along with the amount of precipitation.

From Fig.4-7, it is also found that  $\delta^{18}\text{O}$  decreased with time until the final stage, as predicted by “Rayleigh model of atmospheric vapor condensation”. Judging from the backward trajectories analyses (Fig.4-7)<sup>45)</sup>, the source which brought about the precipitation is near north of Japan Sea. Time-course of  $\delta^{18}\text{O}$  of the sequentially precipitations taken from January 20-21, 2010 is shown in Fig.4-8 along with the amount of precipitation. Contrary to the above case,  $\delta^{18}\text{O}$  generally increased with time until the final stage. Furthermore, the amount of precipitations increased with time until the final stage.

The feature as predicted by “Rayleigh model of atmospheric vapor condensation” was not shown in the series of precipitations, which may be attributable to the

intermittent inflow of air having different origin with relatively large  $\delta^{18}\text{O}$  value during the series of precipitations. Judging from the backward trajectories analyses (Figs. 4-8a,4-8c)<sup>45)</sup>, the source which brought about the precipitation is near Siberia and north of Japan Sea.

Time-course of  $\delta^{18}\text{O}$  of the sequentially precipitations taken from March 4-5, 2010 is shown in Fig.4-9 along with the amount of precipitation. It is found that  $\delta^{18}\text{O}$  increased at first, and then gradually decreased with time (during 21:00-1:00). From the backward trajectories analyses (Figs.4-9a,4-9d)<sup>46)</sup>, it is found that the source which brought about the precipitation changed from (a) (at 19:00) to (b) (at21:00). Then, the remarkable increase of  $\delta^{18}\text{O}$  at 21:00 may be attributable to the supply of the air masses having different origin with high  $\delta^{18}\text{O}$  value.

Furthermore, the amount of precipitations increased with time until the final stage. It is considered that the water vapor was continuously supplied from the same air mass (i.e., the continent of China, Yellow Sea, and Japan Sea) during 21:00-1:00, and then brought about the continuous increase of rainfall.

Considering the above-mentioned, it appears that a decreasing heavy isotope (i.e.,  $\delta^{18}\text{O}$ ) content, as predicted by Rayleigh models of atmospheric vapor condensation, is a predominant feature of sequentially sampled rainfalls, particularly for precipitations taken during passage of typhoons, although further investigations are needed to confirm the relationship between time-course of  $\delta^{18}\text{O}$  and meteorological condition in more detail.

From this work, the sources and passing routes (or the characteristics) of precipitations in Niigata Prefecture could be quantitatively clarified to some extent. The data obtained and the method used in this work can be useful for the preservation of atmospheric environment.

## 4.4 Conclusions

For the investigation of the characteristics, sources and the passing route of precipitations in Niigata Prefecture, time-course of oxygen stable isotopic ratios (i.e.,  $\delta^{18}\text{O}$ ) as well as seasonal variation of  $\delta^{18}\text{O}$  have been examined. It was suggested that decreasing  $\delta^{18}\text{O}$  content with time found in the samples of sequential rainfall for a short period is a predominant feature as predicted by Rayleigh models of atmospheric vapor condensation.

Moreover, it was found that the mean value of  $\delta^{18}\text{O}$  at seaside spots (i.e., Niigata City: -6.93‰) is larger than that of inland spots (Nagaoka City: -7.58‰ or Sanjyo City: -8.68‰), and that the  $\delta^{18}\text{O}$  values varied between -14.57‰ and -3.86‰ in the precipitations of Niigata University.

**Acknowledgments** The present work was partially supported by a Grant-in-Aid for Scientific Research of the Japan Society for the Promotion of Science. Precipitation samples from four sampling points in Niigata Prefecture have been supplied by Niigata Prefectural Research Institute of Public Health and Environmental Sciences.

**Table 4-1 The sampling data of rainfall events from 2009 to 2010 in Niigata University.**

Rainfall Date	Number of samples	Amount of precipitation / mm	Sampling period / h
Jul 27,2009	5	26	10
*Oct 8,2009	5	6.5	10
Nov 11,2009	4	5.5	8
Jan 20-21, 2010	3	6.5	6
Mar 4-5, 2010	4	9.5	8

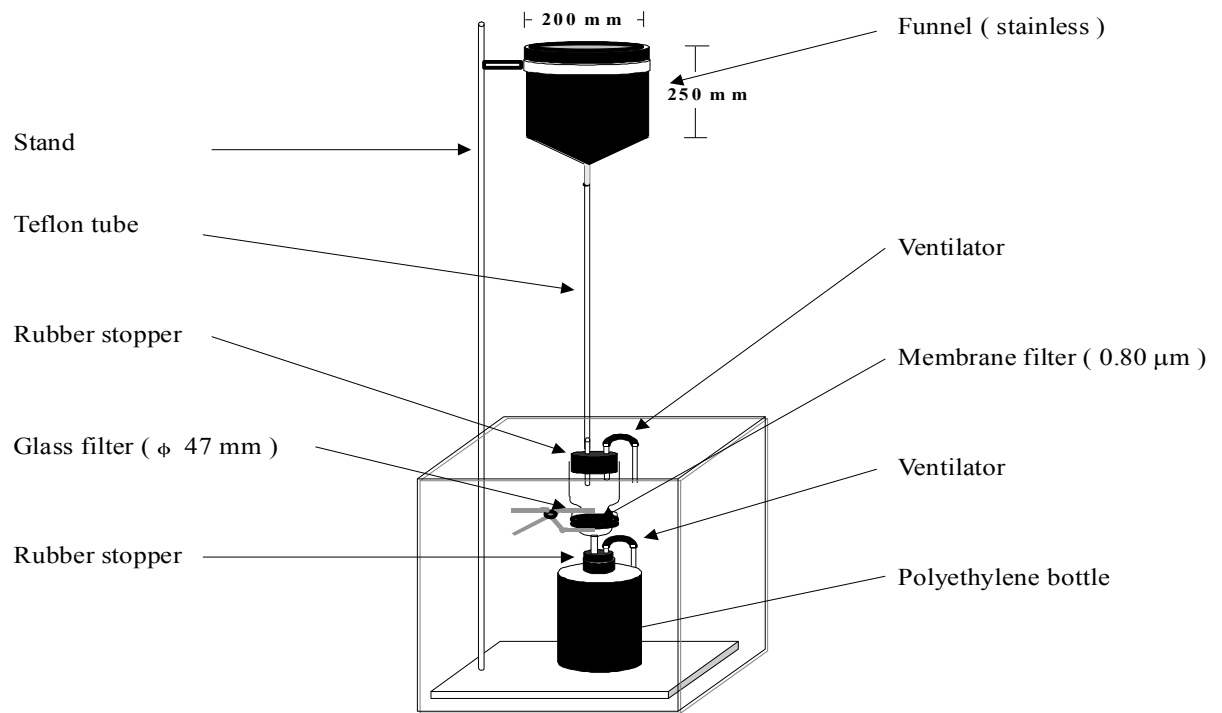
**Table 4-2 The variation of pH and EC in precipitation at Niigata University.**

