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**Land use control on water chemistry of Ohori River,  
Chiba, Japan**

大堀川の水質に与える土地利用の影響について

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## 1. Introduction

### 1.1 Background of the study

Rivers and their catchments are very important part of our natural heritage. Rivers have been utilized by mankind over the centuries to the extent that, very few, if any, are now in their natural condition (Wetzel, 2001). River water chemistry is controlled by many natural and anthropogenic factors. These factors can either be spatially diffused or concentrated. Calculating the inputs by point source is relatively simple as direct measurements can be made at the source, but stream water chemistry by non-point sources is much more difficult (Baker, 2003). Since the river water quality reflects biogeochemical processes in the watershed, the effects of land use may be assessed by exploring the water quality which could be a suitable indicator for monitoring (Hakamata et al., 1992). Water quality “reflects the composition of water as affected by natural processes and by humans’ cultural activities, expressed in terms of measurable quantities and related to intended water use” (Novotny and Chesters, 1981). Land use change is known to influence the biogeochemistry of watersheds (Deocampo, 2004; Tardy et al., 2004; Parr and Manson, 2003). As land use has changed from unaltered natural landscapes to agricultural and urban uses, forests and wetlands have been lost; road density has increased; surface runoff has increased; and anthropogenic chemical and wastewater inputs have increased (Breward, 2003; Parr and Manson, 2003; Lee, 2002; Carpenter et al., 1998). Physical alteration of the landscape also occurs as a result of land use change, affecting the hydrogeologic dynamics of watersheds (Tang et al., 2005; Pijanowski et al., 2002). As a result of these human activities, the conditions of many aquatic environments have been degraded.

Watershed management and catchment scale studies have become increasingly more important in determining the impact of human activity on water quality both within the watershed as well as that of receiving waters. It has been suggested that the relationships between land use and water quality may be obscured by other factors, complicating the development of distinct biogeochemical fingerprints of land use on water quality (Wayland et al., 2003; Mason et al., 1999). Focus on watershed scale investigation is possible due to the recent availability of GIS technology (Ohta et al., 2005; Meador and Goldstein, 2003; Parr and Mason, 2003; Wayland et al., 2003; Lee, 2002). This technology has been used to quantify the spatially-explicit nature of observed water quality based on land use and geology, and to predict the changes of water chemistry resulting from changes in land use (Tang et al., 2005; 2003; Boutt et al., 2001; Wang and Yin, 1997).

The sampling of runoff and storm events is often used to examine the effects of land use on water quality (De Carlo et al., 2004; Steuer et al., 1997; Andoh, 1994). Runoff is an important component of water quality investigations because runoff introduces sediment and mobilizes chemicals directly off the landscape (De Carlo et al., 2004; Steuer et al., 1997; Andoh, 1994).

However, low or base flow in temperate streams is supplied predominately by shallow groundwater discharging to the stream channel (Wayland et al., 2003; Land et al., 2000). Since the shallow groundwater has moved through the landscape in the recent past, it provides a signal that is representative of the surface geology, recent climate and land use (Wayland et al., 2003; Land et al., 2000). Sediment associated analytes may increase during storm events, while many solutes are most concentrated during base flow conditions (Land et al., 2000). Thus base flow chemistry of the dissolved fraction is used to represent the effects of land use characteristics on stream quality in the study site, the Ohori River Basin, Chiba, Japan.

Along with correlation and regression analysis, multivariate statistics facilitate the interpretation of complex hydrochemical data sets. For example, Hierarchical cluster analysis (HCA) can be performed using chemical variables to identify groups of sites that exhibit similar biogeochemical behavior (Hair et al., 1998). Factor analysis (FA), is useful for reducing the number of variables in a data set to a few components or factors that represent most of the variation in the original data, thus simplifying multiple variable interpretation (Hair et al., 1998). Building on the results of the cluster analysis, detailed biogeochemical fingerprints can be developed to identify how the chemical variables behave among the different groups (Wayland et al., 2003).

## *1.2 Scope and importance of the study*

While water quality has improved remarkably during the past decades, Japanese rivers are still heavily impacted by canalization, loss of most dynamic flood plains, flow regulation, invasion by exotic species, and intensive urbanization (Yoshimura et al., 2005). Sudden development of Japanese industry and the increasing standard of living are extending the amount of water usage as well as polluting the usable water resources. For the fundamental solution of aquatic environmental problems, it is necessary to assess the anthropogenic load on the aquatic environment in addition to natural factors and to clarify the chemical process on the surface water. Deterioration in water quality of rivers in the valleys dissecting the urbanized uplands in and around big cities like Tokyo is one of the serious environmental issues. In a study by Terazono (2003) in this upland area, it was found that the basic water quality of spring water is formed in the process of groundwater flow through geology by dissolving of carbonate minerals in layers and the rest of the loads are controlled by land use development in drainage basins. It was also found that the spatial difference of the additional loads is larger than that of basic loads and there were clear relationships between the additional loads and land use. Land use changes of uplands due to urbanization have resulted in degradation in water quality of rivers.

The sampling and analysis design of this study, using the dissolved chemistry and dominant land use, allows for the quantification of the specific contributions of land use on surface water

quality. The analysis of biogeochemical characteristics (major ions) at each of the sites facilitates an in depth investigation of the relationship between land use and surface water chemistry.

### *1.3 Definition of water chemistry*

The definition of 'water quality' or 'water chemistry' is multifarious, and is depending on the purpose of investigations. For example, BOD or COD is widely utilized as an official item related to living environment; heavy metals, such as cadmium or copper are used as chemical indicators in viewpoint of the ecosystem; environmental endocrine disruptor such as dioxin or PCB are applied to know the impact on the human body. The concentration or value of those indexes is so called 'water quality' or 'chemistry' (Anazawa, 2004). In this research, the water chemistry is defined as the "chemicals, which essentially characterize the chemical property of waters". For this sake, the major inorganic ions are adopted as the indicators, i.e., sodium, potassium, magnesium, calcium, chloride, nitrate, sulfate and bicarbonate ion. The reasons for choosing these components are described as follows:

- ✓ Those components are the fundamental and major dissolved components. These components cover over 99% of the total solutes in weight for river water.
- ✓ It is possible for major components to keep the relative analytical error at low level. Moreover, application of statistical methods, which examines the covariance relation between variables, such as multivariate analysis, enables us to minimize the systematic error of the chemical data and to give reliable results.
- ✓ The change of the chemical composition in the stock solution is small during the stock time. Even after several months of sampling, the same analytical results can be obtained. Therefore, reanalysis is also possible to confirm the data reliability.
- ✓ The breakthrough of instrumental analytical techniques, such as ion chromatography enables us to determine the large number of samples on multi-components in the short time.

### *1.4 Comparison between continental and Japanese rivers*

In 1960's, chemical researches on the river water were intensively conducted worldwide for the interest in global material circulation between the continent and ocean. Chemical researches of river water were mainly conducted on the continental rivers with wide catchment area in order to determine the representative chemical composition of world river (e.g. Meybeck, 1979; Gibbs, 1972; Martin and Meybeck, 1979). For example, Livingstone (1963) determined the average chemical composition of world river waters based on over 800 chemical data of the continental river water. The hydrochemical data, which were accumulated in this period, produced many hydrochemical researches; one of the representative works is assumed to be Gibbs (1970). In this

classic paper, he described that the continental aquatic chemistry is mainly controlled by three factors; atmospheric precipitation, carbonate rock weathering, and evapotranspiration and dissolution of evaporate. This model was presented by a plot of total dissolved salts (TDS) against  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  or  $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ , which predicted that water with low TDS and high  $\text{Na}^+$  and  $\text{Cl}^-$  chemically controlled by atmospheric precipitation; water with moderate TDS and high  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  by rock weathering, and water with high TDS and high  $\text{Na}^+$  and  $\text{Cl}^-$  by evaporation. This paper mentioned only little about the weathering of silicate rocks, such as volcanic and metamorphic rocks. Piper (trilinear) diagram and Stiff diagram, which are widely applied for the classification of surface waters in Japan, are also based on the continental water chemistry. These diagrams are lack of silicon from the chemical item, which is a good indicator of silicate weathering. The silicate minerals such as feldspar or quartz are far more resistant to weathering than carbonate minerals, such as calcite or dolomite (White et al., 1999); it is reasonable to focus attention on carbonate weathering for the continental rivers, which flows through sedimentary strata or limestone. On the contrary, as stated above, Japan archipelago differs from continents in geological and hydrological environment, where igneous rocks dominate the geology.

The chemistry of Japanese river water is characterized by the small amount of TDS, low calcium and magnesium concentrations and high silicon in comparison with the world river water. The comparison between chemical and geographical properties gives the general characteristics of chemical mechanism in Japanese river. First, the small amount of TDS would be introduced by the shortness of rivers and rapid flow rate. The low calcium and magnesium and high silicon concentration is reasoned by the geology of catchment area, which is mainly composed of silicate rocks (igneous rocks). The prominent characteristics of Japanese hydrological or hydrochemical environment is supposed to mainly depend on the Japanese topography and geology.

Table 1. Comparison of rivers between continents and Japan

	Continents	Japan
Geographical property:		
Geology	Sedimentary rocks (Limestone and evaporate)	Igneous rocks
Length	Long	Short
Flow rate	Slow	Rapid
Scale	Large	Small
Chemical property:		
Electrical conductivity	High	Low
Hardness	Hard	Soft
Silicon concentration	Low	high

### *1.5 Objectives of the study*

The understanding of linkages between land use and water quality is limited. Research has shown that the source of water in streams during nonstorm periods exhibits spatial and temporal variability. Given the likelihood that baseflow chemistry varies temporarily as well as spatially, it is necessary to examine further the usefulness of the synoptic sampling approach for identifying consistent and reliable hydrochemical fingerprints across a watershed. Therefore the objectives of this study are:

- a) To compare the chemical data collected during four sampling events in an urbanized river basin to characterize the temporal variability of baseflow chemistry.
- b) To quantify the individual effects of land use on stream chemistry and
- c) To identify the dominant land uses which control the surface water chemistry.

## **2. Study area**

### *2.1 Outline of the study area*

The study area is the Ohori River basin, which is located in the northwestern part of the Shimousa Upland and northeastern part of Tokyo Metropolitan Area (Fig. 1). There are two major rivers in the basin named as Ohori and Jiganehori. The Ohori River begins at Aota-shinden, Kashiwa-city, Chiba-prefecture, passes through Nagareyama city and Kashiwa city area and drains into the Teganuma Lake. The river length is 6.9km. The another 6 km long, Jiganehori river originates from at two natural ponds near Kashiwanoha park and drains into Ohori river near Yabatsuka bridge. Many tributaries of the two rivers divide the upland in the basin. The total area of the drainage basin is 31km<sup>2</sup>. The urbanized ratio of this drainage basin at present is higher than 70% and it is a typical city river (FRIR, 2000).

The mean annual temperature from 2001-2006 is 14.8 °C, the average for January is 3.7 °C (minimum) and for August 25.9 °C (maximum) (Fig. 2). The mean annual rainfall is 1461 mm, with minimum values in the February and maximum values in August.

Water sampling stations were located at 24 sites throughout the Ohori river basin (Fig. 1). The sites were selected as the tributaries and mainstream representing the river course. The origin points of Jiganehori river (sites 23 and 24) have less urban impact and the drainage areas are mostly occupied by forest cover.

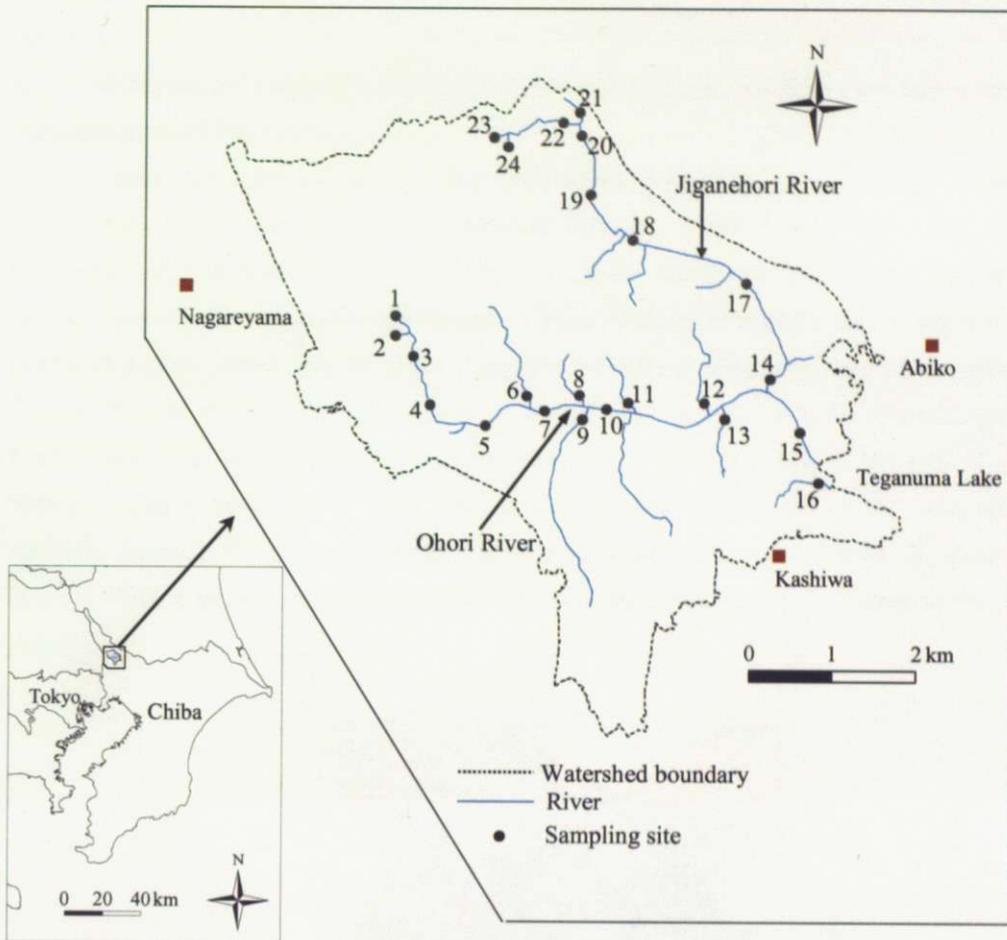


Figure 1. Study area and the location of sampling sites.