Term	pH	EC( $\mu$ S/cm)	Temperature ( $^{\circ}$ C)	Amount(mm)	
1.4-1.11		4.36	190.6	4.1	36.62
1.11-1.18		3.92	191.2	7.9	37.58
1.18-1.25		4.06	79.5	9.4	47.13
1.25-2.1		4.50	109.6	10.3	20.38
2.1-2.9		4.10	146.5	10.7	66.88
2.9-2.16		4.60	36.2	6.0	42.04
2.16-2.23		3.81	113.4	14.6	23.89
2.23-3.2		4.12	44.5	8.7	39.81
3.2-3.9		3.81	59.9	11.3	11.15
3.9-3.16		5.48	46.9	12.5	47.77
3.16-3.23		4.79	71.7	10.0	21.02
3.23-3.30		5.39	81.0	7.0	30.25
3.30-4.6		4.02	17.9	14.6	30.89
4.6-4.13		5.05	36.1	15.0	28.66
4.13-4.20		4.66	66.4	18.8	25.48
4.20-4.27		5.59	19.6	18.5	14.65
4.27-5.4		4.99	52.5	21.0	11.78
5.4-5.11		4.93	22.2	18.5	12.42
5.11-5.18		4.60	16.4	22.1	25.48
5.18-5.25		5.01	6.7	22.3	50.34
5.25-6.1		5.66	28.5	21.7	38.22
6.1-6.8		4.16	36.7	25.3	6.37
6.8-6.15		3.94	32.3	27.9	6.37
6.15-6.22		4.36	14.8	26.5	52.87
6.22-6.29		4.70	9.7	25.2	79.94
6.29-7.13		4.24	29.3	23.3	28.98
7.13-7.20		5.33	9.5	32.0	35.03
7.20-8.3		4.40	13.7	32.0	41.40
8.3-8.17		4.37	14.2	33.2	37.90
8.17-9.7		4.92	18.6	23.0	36.62
9.7-9.14		4.47	32.4	28.2	79.94
9.14-9.21		4.01	15.9	25.7	45.08
9.21-9.28		5.14	24.3	18.8	71.34
9.28-10.5		5.55	27.5	19.0	32.17
10.5-10.12		4.85	18.5	24.4	31.85
10.12-10.19		4.38	68.0	21.6	8.92
10.19-10.26		4.43	88.6	13.4	11.46
10.26-11.2		5.35	97.4	16.3	50.32
11.2-11.9		4.02	120.4	13.0	69.43
11.9-11.16		4.47	190.6	10.0	24.20
11.16-11.23		4.28	49.2	10.2	23.89
11.23-11.30		4.40	94.8	16.1	49.36
11.30-12.7		4.38	202.0	9.0	42.68
12.7-12.14		4.70	105.7	12.1	37.58
12.14-12.20		4.17	70.0	8.50	64.65
12.20-12.28		4.60	157.6	8.0	66.88
12.28-1.4		4.12	131.2	4.8	42.04

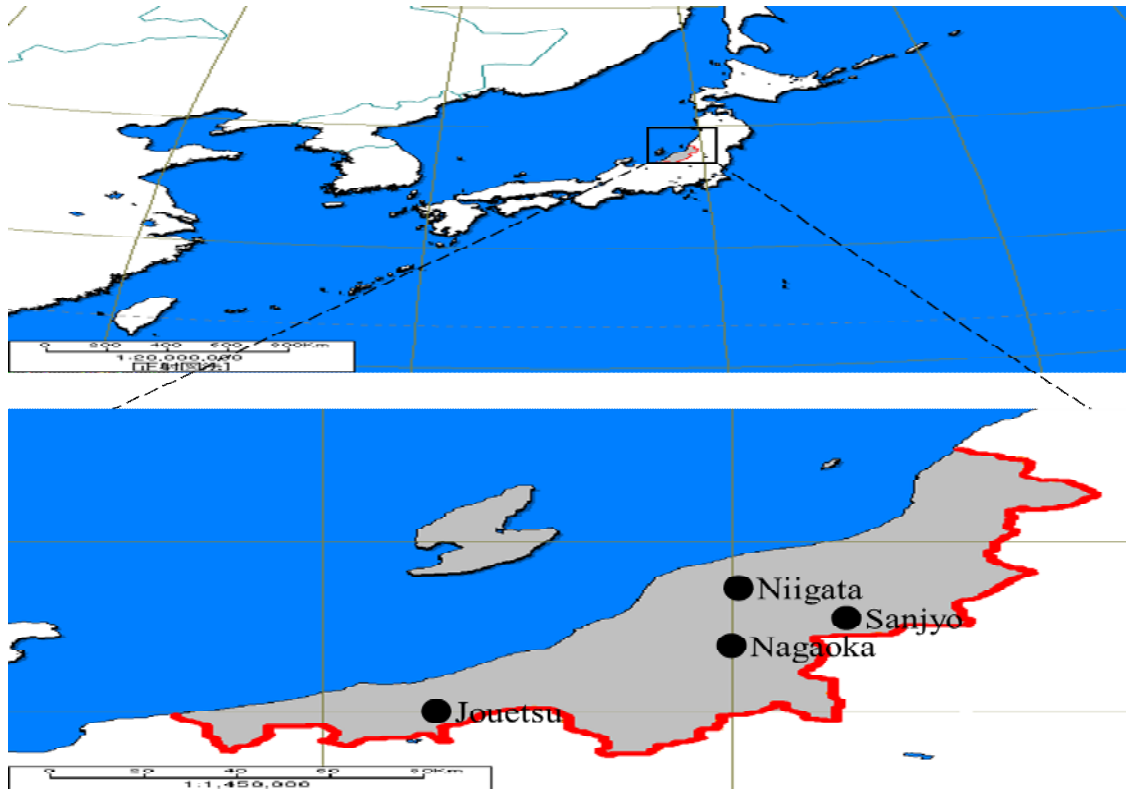


**Table 4-3  $\delta^{18}\text{O}$  value and precipitation amount in 4 points of Niigata Prefecture .**

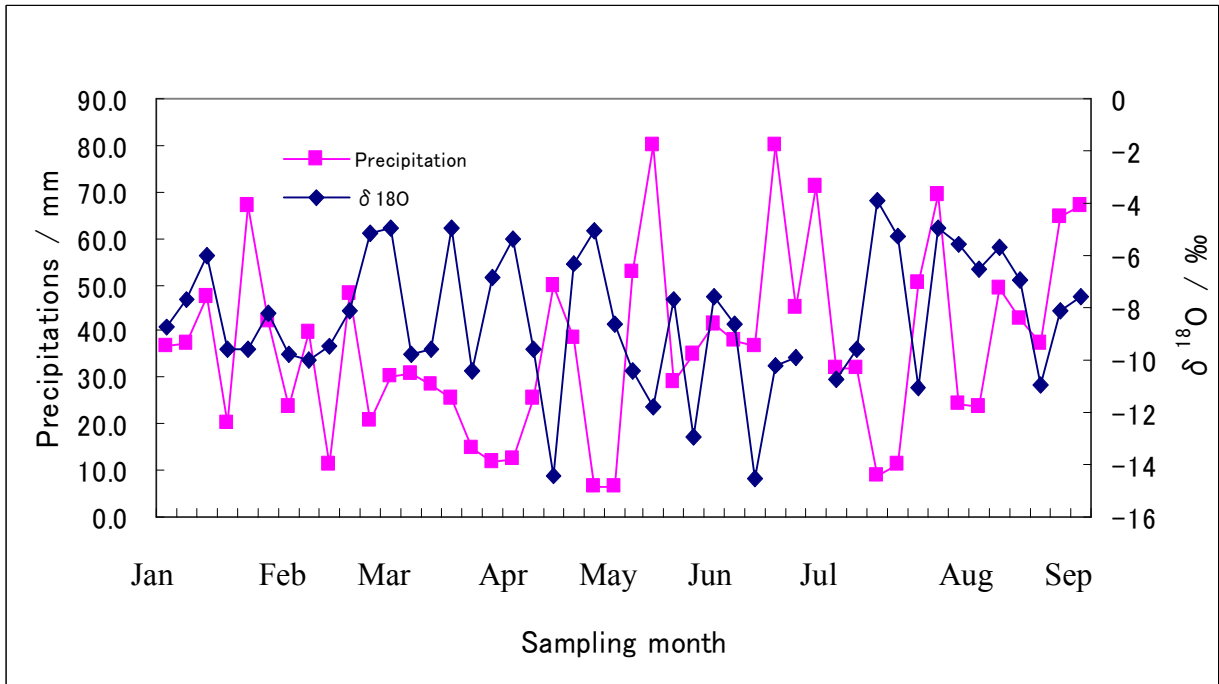
Sampling Date	Niigata		Nagaoka		Jouetsu		Sanjyou	
	$\delta^{18}\text{O}$ (‰)	Precipitation (mm)	$\delta^{18}\text{O}$ (‰)	Precipitation (mm)	$\delta^{18}\text{O}$ (‰)	Precipitation (mm)	$\delta^{18}\text{O}$ (‰)	Precipitation (mm)
3.28-4.11	-6.68	42.1	-7.10	60.2	-6.14	62.1	-5.98	81.7
4.11-4.25	-4.34	22.9	-6.92	39.8	-5.61	30.6	-7.49	33.0
4.25-5.9	-5.98	21.1	-4.26	27.1	-4.19	26.8	-4.43	34.3
5.9-5.23	-5.14	20.0	-5.86	34.6	-5.17	26.1	-7.28	66.8
5.23-6.6	-	4.9	-4.87	16.8	-5.90	25.5	-7.53	56.1
6.6-6.20	-11.22	21.4	-7.60	14.5	-12.83	28.5	-9.32	23.4
6.20-7.4	-7.34	128.3	-6.77	182.2	-7.76	179.9	-7.91	276.1
7.4-7.19	-8.59	69.7	-8.86	100.0	-9.05	92.4	-9.86	126.4
7.19-8.1	-6.47	24.3	-9.73	51.0	-7.88	58.9	-9.57	137.6
8.1-8.17	-7.04	95.8	-8.06	186.3	-14.75	75.5	-8.90	346.7
8.17-8.29	-10.22	47.8	-7.27	170.7	-12.56	96.2	-9.52	88.3
8.29-9.12	-8.17	37.0	-6.33	59.9	-10.81	94.3	-11.73	66.1
9.12-9.26	-4.98	-	-5.60	23.2	-3.04	27.9	-8.37	62.3
9.26-10.11	-5.93	86.4	-5.17	58.6	-1.41	81.2	-8.27	92.6
10.11-10.24	-8.32	59.6	-8.76	74.2	-3.44	72.0	-10.94	104.0
10.24-10.31	-7.80	30.4	-4.37	6.7	-4.77	14.8	-6.00	22.1
10.31-11.7	-5.95	23.3	-6.33	15.0	-7.13	14.0	-7.52	25.4
11.7-11.21	-6.67	73.8	-8.04	180.6	-7.52	176.1	-7.29	162.7
11.21-11.28	-6.84	92.9	-7.75	98.4	-10.87	52.9	-7.94	76.8
11.28-12.5	-7.49	26.6	-8.91	150.0	-8.70	138.5	-7.95	158.6
12.5-12.19	-10.99	134.1	-11.50	224.5	-10.28	134.7	-9.55	180.6
12.19-1.4	-10.02	84.3	-8.70	227.1	-10.22	178.3	-11.06	147.8
1.4-1.16	-10.47	42.3	-9.38	108.6	-10.56	123.2	-12.32	94.6
1.16-1.30	-8.38	6.2	-6.56	71.0	-4.59	69.4	-8.55	51.1
1.30-2.13	-9.54	38.5	-9.74	177.4	-9.13	111.5	-9.39	181.2
2.13-2.27	-6.73	34.7	-7.16	57.6	-6.92	54.5	-7.14	68.4
2.27-3.13	-9.22	67.3	-11.55	79.0	-11.65	99.4	-11.24	71.8
3.13-3.27	-8.68	40.7	-9.06	120.4	-9.70	90.1	-10.04	159.9
Mean	-6.93		-7.58		-7.95		-8.68	
S.D	-5.09		-5.04		-3.71		-5.12	