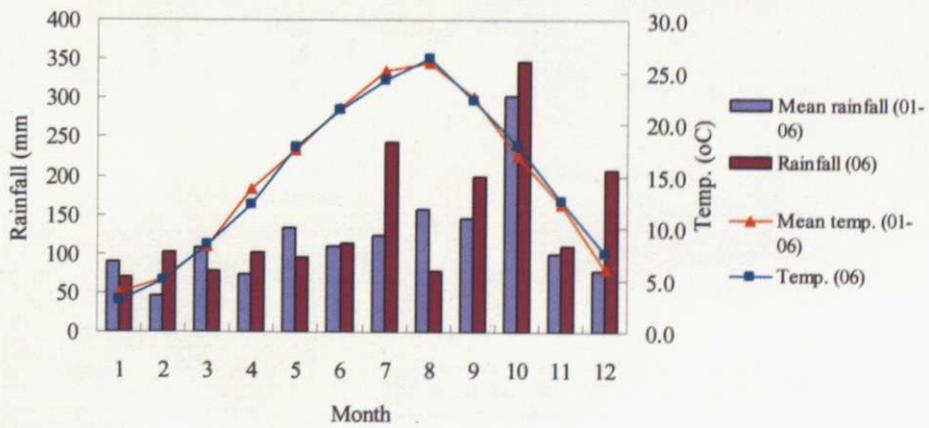


Figure 2. Monthly average temperature and rainfall in the study area.

## 2.2 Geomorphological and geological setting

The landforms in the Ohori River basin consist of upland surfaces with an altitude of 15-30 m and alluvial lowland (2-9m). The Shimousa upland was formed during the Last Interglacial Age and consists of many layers of marine, brackish and alluvial sand clay beds, each of which is almost in horizontal stratum (Fig. 3). They are covered with volcanic ash layers with a maximum thickness of about 5m.

Five units define the geological setting of the site in descending order upto 43m depth which is homogenous throughout the area: Alluvial deposits, Kanto Loam, Joso Clay, Kioroshi Formation and Kamiwashi Formation (Table 2). Quartz and Plagioclase are the most abundant primary minerals throughout the layers. The 3m thick Alluvial-floodplain-marine deposits formed during Holocene period and the main sediments are gravel, sand, mud and peaty soils. After alluvial deposits all other formations were formed during middle to late Pleistocene period. The Kanto Loam is a brownish layer of volcanic ash that extends throughout the area to a depth between 4 and 6 meter. Gravel, sand, mud, peaty soils and volcanic ash are the main sediments and only Quartz is the primary mineral. Clays of Joso Formation occur beneath the Loam in the uplands. With a thickness of 3m, the strata contains high amount of Plagioclase as the primary mineral.

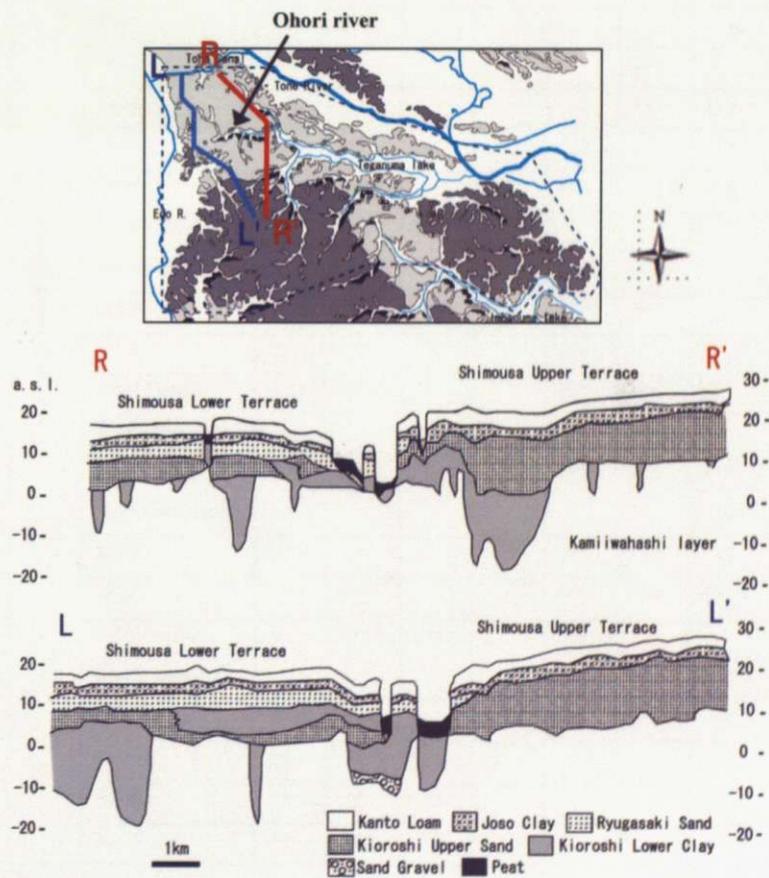


Figure 3. Geological profile of the study area (after Terazono, 2003)

Kioroshi Formation is underlain by an approximately 27m thick layer, consisting of gravel, sand, mud and shell fossil bearing mud. Both Quartz and Plagioclase are major in this formation with secondary minerals like Kaolinite, Montmorillonite and Halloysite. Calcite and Aragonite are found in the shell fossil. Sand is the major sediment of Kamiwashi Formation and found beneath the Kioroshi Formation.

Table 2. Mineral assemblage of sediment and shell fossil in the study area

Depth (m)	Formation	Period	Sediment	Primary Mineral			Secondary Mineral				Shell fossil			
				Quartz	Plagioclase	Magnetite	Goethite	Kaolinite	Montmorillonite	Halloysite	Calcite	Aragonite		
1	Soil	Holocene	Soil	+										
3	(Alluvial)		Soil	+	++									
5	Loam	Middle to late Pleistocene	Ash	+			+							
7	Joso clay		Clay	+	+++									
9			Clay	+	+++				(+)					
11	Kioroshi F.		Sand	++	++									
12			Sand	++	++									
13			Sand	++	+++									
15			Mud	++	++					(+)				
17			Mud	+++	++					(+)	(+)	(+)		
19			Mud	+++	++					(+)	(+)	(+)		
21			Mud	+++	++					(+)	(+)	(+)		
22			Mud (shell fossil bearing)	+++	++	(+)							+	
23			Mud	+++	++					(+)	(+)			
25			Mud	++	+++					(+)				
27			Mud (shell fossil bearing)	+++	+++					(+)	(+)	(+)	+	(+)
29			Mud (shell fossil bearing)	+++	+++					(+)	(+)	(+)	+	(+)
31			Mud	+++	++					(+)	(+)	(+)		
33			Mud	+++	+++					(+)	(+)	(+)		
35			Mud (shell fossil bearing)	+	+++	(+)				(+)				+
37			Mud	+++	+++									
39			Kamiwashi F.	Sand	++	+++	(+)							
41		Sand		+++	++	(+)								
43	Sand	++		+++	(+)									

+++ Major, ++ Common, + Minor, (+) Trace

Source: Muramatsu and Fukuda, 2006

### 3. Methods

#### 3.1 Water sampling and analytical method

Surface water grab samples were collected from 24 sites along the main river and tributaries (Fig. 1) four times from August 2006 to April 2007 during low flow condition, at least one week after heavy rainfall event, if any (Fig. 4). It is assumed that during low or base flow shallow ground water is the major source of water to the stream channel (Land et al., 2000; Grayson et al., 1997). Base flow chemistry is desired as it represents the effects of regional characteristics and land use on stream quality. The sampling occasions were August 1 and 2, 2006 (summer), October 29 and 30, 2006 (fall), January 19 and 20, 2007 (winter) and April 30, 2007 (spring). The sampling was conducted from bridges or other easily accessible locations to facilitate rapid sample collection. Water samples were collected at midstream width by submerging plastic bucket to a depth of 20 to 30 cm. The bucket was rinsed three times with river water before samples were collected. The temperature, pH and EC (Electrical conductivity) were measured in the field by a digital pH meter and EC meter (Horiba D-54). Alkalinity, expressed as  $\text{HCO}_3^-$ , was quantified with a digital titrator (Hach) with 0.16 N HCl, and Bromcresol Green-Methyl Red as an indicator. 100 ml water samples were collected separately at each sampling site using polyethylene bottles. The pre-washed bottles were rinsed with sample water thrice on site before collecting the sample water. The water samples were then brought to the laboratory and stored in a dark and cool room ( $4^\circ\text{C}$ ) until the analyses were completed. In the laboratory, the concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were determined by ion chromatography (Shimadzu SCL-10Asp). TMI (Total major ions) was calculated by adding the concentration of the ions determined by ion chromatography and  $\text{HCO}_3^-$ , measured in the field. The analytical data quality was ensured through careful standardization, procedural blank measurements and duplicate samples.

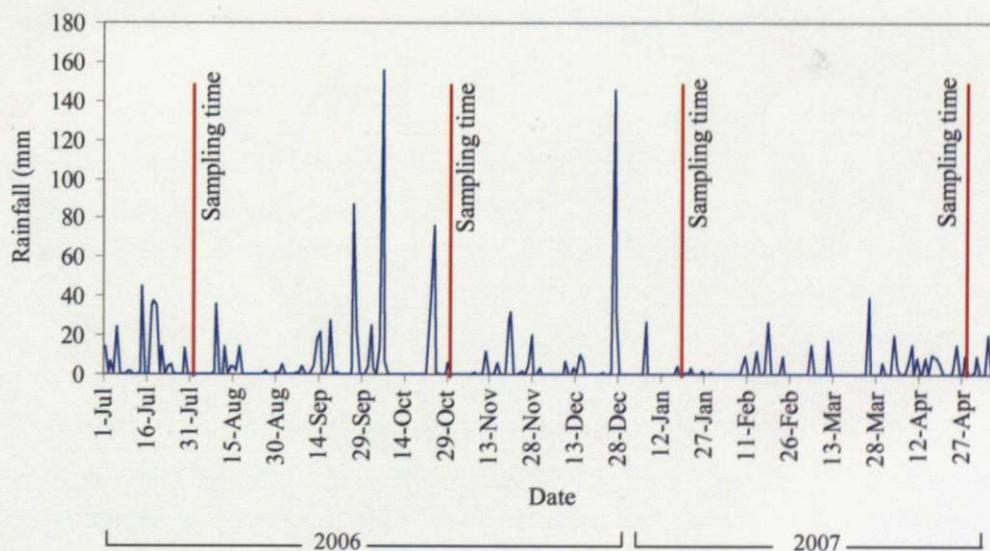


Figure 4. Sampling time and rainfall event.

### 3.2 GIS analysis

ArcGIS 9.1 Desktop GIS software was used to determine the relative composition of land uses within the Ohori River watershed. Raster image of watershed area and drainage divide of sub-watersheds were collected from city office. The divides of drainage basins were confirmed from contour maps and concept of river system. After performing necessary edition, it was digitized with Ground Control Point technique using a 1:25000 scaled topographic map. The resultant polygon data was then overlaid on the digital 10m grid land use map published in 1994 by Geographical Survey Institute of Japan.

The total land use types in the original land use map produced by Geographical Survey Institute of Japan were fifteen which has been manipulated again with similar characteristics and reduced to nine categories. Forest type includes all types of forest, farmland includes paddy field and field, developing area is the sum of empty and the area under construction, industrial area means all types of industry, low-rise residential area includes residences not more than four storied, high-rise residential means densed and tall buildings, commercial area includes all commercial and business center, park is itself park area and others include roads, public facilities area, and water body.

Using ArcView's spatial analyst function the land uses of drainage basins of each sampling site was estimated. The drainage basin of lower reach streams for each sampling site was calculated by including the drainage basins of all upper streams and tributaries. GIS tools were used to calculate the area of each land use types within the sourcshed of sampling sites, which was subsequently divided by the watershed area to derive the percentage of the watershed covered by each type (Fig. 5). A sourcshed is defined as the total area that contributes to a selected drainage point, or sampling site.

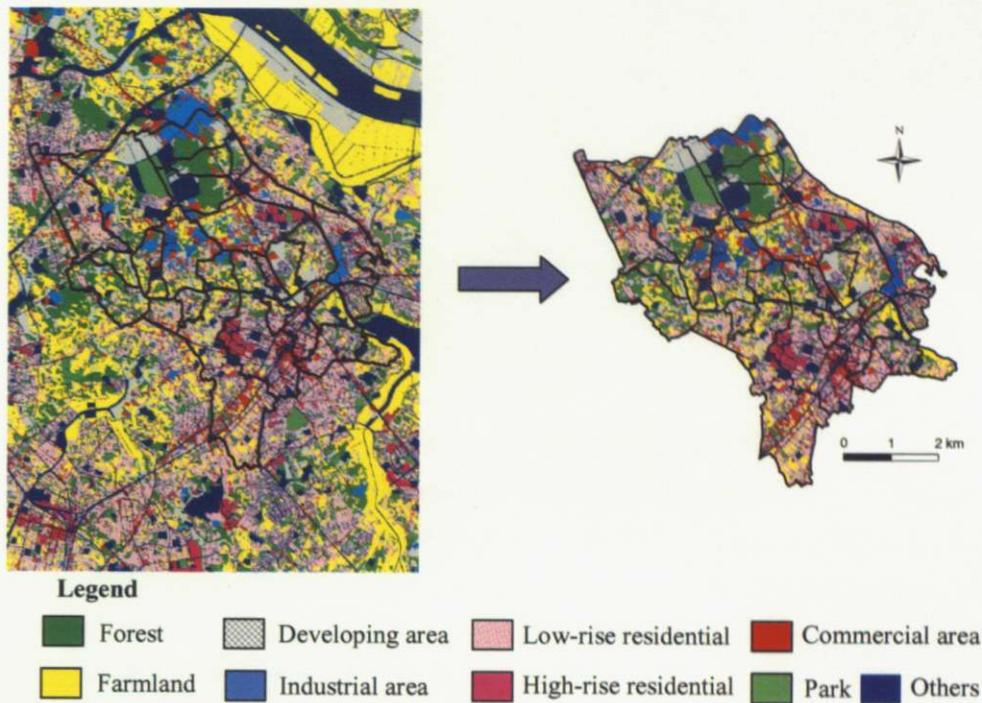


Figure 5. Land use in the Ohori River basin.

### 3.3 Deduction of Tone River effect

In the upper part of Ohori River water about  $0.5 \text{ m}^3/\text{s}$  water is discharged through a pump from a nearby big river, Tone River which increases both the discharge and chemical flux in the river as well as in the lake Teganuma. In order to confirm and maximize the land use effects in the Ohori River itself, the effects of Tone River discharge were deducted in the downstream sampling point of the Ohori mainstream. The mass balance approach is illustrated by the following equation where  $C$  is concentration and  $Q$  is discharge (flow) was used to get the real concentration of ions in the river:

$$C_1Q_1 + C_2Q_2 = C_3Q_3$$

$C_1Q_1$  represents the baseline concentrations and flow, while  $C_2Q_2$  represents the new tailings basin discharge concentration and flow.  $C_3Q_3$  represents the resultant in-stream concentration and flow. Flow is assumed to be conserved such that  $Q_1 + Q_2 = Q_3$ , and thus  $C_3$  can be calculated.

In this research, the concentration of ions of Tone River discharge was determined for each sampling event and the discharge quantity was known. In the downstream sampling point of Ohori River both discharge and concentration of ions was also measured. Discharge ( $Q$ ) was estimated by measuring stream velocity ( $V$ ) and cross sectional area ( $A$ ) of the river channel. Velocity was measured using a current meter (KENEK) by counting the average rotor's number of revolution per unit of time (sec). The cross-sectional area of the river was divided in smaller, discrete areas, where velocity was recorded. Cross-sectional areas were calculated first by multiplying width, and

depth measured at the two extreme sides of each segment when the river bed of the respective section is horizontal. When the depth measured at the two extreme sides is not same, first the area of upper rectangular part and later the triangular part were calculated and added together to get the cross-sectional area. Total river discharge ( $Q = VA$ ) was calculated by adding the partial discharges of each segment. The real discharge of downstream sampling points was calculated by deducting the Tone discharge. Finally, the real concentration of each ion was determined.

$$Q_{ri} = Q_i - Q_t$$

$$C_{ri}Q_{ri} = C_iQ_i - C_tQ_t$$

$$C_{ri} = (C_iQ_i - C_tQ_t)/Q_{ri}$$

$C_i$  : concentration of ions at downstream sampling points of Ohori River

$Q_i$  : discharge measured at downstream sampling points of Ohori River

$C_t$  : concentration of ions of Tone River discharge

$Q_t$  : discharge from Tone River

$C_{ri}$  : real concentration of ions at downstream sampling points of Ohori River

$Q_{ri}$  : real discharge at downstream sampling points of Ohori River

### 3.4 Statistical analysis

Identical statistical analyses were performed on both water quality and land use data. All the data were normally distributed based on the Kolmogorov-Smirnov goodness of fit test. Tests were considered significant at  $p > 0.05$  (Townend, 2002). Analysis of variance (ANOVA) was used to determine whether there was a significant difference between seasonal concentrations of all sampling sites. Multiple comparisons among seasonal mean of each parameter were conducted using Tukey statistical test. The ANOVA and Tukey analysis provided results for each constituent by sampling site and event. The relationship between ion concentration and land use characteristics was revealed by using Pearson's product-moment correlation analysis. The significance of correlation was assigned up to 95% confidence level of t-test and is classified as positive and negative according to the gradient of the regression relationship.

#### *Cluster analysis*

Multivariate statistics like Cluster analysis (CA) was used to classify the water samples into different groups based on the relationships among them and later compared with land use pattern. CA is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behavior of a data set without making a priori assumption about the data, in order to classify the objects of the system into categories or clusters based on their nearness or similarity (Vega et al., 1998). Hierarchical CA was performed on the normalized data set by means of the Ward's method, using Euclidean distances as a measure of similarity. Ward's method is suitable for data sets

which show a well defined group structure (Everitt, 1980). CA was applied to the water quality data set with a view to group the similar sampling sites.

#### Factor analysis

Factor analysis is a common statistical approach for examining and quantifying the factors that control biogeochemical distributions in both surface and ground water (Drever, 1997; Gupta and Subramanian, 1998). It returns a quantitative assessment of the strength of a series of factors in explaining the variance of variables in the dataset. Interpretation of factors can be facilitated by rotating the factors in multidimensional space. Promax rotation with Kaiser normalization was used to maximize the variance of the loadings both among factors and variables. Variable loadings are correlation coefficients between the variable and the factor. Variables that exhibited a rotated loading greater than 0.5 were considered moderately loaded on a factor, while variables with loadings greater than 0.75 were considered strongly loaded on a factor. Values 0.4 to 0.5 have been used as the lower end of moderate loading (Evans et al., 1996; Miller et al., 1997)

### 4. Results

#### 4.1 Analytical accuracy of water quality data

Electrical conductivity (EC) is a measure of a solution's ability to conduct electricity. A good linear correlation between EC and total major ion (TMI), expressed in meq/l confirms the high quality of the data (Mazor, 1997). Conductivity values obtained in the field were plotted against the corresponding TMI concentration and it showed high linear correlation for all season's data (Table 3). The linear correlation with  $R^2$  value of average data is shown in Fig. 6.

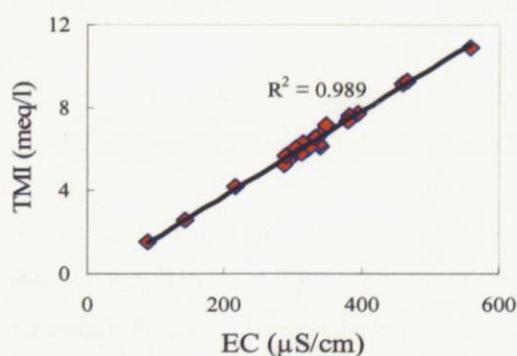


Fig. 6. Relationship between EC and TMI

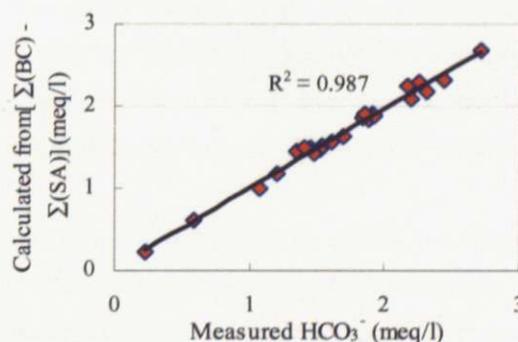


Fig. 7. Relationship between Calculated and measured HCO<sub>3</sub><sup>-</sup>

Alkalinity, expressed as HCO<sub>3</sub><sup>-</sup> was measured in the field during sampling. The measured value should also be linearly correlated with the calculated one. The calculated value is the

difference between sum of base cations and sum of strong acid anions  $\{\sum BC \text{ (Base Cations)} - \sum SA \text{ (Strong Acid anions)}\}$  which concentrations were determined from laboratory analysis. The average correlation ( $R^2$ ) between calculated value and measure value is 0.98 (Fig. 7). The correlation value of individual sampling regime is shown in Table 3.

Table 3. Correlation ( $R^2$ ) between EC and TMI, and measured and calculated  $\text{HCO}_3^-$

	Aug 2006	Oct 2006	Jan 2007	April 2007
EC and TMI	0.98	0.99	0.99	0.98
Measured and Calculated $\text{HCO}_3^-$	0.94	0.99	0.94	0.93

The charge balance, which is calculated by the formula:  $(\text{TZ}^+ - \text{TZ}^-) / (\text{TZ}^+ + \text{TZ}^-) * 100$  between cations and anions (less than 10%) of each sample was within acceptable limit (Singh and Hasnain, 1998), confirming the reliability of the analytical results.

#### 4.2 Spatial and temporal pattern of water quality

The water quality parameters showed considerable variability among the sampling sites and significant temporal variability (Table 4). EC and the concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and TMI showed significant seasonal variation ( $p < 0.05$ ).  $\text{Cl}^-$  was highly variable among the sampling sites in summer; winter and spring while  $\text{NO}_3^-$  in fall.  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  did not vary significantly seasonally and were highest in summer.  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  also did not vary significantly over seasons and were highest in winter. pH did not vary significantly either among the sites or seasonally. Temperature varied significantly only among seasons ( $p < 0.001$ ).

Comparison of means of different seasons showed that the EC value of fall was lower and significantly different from others. Concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  were about half of other three seasons. Due to having similarity, the water quality data of summer, winter and spring were then again subjected to ANOVA test to find out the variability. The results showed that only  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$  and temperature had significant seasonal differences. Then the data were divided into two. One is fall data itself and the average of other three seasons for correlation analysis with the land use variables.

EC of both the tributaries and mainstream of Ohori River measured at different seasons showed that there is distinct difference between fall data and others (Fig. 8), while along the Jiganehori River it is similar except the most downstream point. One week before fall sampling, there was heavy rain which might affect the concentration of ions by dilution. Relatively narrow sized watershed of Jiganehori River might recover the stormwater effect within few days. The water sampling of fall season was done in weekend which might also have some effect.

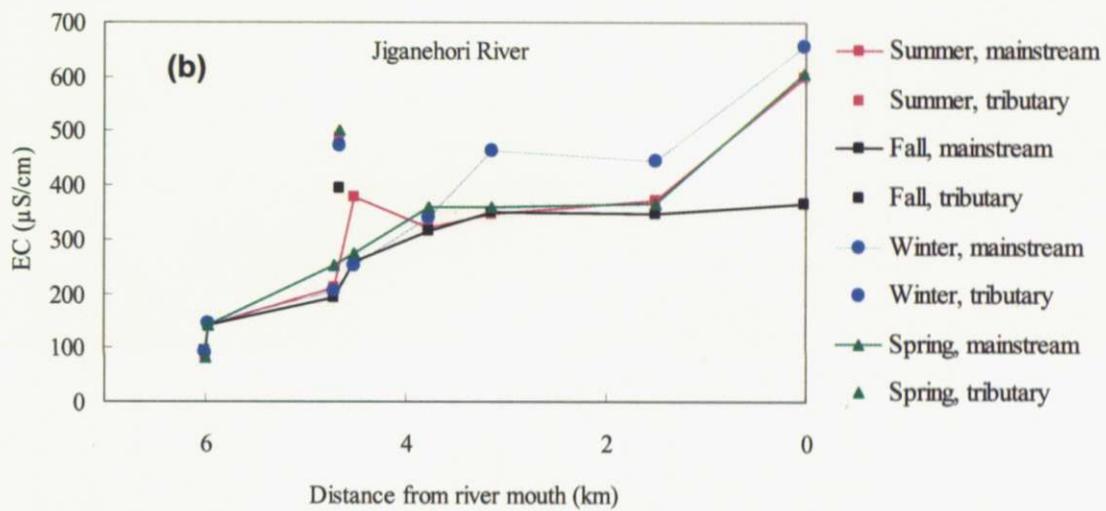
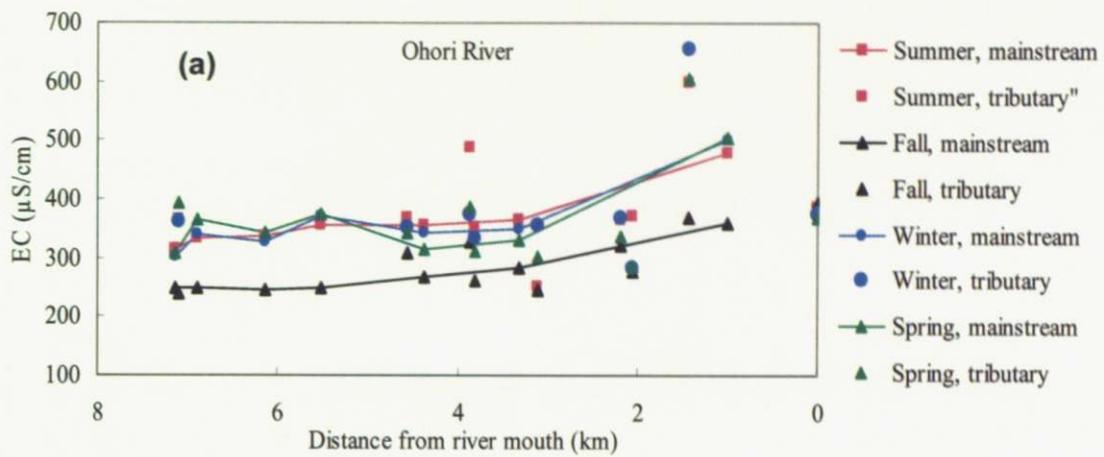


Figure 8. Changes of EC of both mainstream and tributary sampling point of different seasons.