**Fig.4-1 Schematic diagram of the system for rain-water collection.**



**Fig.4-2** Sampling point of precipitation at 5 points in Niigata Prefecture.



**Fig.4-3 Monthly variation of  $\delta^{18}\text{O}$  values and precipitation at Niigata University,2010.**

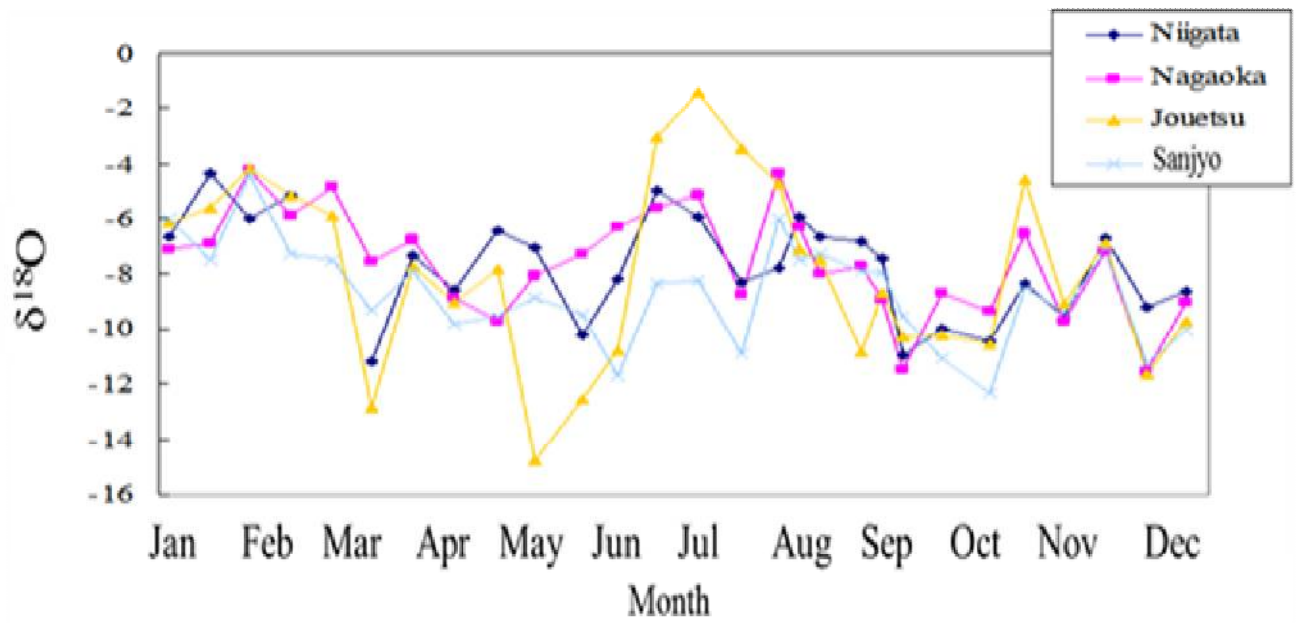
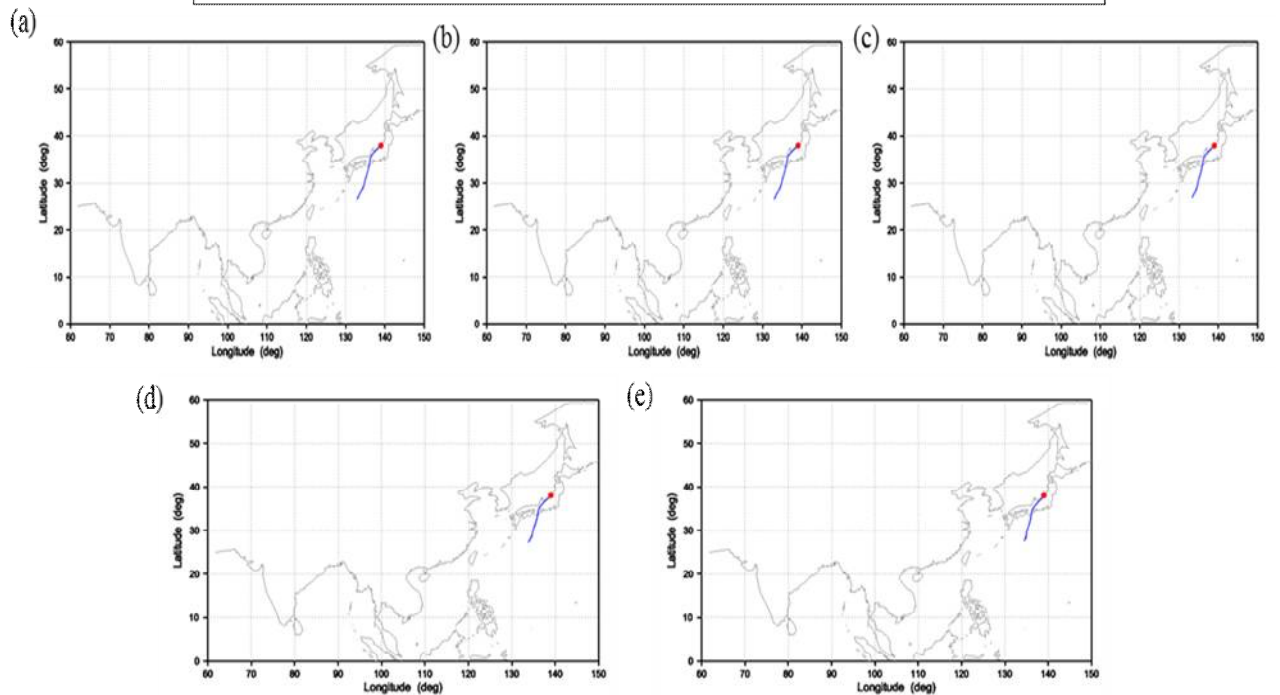
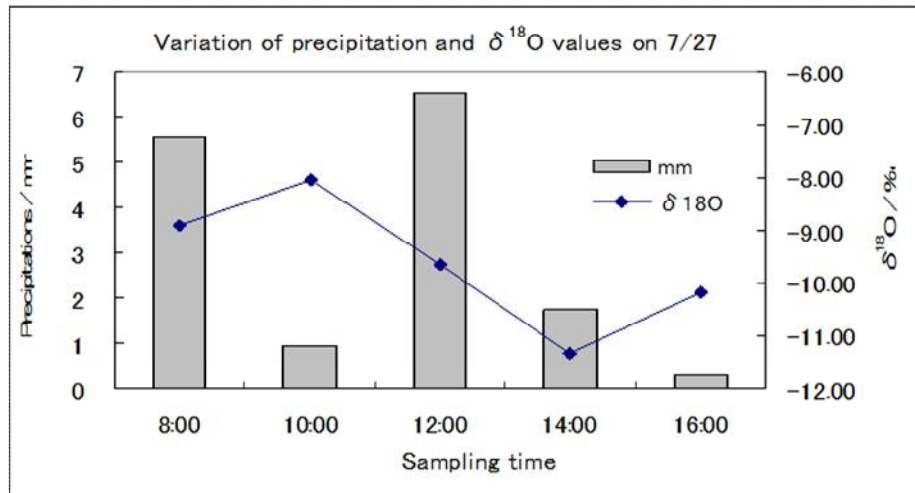
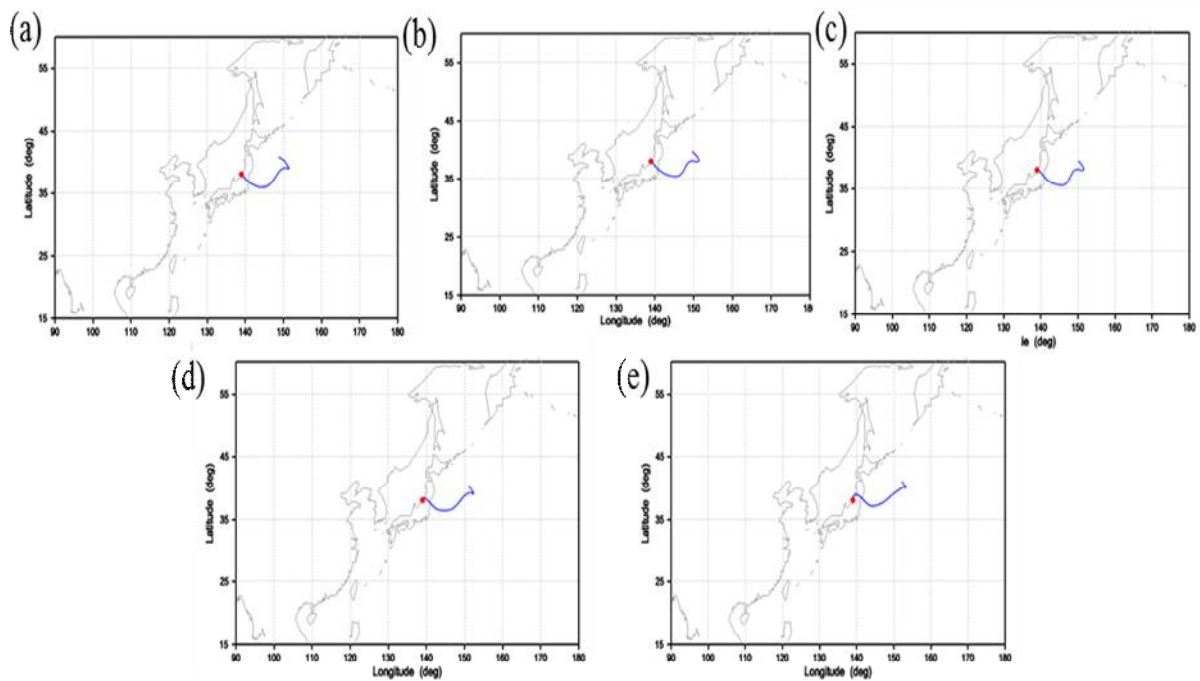
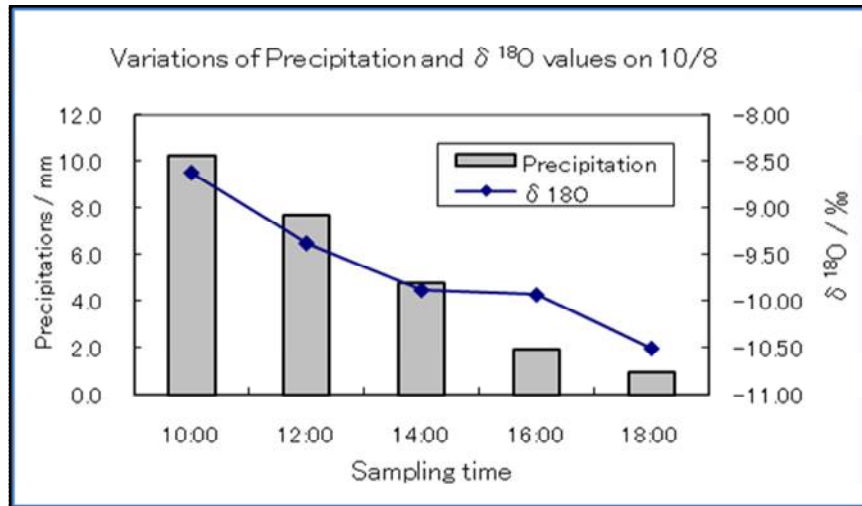