Table 4. Seasonal averages, coefficient of variation [CV(%)], minima and maxima for water quality parameters. The probabilities associated with ANOVA test. Means between the different seasons with same letters (either a, b, or c) indicate that they are not significantly different at  $p=0.05$  level. For example, mean temperature in fall and spring, both of them with c, are not significantly different, but they are significantly different from summer (with a) and winter (with b). Mean temperature between summer (with a) and winter (with b) are significantly different.

	Summer			Fall			Winter			Spring		
	Mean [CV(%)]	Min - Max										
EC ( $\mu\text{S}/\text{cm}$ )	351.7 [31] a	84.5-609.0	280.4 [26] b	94.8-395.0	348.1 [31] a	91.0-600.0	345.1 [33] a	82.2-678.0	345.1 [33] a	82.2-678.0	345.1 [33] a	82.2-678.0
Na <sup>+</sup> (meq/l)	1.31 [56] a	0.30-3.64	0.68 [32] b	0.35-1.05	1.18 [57] a	0.33-3.39	1.31 [61] a	0.30-4.17	1.31 [61] a	0.30-4.17	1.31 [61] a	0.30-4.17
K <sup>+</sup> (meq/l)	0.12 [59] a	0.00-0.37	0.07 [43] b	0.00-0.12	0.10 [44] ab	0.01-0.17	0.11 [49] a	0.00-0.24	0.11 [49] a	0.00-0.24	0.11 [49] a	0.00-0.24
Mg <sup>2+</sup> (meq/l)	0.63 [23] a	0.24-0.95	0.62 [23] a	0.26-0.92	0.68 [22] a	0.27-0.99	0.58 [22] a	0.23-0.89	0.58 [22] a	0.23-0.89	0.58 [22] a	0.23-0.89
Ca <sup>2+</sup> (meq/l)	1.41 [31] a	0.17-2.05	1.36 [33] a	0.20-2.12	1.33 [42] a	0.20-1.95	1.33 [30] a	0.16-1.93	1.33 [30] a	0.16-1.93	1.33 [30] a	0.16-1.93
Cl <sup>-</sup> (meq/l)	0.95 [66] a	0.27-2.99	0.48 [29] b	0.26-0.73	0.90 [60] a	0.27-2.60	0.95 [70] a	0.23-3.38	0.95 [70] a	0.23-3.38	0.95 [70] a	0.23-3.38
NO <sub>3</sub> <sup>-</sup> (meq/l)	0.25 [56] ab	0.04-0.55	0.25 [47] ab	0.05-0.59	0.35 [48] a	0.11-0.85	0.17 [56] b	0.00-0.34	0.17 [56] b	0.00-0.34	0.17 [56] b	0.00-0.34
SO <sub>4</sub> <sup>2-</sup> (meq/l)	0.50 [62] a	0.06-1.69	0.49 [26] a	0.12-0.67	0.51 [27] a	0.10-0.69	0.46 [33] a	0.07-0.69	0.46 [33] a	0.07-0.69	0.46 [33] a	0.07-0.69
HCO <sub>3</sub> <sup>-</sup> (meq/l)	1.89 [35] a	0.24-2.86	1.46 [38] a	0.24-2.78	1.66 [36] a	0.22-2.90	1.61 [34] a	0.22-2.60	1.61 [34] a	0.22-2.60	1.61 [34] a	0.22-2.60
TMI (meq/l)	7.07 [33] a	1.44-12.3	5.40 [28] b	1.66-8.07	6.70 [33] ab	1.59-11.85	6.51 [34] ab	1.40-12.59	6.51 [34] ab	1.40-12.59	6.51 [34] ab	1.40-12.59
pH	7.33 [9] a	5.71-8.88	7.16 [9] a	5.79-8.50	7.13 [8] a	5.71-8.44	7.54 [12] a	4.66-9.33	7.54 [12] a	4.66-9.33	7.54 [12] a	4.66-9.33
Temp (°C)	22.37 [8] a	17.8-25.9	19.12 [4] c	17.3-20.3	9.91 [20] b	6.6-13.7	18.12 [13] c	13.8-23.0	18.12 [13] c	13.8-23.0	18.12 [13] c	13.8-23.0

\* all seasons

\*\* three seasons (except Fall)

### 4.3 Chemical characteristics

The chemical composition of water in the Ohori River basin is variable with electrical conductivity ranging from 84.5 to 609  $\mu\text{S}/\text{cm}$  in summer; 94.5 to 395  $\mu\text{S}/\text{cm}$  in fall; 91 to 600  $\mu\text{S}/\text{cm}$  in winter and 82.2 to 678  $\mu\text{S}/\text{cm}$  in spring (Table 4). Tributaries have high EC comparing the value measured along the mainstream. Like many other major river studies (Cameron et al., 1995; Karim and Veizer, 2000; Douglas et al., 2002), EC in the Ohori River basin increases from headwaters to river mouth. This is because the number of tributaries and the intensity of anthropogenic activity increase downstream. The highest EC value measured at sampling station 21 in fall and at 14 in other three seasons. The high values at site 14 were most likely caused by the industries located upstream of this sampling point. EC below 100  $\mu\text{S}/\text{cm}$  was always recorded at site 24 which is a spring and the headwater of Jiganehori River. The Ohori River water is slightly acidic to alkaline. The highest (9.33) and lowest (4.66) value pH were found during spring sampling.

There was no significant seasonal variation of mean value of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ . The highest value  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  were recorded during winter,  $\text{Ca}^{2+}$  during fall and  $\text{SO}_4^{2-}$  during summer season.  $\text{Na}^+$  and  $\text{Cl}^-$  concentration were highest during spring season, reaching 4.17 and 3.38 meq/l respectively. Except  $\text{Cl}^-$  and  $\text{NO}_3^-$  the lowest values of other ion concentration were recorded at site 24 in all seasons.

The average concentrations of ions of Ohori River were higher than that of Japan and world average data (Table 5). According to the recommended value set by World Health Organization and European Community, the concentration of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  were within the desirable limits (Table 6).

Table 5. Comparison of average concentration (meq/l) of major ion and EC ( $\mu\text{S}/\text{cm}$ ) of this study with previous Japan and World data.

References	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	EC
This study	1.26	0.11	0.63	1.36	0.93	0.26	0.49	1.72	348
Japan									
Kobayashi (1961)	0.29	0.03	0.16	0.43	0.16	0.004	0.22	0.51	
Sugawara (1969)	0.22	0.02	0.19	0.31	0.14		0.22		
Konohira* (2006)	0.21	0.02	0.10	0.26	0.12	0.025	0.12	0.34	70.1
World									
Livingstone (1963)	0.27	0.06	0.33	0.75	0.22	0.003	0.23	0.96	
Meybeck (1979)	0.31	0.03	0.30	0.73	0.23		0.24	0.87	
Gibbs (1972)	0.30	0.05	0.32	0.75	0.23		0.22	0.92	

\*The study was carried out mostly in the mountainous rivers.

Table 6. Recommended water quality criteria

Quality factor	Desirable limit	Maximum permissible limit	Orgazination/Body
Range of pH	7.0 – 8.5	6.5 – 9.2	WHO
EC ( $\mu\text{S}/\text{cm}$ )	750	2500	WHO
$\text{Na}^+$ (meq/l)	2.17	7.61	WHO
$\text{Ca}^{2+}$ (meq/l)	3.74	9.98	WHO
$\text{Cl}^-$ (meq/l)	7.05	16.92	WHO
$\text{NO}_3^-$ (meq/l)	0.40	0.81	EC

WHO, World Health Organization; EC, European Community

The chemical types of average (three seasons) water quality of each sampling point are plotted with hexadiagram (Fig. 9). The water quality along Ohori River mainstream is  $\text{Ca-HCO}_3$  type except the most downstream point which is  $\text{Na-HCO}_3\text{-Cl}$  type. The concentration of ions increased in the downstream. The excess Na and Cl are added from the tributaries. The upper part of Jiganehori River has  $\text{Ca-HCO}_3$  type and it changes to  $\text{Na-Cl-HCO}_3$  type. Tributaries have different water quality type like  $\text{Na-Ca-HCO}_3$ ,  $\text{Na-HCO}_3$ ,  $\text{Na-Cl-HCO}_3$ ,  $\text{Na-NO}_3$  and  $\text{Ca-HCO}_3$ . The water quality of  $\text{Ca-HCO}_3$  is regarded as mostly affected by water-rock interaction while other types are mostly affected by anthropogenic inputs. The hexadiagram of water quality type indicates that both natural and various anthropogenic inputs are involved in controlling the chemical composition of the water in the Ohori River basin.

Significant correlations among water quality parameters suggested they have multiple sources (Table 7).  $\text{Na}^+$  showed high correlation with  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$ ,  $\text{K}^+$  with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  with  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  with  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ , and  $\text{NO}_3^-$  with  $\text{SO}_4^{2-}$  indicating their common sources. There was significant correlation between TMI and all ions except  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  which might have some specific sources.

Table 7. Correlation coefficient matrix of water quality parameters\*

	EC	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	TMI
EC	1.00									
$\text{Na}^+$	<b>0.91</b>	1.00								
$\text{K}^+$	<b>0.84</b>	<b>0.74</b>	1.00							
$\text{Mg}^{2+}$	<b>0.66</b>	0.37	<b>0.43</b>	1.00						
$\text{Ca}^{2+}$	<b>0.71</b>	0.37	<b>0.63</b>	<b>0.84</b>	1.00					
$\text{Cl}^-$	<b>0.86</b>	<b>0.94</b>	<b>0.66</b>	0.37	0.36	1.00				
$\text{NO}_3^-$	0.20	0.05	0.30	0.24	0.23	-0.15	1.00			
$\text{SO}_4^{2-}$	0.39	0.21	<b>0.44</b>	0.39	<b>0.50</b>	-0.02	<b>0.64</b>	1.00		
$\text{HCO}_3^-$	<b>0.90</b>	<b>0.72</b>	<b>0.75</b>	<b>0.79</b>	<b>0.87</b>	<b>0.68</b>	0.09	0.36	1.00	
TMI	<b>0.99</b>	<b>0.89</b>	<b>0.83</b>	<b>0.69</b>	<b>0.74</b>	<b>0.84</b>	0.17	0.39	<b>0.94</b>	1.00

\*Bold values are significant at 5% level of t-test

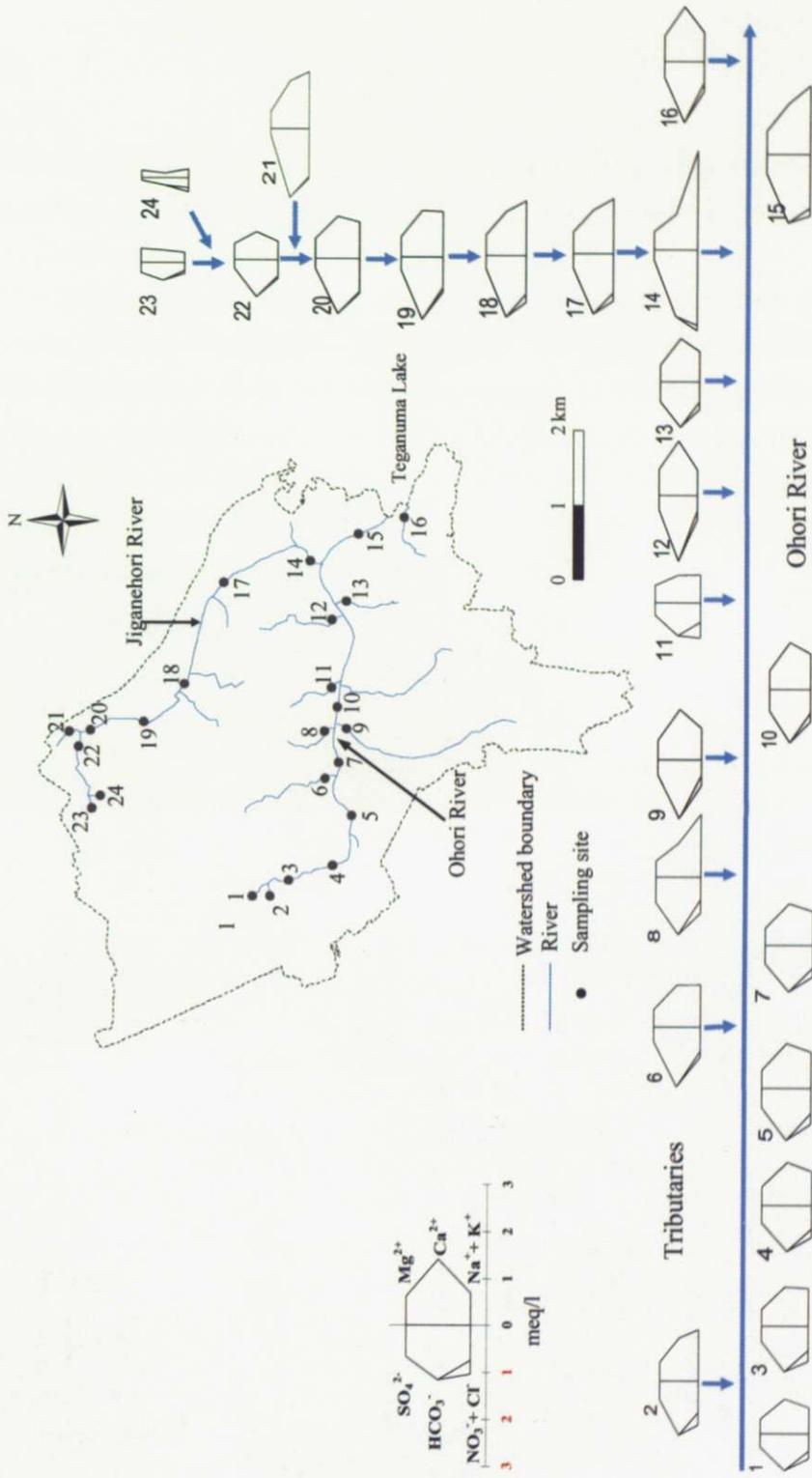


Figure 9. Hexadiagram of water quality of individual sampling point

#### 4.4 Loading, concentration and discharge

In reviewing and conducting watershed-water quality studies, it is important to differentiate between the effects of land use on subsequent instream concentrations and effects on loading. Calculations of loading are more appropriate from the perspective of impacts on downstream areas, particularly receiving waters such as lakes and reservoirs (Schlosser and Karr, 1981). Johnson et al. (1997) and Osborne and Wiley (1988) affirm that concentration data should be used when examining landscape influence on water quality. The assertion is that concentration is more directly linked to the 'integrity' of the system than loading.

In August 2006, discharge was measured from fifteen points at the time of sampling. Loading of each chemical was calculated by multiplying the concentration with discharge. The results show that no correlation was found between concentration and discharge (Table 8). Discharge and loading are dependent on the size of the watershed and hence shows significant relationship. So the concentration of water quality chemicals is independent and we can analyze the water quality in terms of concentration of different sized watersheds at the same time. Fig.10 shows the relationship between discharge, loading and concentration.

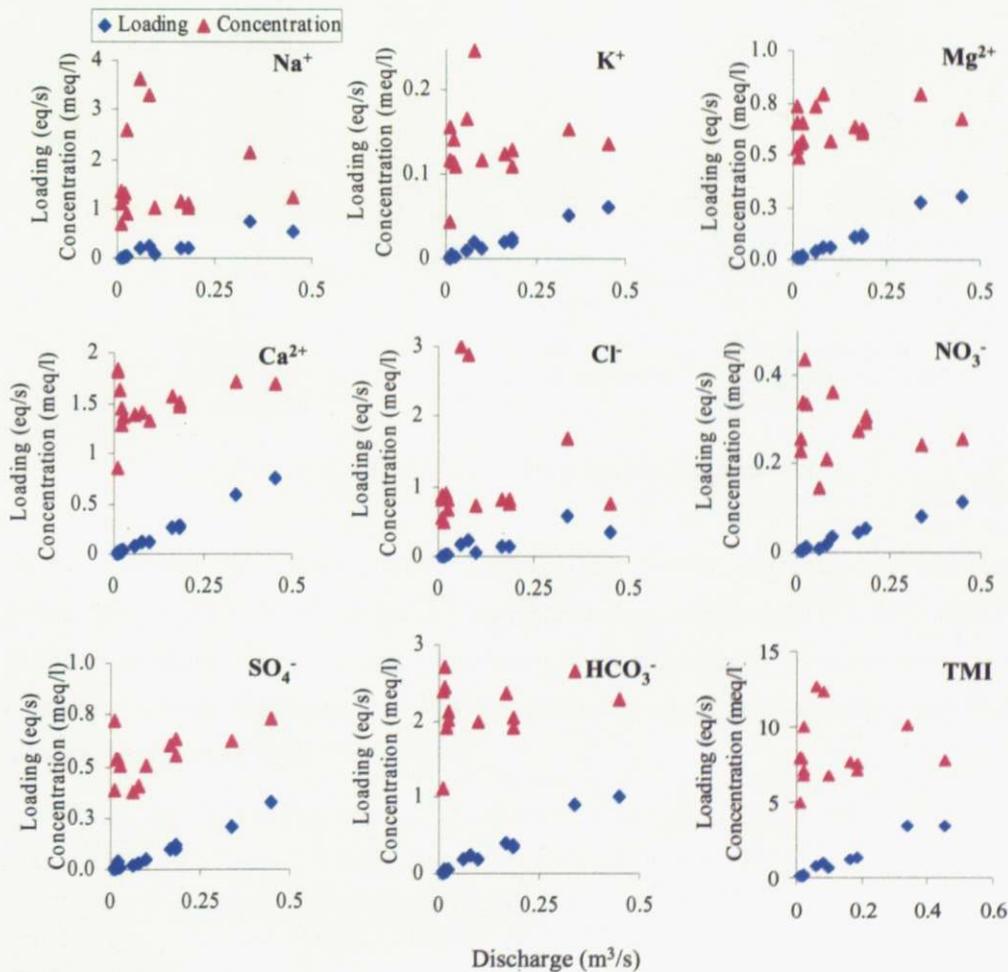


Figure 10. Relationship between discharge, loading and concentration

Table 8. Correlation relationship between discharge and loading, and discharge and concentration.

	Discharge								
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TMI
Loading	<b>0.90*</b>	<b>0.98</b>	<b>0.99</b>	<b>0.99</b>	<b>0.84</b>	<b>0.99</b>	<b>0.98</b>	<b>0.99</b>	<b>0.98</b>
Concentration	-0.04	-0.01	0.33	0.37	0.04	-0.34	0.04	0.11	0.06

\*Bold values are significant correlation at  $p < 0.01$

#### 4.5 Land use characteristics

The land use in the Ohori River basin has been changed greatly over time (Fig. 11) and is still changing due to urbanization. Forest, farmland and the area under development are decreasing while urban coverage like residential, commercial and industrial area increasing.

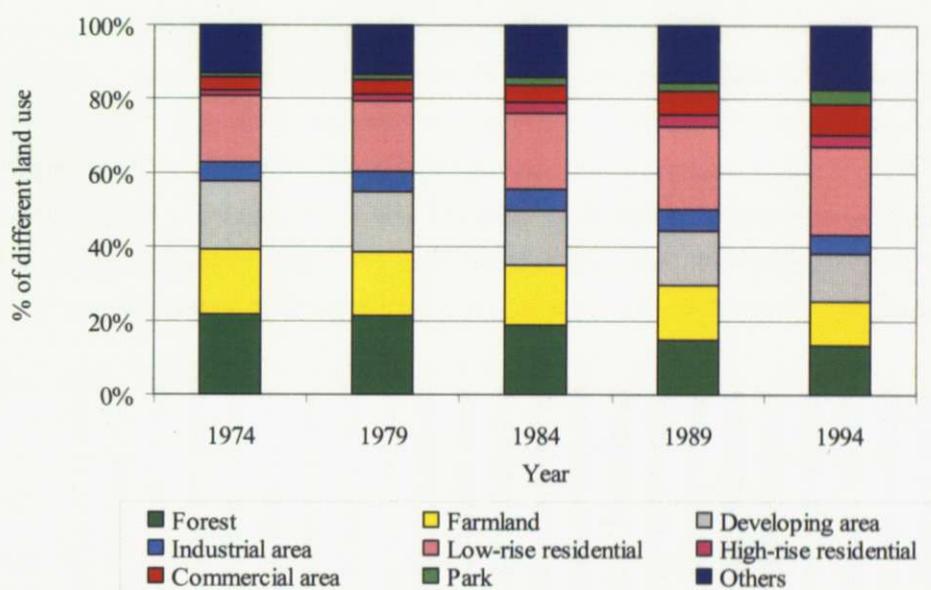


Figure 11. Land use of different years in the Ohori River basin

In the year 1974 the amount of forest coverage was 21.69% which has been changed to 13.19% in 1994 (Table 9). Farmland and developing area changed from 17.54% to 11.95% and 18.45% to 12.99% respectively. There was very little change in the proportion of industrial area over the time period. Low-rise residential and high-rise residential area increased 5.88% and 1.77%. Commercial area changed from 3.70% to 8.15%.

Table 9. Land use changes in the Ohori River basin

	1974	1979	1984	1989	1994	Change
	(%)	(%)	(%)	(%)	(%)	1994-1974(%)
Forest	21.69	21.14	18.67	14.90	13.19	-8.50
Farmland	17.54	17.66	16.36	14.63	11.95	-5.59
Developing area	18.45	16.22	14.62	14.82	12.99	-5.46
Industrial area	5.19	5.28	5.80	5.77	5.25	0.07
Low-rise residential	17.86	19.16	20.58	22.54	23.73	5.88
High-rise residential	1.60	1.87	2.88	3.08	3.37	1.77
Commercial area	3.70	4.00	4.92	6.58	8.15	4.45
Park	1.08	1.23	2.01	2.07	3.98	2.90
Others	12.90	13.43	14.17	15.63	17.39	4.49

According to the land use of 1994, approximately 61% of Ohori River watershed was covered with urban land uses. Farmland area accounted for 12%, while forest and park areas accounted for approximately 17%. The remaining land was distributed among roads, water bodies and others. The proportion of forests in the drainage basins of sampling sites ranged from 2.47 to 86.2% with the highest being in watershed 24 (Fig. 12). The range of farmlands distributed in the basins was 0–18.5%. The proportion of urban land uses like industrial area, low-rise residential, high-rise residential and commercial area ranged from 0.04–29%, 0–42%, 0–5% and 0–16% respectively.

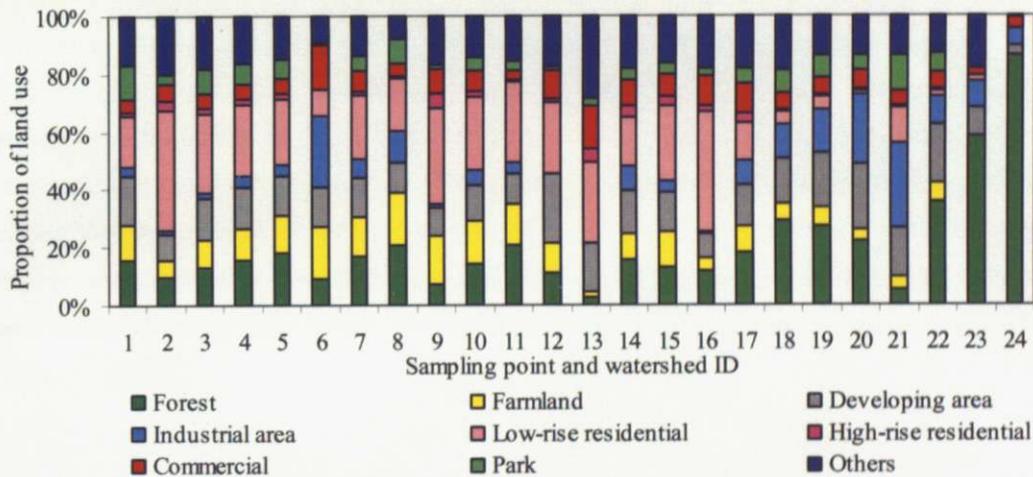


Figure 12. Land uses in the drainage area each sampling point.

Significant negative correlation between forest and urban coverage indicates that urban area has low forest coverage (Table 10) in the sub-watersheds. High-rise residential area was positively correlated with commercial and low-rise residential area.