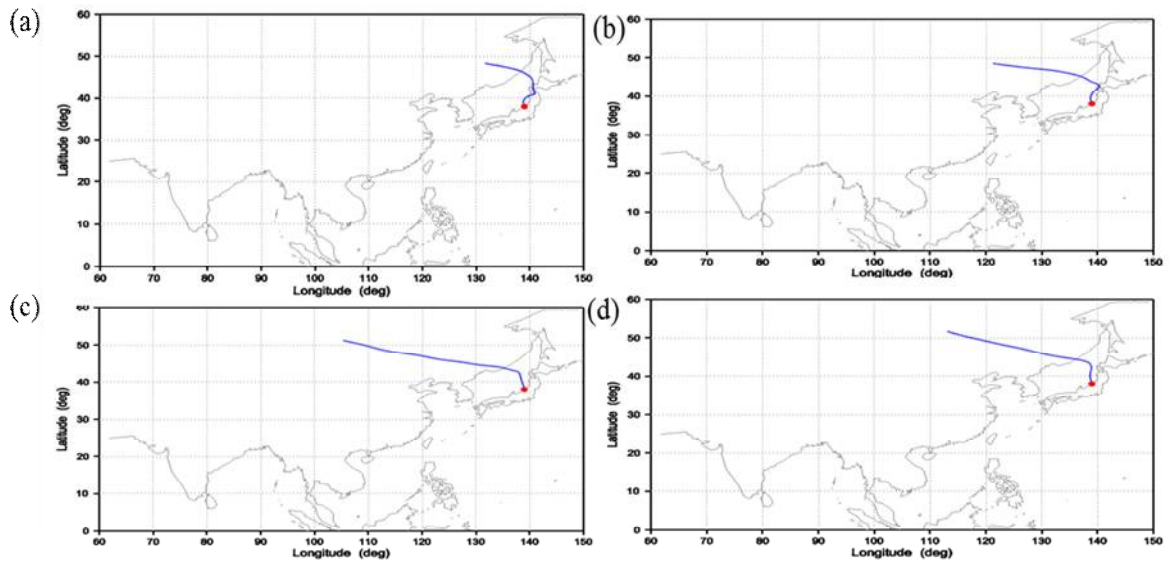
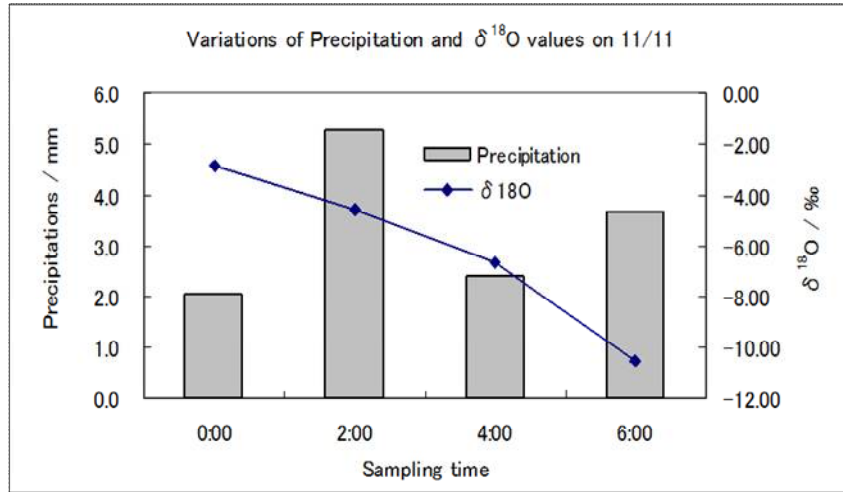
Fig.4-4 The variation of  $\delta^{18}\text{O}$  values in precipitation at 4 Points in Niigata Prefecture, 2005-2006.



**Fig. 4-5 Time-course of  $\delta^{18}\text{O}$  and precipitation values from 8:00 to 16:00 on July 27, 2009 in Niigata University. Three-day 3D-wind backward trajectory on July 27, 2009 at (a) 8:00; (b) 10:00; (c) 12:00; (d) 14:00; (e) 16:00.**