Table 10. Correlation coefficient matrix of land use characteristics.\*

	Forest	Farm land	Devel- oping	Industrial	Low- rise res	High- rise res	Comm ercial	Park	Others
Forest	1.00								
Farmland	<b>-0.48</b>	1.00							
Developing	-0.38	-0.02	1.00						
Industrial	0.03	<b>-0.06</b>	0.31	1.00					
Low-rise res	<b>-0.62</b>	0.32	-0.27	<b>-0.65</b>	1.00				
High-rise res	<b>-0.53</b>	0.11	-0.07	<b>-0.46</b>	<b>0.61</b>	1.00			
Commercial	<b>-0.49</b>	0.17	0.16	0.00	0.25	<b>0.40</b>	1.00		
Park	-0.30	0.10	0.38	0.30	-0.11	-0.12	-0.39	1.00	
Others	<b>-0.56</b>	-0.18	0.30	<b>-0.40</b>	<b>0.47</b>	<b>0.61</b>	0.32	0.04	1.00

\*Bold values are significant at 5% level of t-test

#### 4.6 Land use-water quality relationship

The correlation coefficients between ion concentrations (in milliequivalent unit) and land use characteristics (in percent) are shown in Table 11 and 12. The correlations were better explained by the average water quality data of summer, winter and spring than the fall data. Forest area was negatively correlated with all ions in both cases. Farmland showed significant positive correlations with mean concentrations of  $K^+$ ,  $NO_3^-$  and  $SO_4^{2-}$  but only with  $NO_3^-$  in the case of fall season data. Urban developing area was positively correlated with  $Ca^{2+}$  and  $HCO_3^-$ . Industrial area showed significant positive correlation with fall  $Na^+$  concentrations while the correlation was very weak with the average data. Low-rise residential area showed positive significant correlations with the average concentrations of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $NO_3^-$  and  $SO_4^{2-}$  while high-rise residential area was positively correlated with  $K^+$  and  $Ca^{2+}$ . There were no significant correlations between fall water quality data and residential land use except  $NO_3^-$  which showed significant positive correlation with low-rise residential area.  $Mg^{2+}$ ,  $Ca^{2+}$  and  $HCO_3^-$  were positively correlated with commercial land use in case of average water quality data and the fall data showed significant correlations with  $Ca^{2+}$  and  $SO_4^{2-}$ .

Table 11. Relationships between major ion concentrations and land use characteristics\*. The water quality data is the mean concentration of summer, winter and spring season.

	EC	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TMI
Forest	<b>-0.67</b>	-0.37	<b>-0.66</b>	<b>-0.68</b>	<b>-0.85</b>	-0.30	-0.36	<b>-0.61</b>	<b>-0.73</b>	<b>-0.67</b>
Farmland	0.37	0.24	<b>0.52</b>	0.25	0.38	-0.04	<b>0.60</b>	<b>0.61</b>	0.36	0.36
Developing area	0.22	0.07	0.09	0.37	<b>0.41</b>	0.15	-0.30	-0.05	0.39	0.25
Industrial area	0.14	0.26	0.06	-0.12	-0.01	0.30	<b>-0.57</b>	<b>-0.38</b>	0.25	0.16
Low-rise residential area	0.34	0.08	0.35	<b>0.48</b>	<b>0.54</b>	-0.01	<b>0.70</b>	<b>0.62</b>	0.29	0.32
High-rise residential area	<b>0.46</b>	0.35	<b>0.60</b>	0.32	<b>0.44</b>	0.36	0.26	0.35	0.37	<b>0.46</b>
Commercial area	0.27	0.14	0.33	<b>0.41</b>	<b>0.48</b>	0.12	-0.03	0.31	<b>0.43</b>	0.33
Park	0.36	0.30	0.28	0.05	0.28	0.29	-0.02	0.09	0.31	0.32
Others	0.29	0.10	0.31	<b>0.44</b>	<b>0.42</b>	0.15	0.19	0.33	0.25	0.28

\*Bold values are significant at 5% level of t-test

Table 12. Relationships between major ion concentrations of fall season and land use characteristics\*.

	EC	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TMI
Forest	<b>-0.70</b>	<b>-0.40</b>	<b>-0.62</b>	<b>-0.56</b>	<b>-0.79</b>	-0.30	-0.26	<b>-0.77</b>	<b>-0.63</b>	<b>-0.69</b>
Farmland	0.28	0.16	0.22	0.21	0.27	0.09	<b>0.59</b>	0.36	0.11	0.25
Developing area	0.30	0.14	0.36	0.31	<b>0.41</b>	0.09	-0.38	0.32	<b>0.45</b>	0.35
Industrial area	0.23	<b>0.44</b>	0.27	0.24	0.13	0.24	<b>-0.46</b>	0.15	0.35	0.25
Low-rise residential area	0.29	-0.02	0.13	0.20	0.39	-0.01	<b>0.58</b>	0.29	0.15	0.26
High-rise residential area	0.26	0.03	0.32	0.12	0.38	0.10	0.13	0.37	0.21	0.26
Commercial area	<b>0.42</b>	0.27	0.23	0.38	<b>0.45</b>	0.29	0.07	<b>0.60</b>	0.34	<b>0.42</b>
Park	0.36	0.38	<b>0.54</b>	0.18	0.37	0.26	-0.18	0.26	<b>0.41</b>	0.37
Others	0.28	0.04	0.31	0.23	0.36	0.12	0.02	<b>0.45</b>	0.23	0.27

\*Bold values are significant at 5% level of t-test

#### 4.7 Factor analysis of combined water quality and land use data

Most factor analyses reported in the literature use only water quality data to identify factors that explain the dominant controls on stream chemistry. In this research, factor analysis was performed on a database of land use and chemical species. Using land use distributions together with water chemistry is a relatively novel approach that mixes two types of data (chemical concentrations and land use proportions). For the R-mode factor analysis, water quality data for each sampling point were merged with land use distributions for the corresponding sourceshed; the resulting database contained the proportion of each land use in the sourceshed contributing to

the sampling point and the average water quality data. The land uses were categorized again to a small number of groups (Table 13). The database was structured so that columns contained water quality and land use variables, and rows contained sample locations.

Table 13: Description of land use classification for factor analysis

Land use category	Description
Forest	All types of forest
Farmland	Paddy field and field
Empty and Developing	Empty and urban developing area
Urban	Both low-rise and high-rise residential area, industrial area, commercial area, parks, public facilities area
Others	Roads, water bodies

Table 14. Factors for water quality and land use datasets. Factor loadings  $>0.5$  or  $<-0.5$  are shown. Number in italic type indicate loadings  $>0.75$  or  $<-0.75$ . Cumulative percentage of variability in the data is explained by factors is shown in the last line.

	Factor		
	1	2	3
EC	<i>0.98</i>	0.66	
Na <sup>+</sup>	<i>0.94</i>		
K <sup>+</sup>	<i>0.86</i>	0.57	0.57
Mg <sup>2+</sup>	0.58	<i>0.82</i>	
Ca <sup>2+</sup>	0.65	<i>0.93</i>	
Cl <sup>-</sup>	<i>0.90</i>		
NO <sub>3</sub> <sup>-</sup>			<i>0.88</i>
SO <sub>4</sub> <sup>2-</sup>		0.56	<i>0.85</i>
HCO <sub>3</sub> <sup>-</sup>	<i>0.89</i>	<i>0.78</i>	
TMI	<i>0.98</i>	0.68	
PH	0.63	<i>0.81</i>	0.54
Forest	-0.62	<i>-0.93</i>	-0.61
Farmland			<i>0.80</i>
Empty and Developing		0.53	
Urban	0.64	<i>0.82</i>	0.55
Others		0.70	
Cumulative variance, %	54.6	70.2	81.5

Factor analysis on the combined datasets provided three factors with eigenvalue  $>1$  that can explain approximately 82% of the variability of the data (Table 14). Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>

exhibited strong positive loadings on Factor I, while  $Mg^{2+}$ ,  $Ca^{2+}$  and proportion of urban had moderate positive loading. Factor II had strong loadings of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $HCO_3^-$  and proportion of urban, and moderate positive loadings on  $K^+$ ,  $SO_4^{2-}$ , urban and developing land use. Proportion of farmland had strong positive loading on Factor III, along with  $NO_3^-$  and  $SO_4^{2-}$ , and  $K^+$  and urban had moderate loadings. Proportion of forest showed strong negative loading on Factor II and moderate negative loading on Factor I and Factor III.

#### *4.8 Groupings of water quality*

Results of Cluster analysis for the 24 water samples using their chemical components were illustrated with a tree dendrogram (Fig. 13). The optimum number of clusters was identified based on the point where the percentage of variation for each additional cluster failed to decrease dramatically. Using a criterion value of the rescaled distance between 15 and 20, the samples were classified into three groups.

A simple rating procedure was developed to establish relative water quality levels based on the measured water quality data. The complete data set of each chemical was pooled and sorted in ascending order. Then the data were divided into thirds. The lowest third was defined as low, the middle third as moderate, and the highest third as high concentrations. Finally, the cluster's mean concentrations for each chemical were compared to the concentration ranges obtained in the rating procedure in order to classify the concentration levels in one of the three groups (low, moderate, and high).

The average concentrations of the studied components and their speciation with water quality description were presented in Table 15. Cluster 1 showed low concentration of all chemical constituents and relatively good water quality. The sampling sites under this group were upstream points of Jiganehori River and two of them were spring. The average land use of these sites indicated that most part of the watersheds was occupied by forest coverage and less urban effect (Fig. 13). Cluster 2 included most of the sampling sites and the water quality was characterized by high concentration of  $NO_3^-$  and  $SO_4^{2-}$  and moderate concentration of other parameters. More urbanized land use with less forest coverage characterized the land use in this cluster. The percent of farmland, low-rise residential and commercial land use were highest in this cluster among the clusters. Cluster 3 had the least forest cover and highest industrial area among clusters. The high EC in this cluster was due to excess concentration of  $Na^+$  and  $Cl^-$ . Sampling site 14 and 21 under this cluster had distinct industrial land use background in the watershed.

Table 15. Description and interpretation of cluster analysis

Clusters	Sampling sites	Water quality chemicals										Water quality description
		EC	TMI	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	
1	22, 23, 24	150.72	2.80	0.42	0.02	0.43	0.53	0.37	0.10	0.23	0.70	All parameters at lowest range
2	1-13, 16-18, 19, 20	349.75	6.77	1.17	0.12	0.65	1.44	0.81	0.30	0.54	1.76	NO <sub>3</sub> <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> at highest range, the others at moderate range
3	14,15,21	537.30	10.62	2.67	0.16	0.74	1.67	2.23	0.17	0.44	2.54	NO <sub>3</sub> <sup>-</sup> at lowest range, SO <sub>4</sub> <sup>2-</sup> at moderate range, the others at highest range

Note: All concentrations are mean value of each cluster and expressed in meq/L except for EC which is expressed in  $\mu\text{S}/\text{cm}$ .

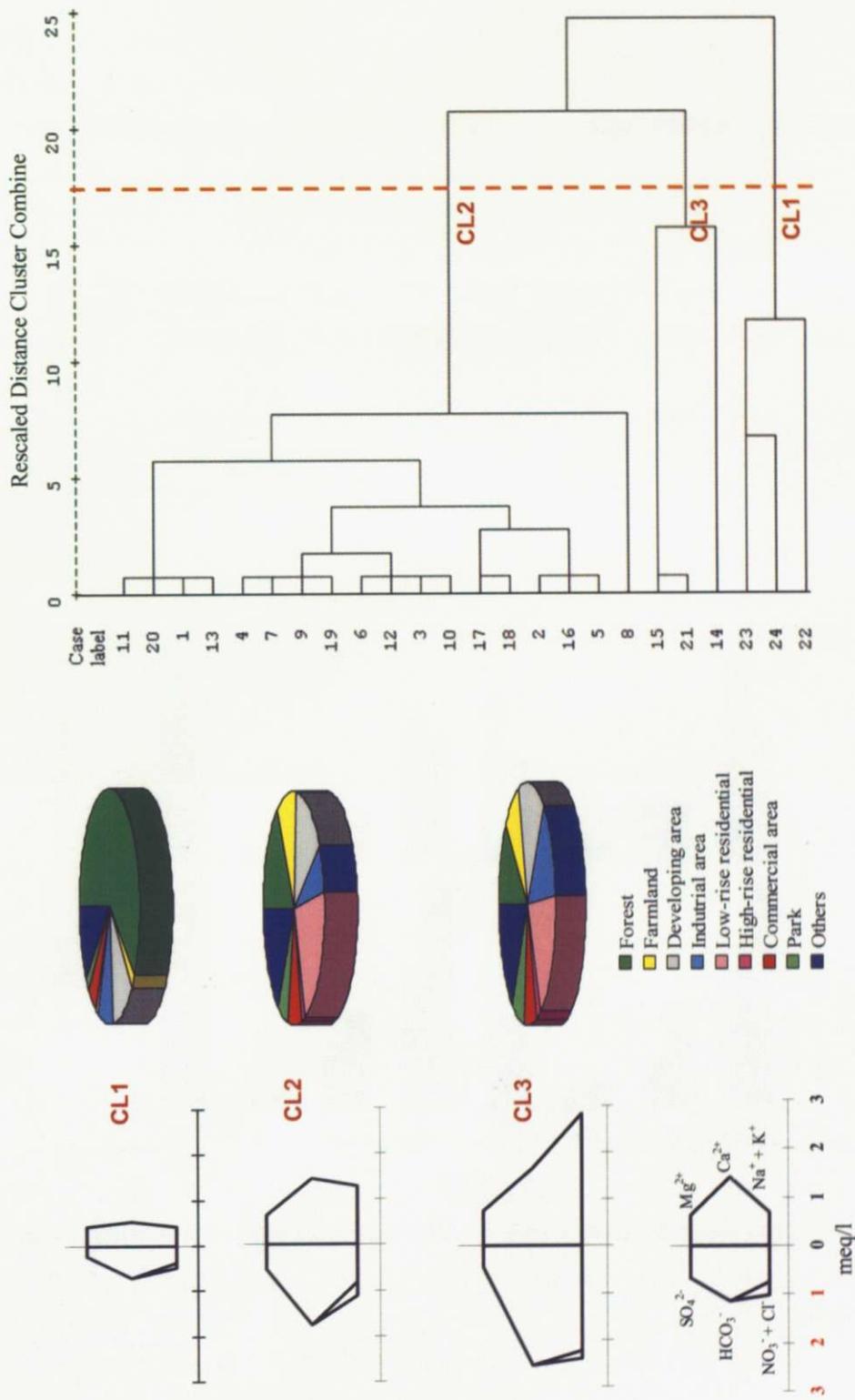


Figure 13. Dendrogram from cluster analysis, hexadiagram of each cluster water quality and average land use pattern.

#### 4.9 Effects of Tone River discharge

The concentrations of ions of Tone River water discharged at the upstream of Ohori River were lower than that of Ohori River downstream point (Table 16) except  $\text{SO}_4^{2-}$ , which had very similar value. The water discharged from Tone River remained constant at  $0.5\text{m}^3/\text{s}$  and higher than the average discharge produced by Ohori River itself. The combined concentration was lower than Ohori River but the total chemical flux of each ion to Teganuma Lake was higher (Fig. 14)

Table 16. Major ion concentration and chemical flux from Ohori River and Tone River discharge.

		$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$
Concentration (meq/l)	Ohori River	2.20	0.17	0.82	1.74	1.88	0.25	0.66	2.13
	Tone River	0.74	0.08	0.41	1.08	0.55	0.20	0.64	0.83
Flux (eq/s)	Ohori River	1.03	0.08	0.38	0.82	0.88	0.12	0.31	1.00
	Tone River	0.37	0.04	0.21	0.54	0.28	0.10	0.32	0.41

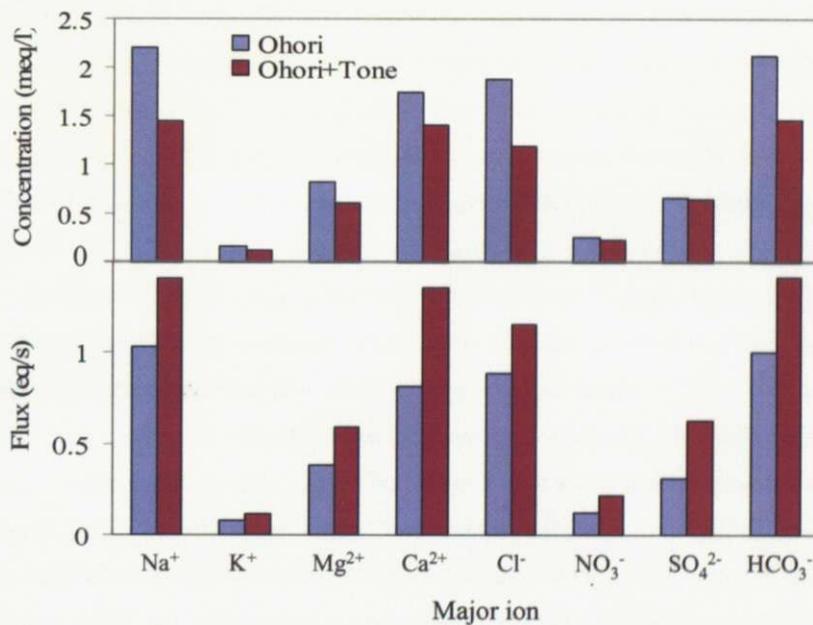


Fig. 14. Effect of Tone River discharge on the concentration and chemical flux to Teganuma Lake.

## 5. Discussion

Most seasonal variations in river water chemistry are driven by climatic and biotic factors and are therefore largely governed by the processes that are taking place in the terrestrial part of the watershed (Moldan and Cerny, 1994). In this study, water quality showed slight seasonal difference in the concentration and interactions with land use characteristics. Relationship between water quality and land use variables was better explained with the average of summer, winter and spring water quality data rather than fall data. This may have been the result of relatively higher discharge within watersheds affected by the heavy rainfall one week before sampling. In fall, low value of EC resulted from the low concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  while other ion concentrations remained close to other season's value.  $\text{Na}^+$  and  $\text{Cl}^-$  tend to vary with season and usually decline with increasing discharge (Markich and Brown, 1998). There might have some other effect like 'weekend effect' in declining their concentration when some industries remain closed and in fall the water samples were collected in weekend.

The correlation analysis results of this study suggest that, using the watershed land use variables, urban land uses are the most important predictor of water quality variability. This relationship may have been highly influenced by point source (which later mix with the river and diluted) as well as non-point source pollution that is commonly associated with urbanized areas. After urban land use, agriculture appeared important in determining water quality.

Examination of the relationships between major inorganic ion concentrations and land use characteristics revealed multiple controls on ion concentrations related to sources. Forested land use was negatively correlated with all land uses while Ding et al. (2006) found positive correlation with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$ . Forests intake nutrients for their growth and function and in forested land use chemical weathering is the only available source of ion supply.  $\text{Na}^+$  and  $\text{Cl}^-$  did not show significant positive correlations with land use characteristics but showed weak positive correlations with industrial area and high-rise residential area. Although these two ions were not significantly correlated with industrial land use, their excess concentration found at sampling point 14 and 21 resulted from industries. The nature and concentration of effluent depend on the type of industry. Some industries with small area relative to the area of respective watershed discharge high concentration of ions while some big industries do not. This point source nature of industrial land use might not result good correlations.  $\text{Na}^+$  and  $\text{Cl}^-$  likely come from domestic effluents, industries and roads.  $\text{Cl}^-$  concentration seems to be a general indicator of any non-forested land and it could be used as a good surrogate indicator for general human disturbance in the watershed (Herlihy et al., 1998).

Residential area and farmland are positively correlated with  $\text{K}^+$ . In manure and commercial fertilizers,  $\text{K}^+$  is an essential nutrient, while  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are less important constituents (Van der Weijden and Pacheco, 2006). The possible sources of  $\text{K}^+$  are domestic effluents and fertilizers used in agricultural land and home garden.  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were positively correlated with mostly

urban coverage like residential area, commercial and urban developing area. They might come from salts in domestic wastewater, concrete structure and fertilizers used in agricultural land. Relatively small temporal and spatial variation of these ions also indicated their natural origin which resulted from weathering of carbonate and silicate minerals.

$\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  showed significant positive correlations with farmland and low-rise residential area.  $\text{NO}_3^-$ -N and agricultural land use relationship has been frequently reported in the previous studies (Smart et al., 1985; Neill, 1989; Sauer et al., 2001; Woli et al., 2004). It likely comes from fertilizers used in agricultural land and in home gardens, biological activity of plants and domestic effluents. Sources of  $\text{SO}_4^{2-}$  include sulfuric salts in domestic wastewater and fertilizer. Natural processes such as the chemical weathering of rocks and dissolution of atmospheric and soil  $\text{CO}_2$  gas could be the mechanism which supplies  $\text{HCO}_3^-$  to surface and groundwater. In the present study  $\text{HCO}_3^-$  shows weak positive correlations with all land uses except forest. So, the potential anthropogenic sources of  $\text{CO}_2$  are (a)  $\text{CO}_2$  gas originating from municipal wastes and (b)  $\text{CO}_2$  gas due to the oxidation organic materials leaked from sewage systems.

Factor analysis on combined datasets of water quality and land use produced three statistically significant factors that could be clearly interpreted in light of land use controls on water quality. The results also supported the correlation analysis results. Urban and urban developing areas are associated with high concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and EC which was explained by first two factors. Other researchers have observed similar loadings of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  on a factor, which they interpreted as a mineral weathering signal (Schot and van der Waal, 1992; Puckett and Bricker, 1992); however, land use variables were not included in their analyses. Another important factor can be explained by the coverage of farmland which is associated with high concentration of  $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

Cluster analysis on water quality variables produced three distinct clusters and the water quality of each cluster reflected the land uses in the watershed even though land use distributions were not included as variables in the cluster analysis. Cluster 1 indicated relatively good water quality and formed when the sourcesheds of sampling points occupied mostly forested land use. There was big difference in the water quality of cluster 2 and cluster 3 but the land uses almost similar. The difference in the water quality was due to industrial land use. The effect of industrial land use on the concentration of ions is already discussed above.

There was no evidence that the concentration of major ion found in this study exceeded the acceptable limit or water quality standard. Major ion concentrations might play an important role in the ecology of the river system, for instance, by serving as a trigger for processes related to the reproduction of fish (Smolders et al., 2004). Many species from rivers that show a strong seasonal variation in discharge show synchronized reproduction at the onset of the rainy season (Bayley, 1973; Payne and Harvey, 1989; Winemiller, 1989; Paugy, 2002), for instance due to a strong drop of conductivity (Ramnarine, 1995; Kirschbaum, 1979). The present results show that the conductivity as well as the concentration of some ions dropped at fall sampling event which has

been partly discussed as the effect of rainfall one week before sampling. Such a change in conductivity and ion concentrations might well serve as a trigger for spawning behavior at the onset of rainy season. High concentration of dissolved ions may also affect the speciation of toxic metals and the toxicity of these metals (Smolders et al., 2004). Complexation of metals by inorganic ligands such as  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$  may strongly limit the bioavailability and toxicity of metals (Playle, 1998; Bury et al., 1999; Bianchini and Bowles, 2002). Cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  reduce the toxic effects of metals for fish by competition for metal binding sites at negatively charged fish gills (Pagenkopf, 1983; Playle, 1998).

## 6. Conclusion

The primary objective of this research was to identify consistent geochemical fingerprints of land use in surface water chemistry with seasonal sampling and watershed land use analysis. Four seasonal sampling events had been conducted and the results showed that the concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and conductivity varied significantly while others did not. The conductivity measured at different seasons showed that only fall mean varied significantly from others. There was no significant difference between the mean value of summer, winter and spring. Comparison of mean of all solutes among those three seasons showed no significance difference except  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$ . Therefore, the water quality data were divided into two groups: 1) average of summer, winter and spring and 2) fall data and were used to find out the relationship with watershed land uses. The average water quality data was found better to explain the relations

Forested areas had lower levels of inorganic ions and were found to maintain the water quality as it is inversely related with almost all ion concentrations. Farmland coverage was associated with elevated levels of  $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentration. Residential areas were associated with higher concentration of  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , commercial area with  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , and urban developing area with  $\text{Ca}^{2+}$ . Although weak positive correlations were found between proportion of industrial area, and  $\text{Na}^+$  and  $\text{Cl}^-$ , their excess concentrations were found in the sampling sites near industrial area. Water quality clusters were also found to be highly influenced by the land uses. Factor analysis on the combined dataset of water quality and land use showed two major factors like farmland and urban land use controlling the river water chemistry. It is becoming clear that there are distinctive and consistent patterns to the impacts of land use on water quality. However, the results of this study do not fully comply with other research which merit further research.

Future work to incorporate the effects of changing land use, characterize the base flow chemistry of urban streams, and compare biogeochemical fingerprints from different watersheds should lead to improvements in this method and greater understanding of the processes that relate land use and surface water chemistry. With the changes of land use pattern in future, the levels of contaminants will be changed accordingly. Hence future land development and management should be considered with care. With a better land use planning, we may be able to curtail some of

the water quality problems. Since water quality is maintained or improved due to increase of forest area in the drainage basin, the protection of this form of land use should be encouraged. Planned urban settlements should also be emphasized.

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# Land use control on water chemistry of Ohori River, Chiba, Japan

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**Keywords:** River water, inorganic ion, land use, urbanization, GIS

## 1. Introduction

River water chemistry is controlled by numerous natural and anthropogenic factors. Land use impact on stream chemistry can either be spatially diffused or concentrated (point source). Land use change is known to influence the biogeochemistry of watersheds. Due to changes of land use from unaltered natural landscapes to agricultural and urban uses, forests and wetlands have been lost; road density has increased; surface runoff has increased; and anthropogenic chemical and wastewater inputs have increased. As a result of these human activities, the conditions of many aquatic environments have been degraded. There are a number of studies focused on areas in the vicinity of pollution sources or specific land use like agricultural lands. However, the effects of multiple land use on the water quality and their controls have not been systematically examined yet. Watershed management and catchment scale studies have become more important in determining the impact of human development on water quality. Therefore, in this research, river water quality will be discussed in relation to land uses in an upland urbanized river basin by analyzing concentrations of major inorganic ion.

## 2. Study Area

The study area is the Ohori River basin, which is located in the northwestern part of the Shimousa Upland, Chiba Prefecture. Landforms of the basin consist of upland surfaces (15-30 m) and alluvial lowland (2-9m). The length of the Ohori River is 6.9 km and the major tributary, Jiganehori River is 6 km. Many other tributaries of the two rivers divide the upland in the basin. The total area of the drainage basin is 31km<sup>2</sup>. The land use in the Ohori River basin is complex with forests, farmland, residential, industrial and commercial area, parks etc.