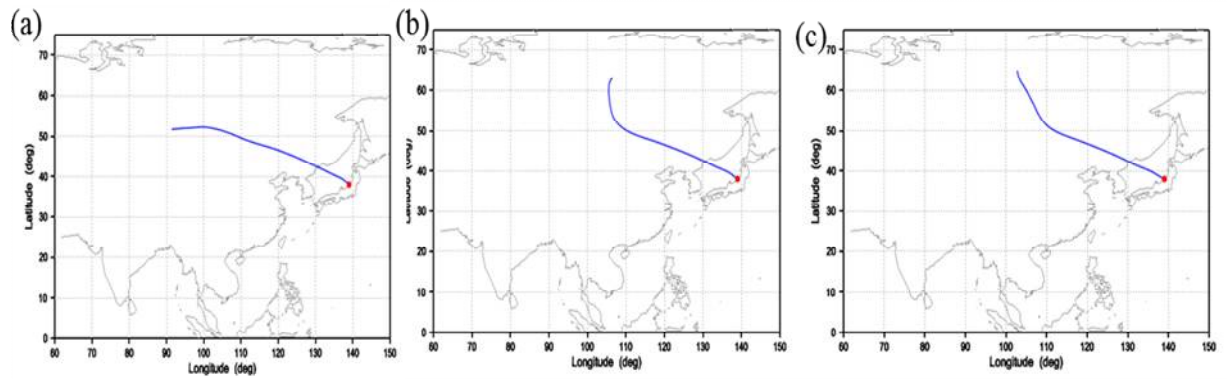
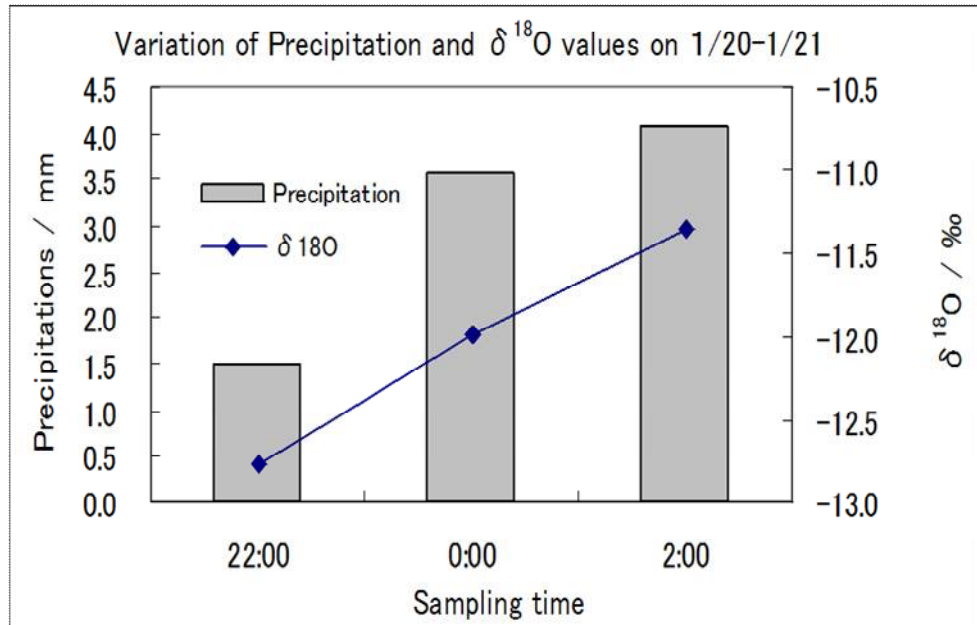


**Fig.4-6 Time-course of  $\delta^{18}\text{O}$  and precipitation values from 10:00 to 18:00 on October 8, 2009 in Niigata University. Three-day 3D-wind backward trajectory on October 8, 2009 at (a) 10:00; (b) 12:00; (c) 14:00; (d) 16:00; (e) 18:00.**

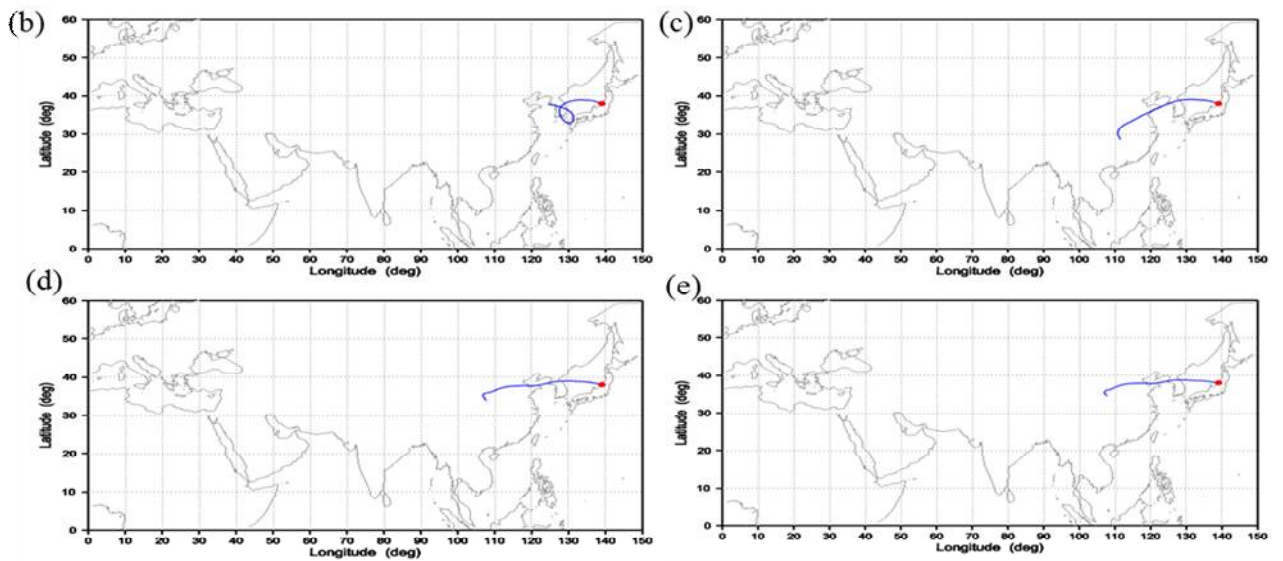
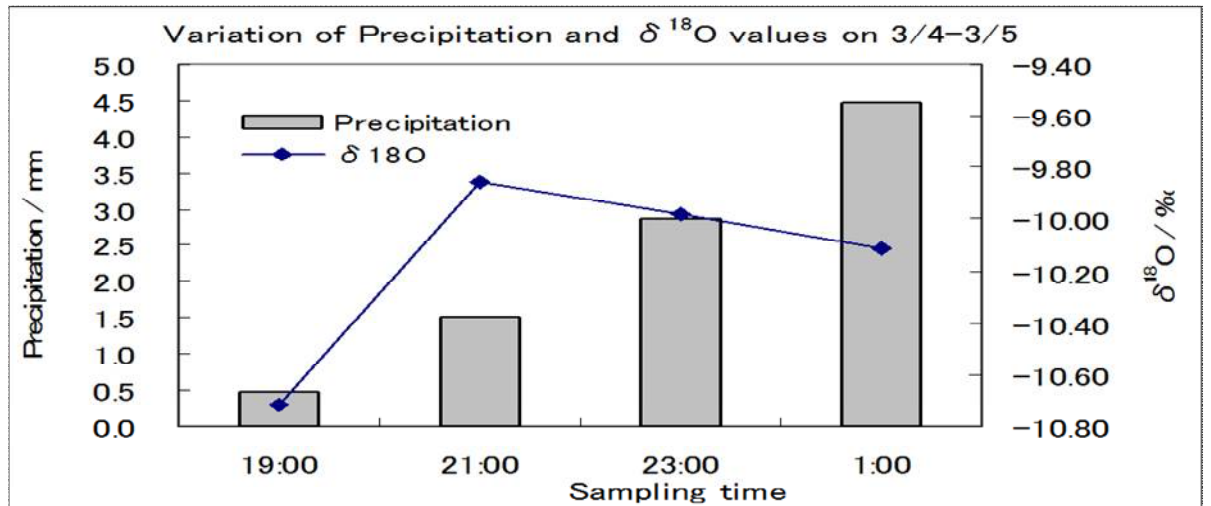


**Fig.4-7 Time-course of  $\delta^{18}\text{O}$  and precipitation values from 0:00 to 6:00 on November 11, 2009 in Niigata University. Three-day 3D-wind backward trajectory on November 11, 2009 at (a) 0:00; (b) 2:00; (c) 4:00; (d) 6:00.**





**Fig.4-8 Time-course of  $\delta^{18}\text{O}$  and precipitation values from 22:00 on January 20 to 2:00 on January 21 in Niigata University in 2010. Three-day 3D-wind backward trajectory on January 20-21, 2010 at (a) 22:00; (b) 0:00; (c) 2:00.**



**Fig.4-9 Time-course of  $\delta^{18}\text{O}$  and precipitation values from 19:00 on March 4 to 1:00 on March 5 in Niigata University in 2010. Three-day 3D-wind backward trajectory on March 4-5, 2010 at (a) 19:00; (b) 21:00; (c) 23:00; (d) 1:00.**

# **Chapter 5      Conclusions**

For the investigation of the characteristics of lagoon waters in Sakata, Toyanogata in Niigata Prefecture, Japan and Zhalong Wetland in Heilongjiang Province, China, oxygen and hydrogen stable isotopic ratios (i.e.,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) and the values of pH, DO and DOC have been regularly examined. Furthermore, the concentrations of chromium (Cr) as well as those of major ions, the nutrients such as nitrogen (N) and phosphorus (P) in these water samples were determined. In addition, to survey the influence of rainfall event on these lagoons and the surrounding rivers,  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , the concentration of major ions, nutrients, and heavy metals such as Cr in these water samples after rainfall were also determined as well as those in normal samples.

The results obtained through this work are summarized as follows:

- (1)  $\delta^{18}\text{O}$  values of sample waters in Zhalong Wetland are generally large probably because of the effect of evaporation, whereas those of Sakata lagoon are large which may be due to the biological process such as the activity of plankton.  $\delta\text{D}$  value of water samples in Sakata was generally larger than that in Toyanogata similarly to the case of  $\delta^{18}\text{O}$ , though remarkable large difference among samples was not found. It was suggested that the biological process such as the activity of *Crustacea* plankton as well as the recharge from surrounding groundwater is active in Sakata.
- (2) It is quantitatively revealed that the water quality of lagoon (Sakata and Toyanogata) waters in Niigata Prefecture is better than that of Zhalong Wetland in China. Particularly, self-purification is active because of the biological process in Sakata.
- (3) For all of the investigated water samples, the concentration of Cr (III) species is higher than that of Cr (VI) species. The ratio of Cr (III) to Cr (VI) is generally larger with increasing the depth, although significant differences cannot be detected. The ratio of Cr (III) to Cr (VI) can be a good indicator for represent the oxidation-reduction state at the spot.
- (4) It was found that pH value of lagoon water samples is 6.5-8.5 (which is generally

larger than that of river water), and that pH at the spot of S1 (downstream point of Lower Lagoon (Shitakata)) is remarkably high (9.0-10.5). The value of DO in Sakata is relatively large in summer in spite of large value of DOC in summer. Moreover, the eutrophication is not relatively large in spite of high concentrations of chlorophyll a. These things might be attributable to photosynthesis due to aquatic plant and phytoplankton. Self-purification is active because of the biological process in Sakata.

(5) Lagoon water has the chemical characteristics contrasting to groundwater with a focus on river water from the viewpoint of pH (acidity or alkalinity) and DO. These matters can be closely related to the biological activity such as photosynthesis due to aquatic plant and phytoplankton and the activity of *Crustacea* plankton etc. in lagoon.

(6) After rainfall events, the following matters were considered.

1.  $\delta^{18}\text{O}$  of sample at S3 increased after rainfall events as well as those of samples in Toyonogata.
2. The concentrations of  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  increased after rainfall events at S3.
3. The concentration of total Cr and the percentage of “suspended” remarkably increased after rainfall event. The concentration of Cr(III) is larger than that of Cr(VI) species in our samples.

It is suggested that the increase of dissolved components may be caused by the supply from surrounding soil (or rock) due to the rainfall event instead of the direct inflow of precipitation.

The data obtained and the method used in this work can be useful for environmental preservation or recovery of resources.

## References

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## Acknowledgements

Look back the past three years that I studied in Kano Lab, let me express my deepest gratitude to Associated Professor Naoki Kano for his sincerely guidance, valuable advice and encouragement throughout my doctoral course of study at the Graduate School of Science and Technology, Niigata University, Japan. I am extremely thanks to Professor Hiroshi Imaizumi my vice director who gave me lots of help.

I would like to thank Professor Mineo Sato, Professor Tatsuya Kodama and Professor Kazuaki Yamagiwa for their advices and suggestions for this thesis.

I also want to give my thanks to Associate Professor Naoki Watanabe of Research Center for Natural Hazards and Disaster Recovery in Niigata University for permitting the use of the facilities and mass spectrometers.

Many thanks to my co-members in our Lab who give me experiment training and offering helpful advices through my course of study.

Finally, I want give my best thanks to my parents who always support my studying abroad.