## 3. Methodology

Surface water grab samples were collected from 24 sites along the main river and tributaries four times from August 2006 to April 2007 during base flow condition. Water temperature, Electrical conductivity (EC), pH and Alkalinity (HCO<sub>3</sub><sup>-</sup>) were measured in the field. Major inorganic ion (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) concentrations were determined by ion-chromatography in the laboratory. To analyze the land use, detailed digital information published by Geographical Survey Institute of Japan in 1994 was used. Drainage divide map of subwatersheds was collected from City Office and land use proportion of sourcesheds of each sampling site was calculated by GIS.

#### 4. Results and discussion

The water quality parameters showed considerable variability among the sampling sites and significant temporal variability. EC and the concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and TMI showed significant seasonal variation. Comparison of means of different seasons showed that the EC value of fall was lower and significantly different from others. Concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  were about half of other three seasons. The average water quality data of summer, winter and spring showed significant difference only in  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$  concentration and temperature.

The water quality of Ohori River mainstream changed from  $\text{Ca-HCO}_3$  type to  $\text{Na-HCO}_3\text{-Cl}$  type. Tributaries had unique characteristics, which water quality types were  $\text{Ca-HCO}_3$  type,  $\text{Na-HCO}_3$  type,  $\text{Na-Ca-HCO}_3$  type,  $\text{Na-NO}_3$  type and  $\text{Na-Cl-HCO}_3$  type. EC in the Ohori River basin increased from headwaters to river mouth. This is because the number of tributaries and the intensity of anthropogenic activity increase downstream.

Relationship between water quality and land use variables was better explained with the average of summer, winter and spring water quality data rather than fall data. This may have been the result of relatively higher discharge within watersheds affected by the heavy rainfall one week before fall sampling and to some extent by 'weekend effect' where the samples were collected in weekend. Forest area was negatively correlated with all ions (Table 1). Farmland showed significant positive correlations with mean concentrations of  $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  but only with  $\text{NO}_3^-$  in the case of fall season data. Urban developing area was positively correlated with  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ . Industrial area showed significant positive correlation with fall  $\text{Na}^+$  concentrations while the correlation was very weak with the average data. Low-rise residential area showed positive significant correlations with the average concentrations of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  while high-rise residential area was positively correlated with  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ . There were no significant correlations between fall water quality data and residential land use except  $\text{NO}_3^-$ .  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  were positively correlated with commercial land use in case of average water quality data and the fall data showed significant correlations with  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ . The cluster analysis on water quality variables produced three distinct clusters and the water quality of each cluster reflected the dominant land uses in the watersheds. Factor analysis on the combined dataset of water quality and land use showed two major factors like farmland and urban land use controlling the river water chemistry.

Table 1. Relationships between major ion concentrations and land use characteristics (indicated by correlation coefficient,  $r$ ). The water quality data is the mean concentration of summer, winter and spring season. Bold values are significant correlation at  $p \leq 0.05$

	EC	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	TMI
Forest	<b>-0.67</b>	-0.37	<b>-0.66</b>	<b>-0.68</b>	<b>-0.85</b>	-0.30	-0.36	<b>-0.61</b>	<b>-0.73</b>	<b>-0.67</b>
Farmland	0.37	0.24	<b>0.52</b>	0.25	0.38	-0.04	<b>0.60</b>	<b>0.61</b>	0.36	0.36
Developing area	0.22	0.07	0.09	0.37	<b>0.41</b>	0.15	-0.30	-0.05	0.39	0.25
Industrial area	0.14	0.26	0.06	-0.12	-0.01	0.30	<b>-0.57</b>	-0.38	0.25	0.16
Low-rise res. area	0.34	0.08	0.35	<b>0.48</b>	<b>0.54</b>	-0.01	<b>0.70</b>	<b>0.62</b>	0.29	0.32
High-rise res. area	<b>0.46</b>	0.35	<b>0.60</b>	0.32	<b>0.44</b>	0.36	0.26	0.35	0.37	<b>0.46</b>
Commercial area	0.27	0.14	0.33	<b>0.41</b>	<b>0.48</b>	0.12	-0.03	0.31	<b>0.43</b>	0.33
Park	0.36	0.30	0.28	0.05	0.28	0.29	-0.02	0.09	0.31	0.32
Others	0.29	0.10	0.31	<b>0.44</b>	<b>0.42</b>	0.15	0.19	0.33	0.25	0.28

# 大堀川の水質に与える土地利用の影響について

2007年9月

新領域創成科学研究科自然環境学専攻

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## 1. はじめに

河川水質は多くの自然起源物質や人為起源物質によって規定される。また、河川水質に影響する負荷源は、大きく点源負荷と面源負荷に分かれる。

土地利用の変化は流域の生物地球化学要因を変化させる。例えば農地や都市の増加によって森林や湿地は消滅する。道路面積は増加し、表層からの流出は増加し、化学物質や下水の流入が増える。こうした人間活動の結果、水環境は多方面で悪化してきた。

このような状況のもと、例えば農地における汚染物質などの、特定の土地利用域における汚染物質を対象とした研究は多いが、多数の土地利用が混在した地域で土地利用が水質にどう関わってくるのかを検討した研究は少ない。流域管理や流域規模に根ざした研究は、人間の開発が水質に及ぼす影響に着目した場合に重要になる。

以上から本研究では、都市化した台地を流れる河川の水質と土地利用との関係について、主要無機イオン濃度を分析して議論した。

## 2. 研究地域

研究地域は千葉県の、下総台地北西部に位置する大堀川流域とした。下総台地は標高15-30mの台地面と2-9mの低地部からなる。大堀川の流路長は6.9kmで、主要な支流である地金堀川の長さは6kmである。また、多くの谷が台地面を刻む。流域面積は31km<sup>2</sup>で多様な土地利用を有し、森林、農地、宅地、工業用地、商業用地、公園等からなり、流域の都市域は70%以上になる。

## 3. 方法

2006年8月から2007年4月までの平水時に4回にわたり流域の本流や支流の24地点において表層水を採水した。水温、伝導度 (EC)、アルカリ度 (重炭酸濃度に換算) を現場で測定し、実験室でイオンクロマトを用いて主要無機イオン (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>+</sup>, Mg<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>) を測定した。土地利用の解析には1994年国土地理院発刊の10mメッシュ土地利用図を用いた。流域図は柏市役所から入手し、支流流域の土地利用構成はGISを用いて算出した。

#### 4.結果と考察

水質は採水地点間で大きく異なり、採水時期によっても変化があった。EC と  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  と TMI は季節変化が大きかった。特に、秋期のECは他の時期の平均値と比べ明らかに低い値を示し、 $\text{Na}^+$  と  $\text{Cl}^-$  は他の季節の半分だった。これに対し春期、夏期、冬期では、異なっていたのは  $\text{Mg}^{2+}$  と  $\text{NO}_3^-$  の濃度と温度だけだった。

大堀川本流の水質は  $\text{Ca-HCO}_3$  型から  $\text{Na-HCO}_3\text{-Cl}$  型に変化した。支流はそれぞれ型が異なっていて、 $\text{Ca-HCO}_3$  型,  $\text{Na-HCO}_3$  型,  $\text{Na-Ca-HCO}_3$  型,  $\text{Na-NO}_3$  型,  $\text{Na-Cl-HCO}_3$  型などだった。大堀川のECは源流から最下流部にかけて上昇した。これは、下流において支流の流入が増えるのと、人間活動が活発化する為であると考えられた。

水質と土地利用の関係は、夏期、冬期、春期のデータについては対応を説明できた。秋期に採ったサンプルが他の季節とは異なっていた原因として、採水 1 週間前に流域にあった降雨の影響を受けていた可能性と、週末に採水したことによる「週末効果」が反映されていた可能性の、2通りの可能性が考えられた。

森林は全てのイオンと負の相関を示した (Table 1)。農地は  $\text{K}^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  と高い正の相関を示したが、秋期のデータでは  $\text{NO}_3^-$  以外関係性が認められなかった。都市開発域は  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  と正の相関があった。工業用地は秋期に  $\text{Na}^+$  と高い正の相関があったが、通年平均では、この相関は小さくなった。低層住宅地での平均水質は  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  と高い正の相関を示したが、高層住宅地では  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  と正の相関を示した。秋期においては宅地と  $\text{NO}_3^-$  との関係性を除いて土地利用との水質の関係性はみられなかった。平均水質は  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  が商業用地と高い相関を示し、秋期の水質は  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  が商業用地と高い関係性を示した。

水質濃度を変量にクラスター分析をした結果、水質は大きく 3 つの群に分かれ、各々の水質は卓越する土地利用と対応していた。水質データと土地利用を変量に因子分析を行った結果、農地と都市が河川水質を規定していることが示された。

表 1. 主要イオン濃度と土地利用特徴の関係 (値は r 値)。水質データは夏期、冬期、春期データの平均値である。また、太字は  $p \leq 0.05$  で高い相関を示す。

	EC	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	TMI
森林	<b>-0.67</b>	-0.37	<b>-0.66</b>	<b>-0.68</b>	<b>-0.85</b>	-0.30	-0.36	<b>-0.61</b>	<b>-0.73</b>	<b>-0.67</b>
農地	0.37	0.24	<b>0.52</b>	0.25	0.38	-0.04	<b>0.60</b>	<b>0.61</b>	0.36	0.36
造成地	0.22	0.07	0.09	0.37	<b>0.41</b>	0.15	-0.30	-0.05	0.39	0.25
工業用地	0.14	0.26	0.06	-0.12	-0.01	0.30	<b>-0.57</b>	-0.38	0.25	0.16
低層住宅	0.34	0.08	0.35	<b>0.48</b>	<b>0.54</b>	-0.01	<b>0.70</b>	<b>0.62</b>	0.29	0.32
高層住宅	<b>0.46</b>	0.35	<b>0.60</b>	0.32	<b>0.44</b>	0.36	0.26	0.35	0.37	<b>0.46</b>
商業用地	0.27	0.14	0.33	<b>0.41</b>	<b>0.48</b>	0.12	-0.03	0.31	<b>0.43</b>	0.33
公園	0.36	0.30	0.28	0.05	0.28	0.29	-0.02	0.09	0.31	0.32
その他	0.29	0.10	0.31	<b>0.44</b>	<b>0.42</b>	0.15	0.19	0.33	0.25	0.28

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APPENDIX

Water quality data

Sampling date: Aug. 1 and 2, 2006

ID	Site name	EC [ $\mu$ S/cm]	Temp. °C	pH	Na <sup>+</sup> [meq/l]	K <sup>+</sup> [meq/l]	Mg <sup>2+</sup> [meq/l]	Ca <sup>2+</sup> [meq/l]	Cl <sup>-</sup> [meq/l]	NO <sub>3</sub> <sup>-</sup> [meq/l]	SO <sub>4</sub> <sup>2-</sup> [meq/l]	HCO <sub>3</sub> <sup>-</sup> [meq/l]	TMI [meq/l]
1	Mita east	314.0	21.2	7.15	0.92	0.11	0.57	1.36	0.68	0.33	0.51	1.44	5.92
2	Mita west	364.0	22.5	7.22	1.31	0.14	0.56	1.29	0.90	0.44	0.54	1.50	6.68
3	Komagi upper	334.0	21.8	7.18	1.04	0.12	0.57	1.33	0.74	0.36	0.50	1.58	6.24
4	Komagi	336.0	22.0	7.25	1.01	0.11	0.61	1.47	0.75	0.29	0.56	1.65	6.45
5	Shim komagi	355.0	21.9	7.28	1.11	0.13	0.63	1.52	0.82	0.31	0.63	1.79	6.93
6	Shim komagi trib.	368.0	20.9	7.89	1.38	0.16	0.54	1.81	0.87	0.23	0.38	2.45	7.82
7	Shimbashi	355.0	22.0	7.42	1.14	0.13	0.64	1.56	0.82	0.28	0.60	2.03	7.20
8	Nishimae	489.0	22.2	7.59	2.59	0.11	0.65	1.46	0.80	0.55	1.69	2.13	9.98
9	Uchino	353.0	22.6	7.69	1.25	0.37	0.49	1.62	0.50	0.34	0.53	2.50	7.60
10	Takadabashi	365.0	23.1	7.52	1.22	0.14	0.68	1.69	0.76	0.26	0.73	2.27	7.75
11	Yanaka ue	251.0	20.5	7.45	0.70	0.04	0.66	0.86	0.54	0.55	0.38	0.94	4.67
12	Hanaka	364.0	21.5	7.75	0.77	0.08	0.95	2.05	0.49	0.32	0.53	2.66	7.85
13	Matsugasaki	372.0	23.6	8.34	1.13	0.12	0.73	1.83	0.82	0.26	0.72	2.39	8.01
14	Jigane hori	609.0	25.9	8.88	3.64	0.17	0.73	1.40	2.99	0.14	0.38	2.86	12.31
15	Kita kashiwa	479.0	24.6	7.42	2.15	0.15	0.79	1.72	1.69	0.24	0.62	2.66	10.03
16	Kashiwa furusato	386.0	20.5	7.39	0.99	0.07	0.94	1.96	0.82	0.31	0.52	2.24	7.85
17	Matsuba chuo	373.0	24.0	7.41	1.50	0.15	0.70	1.43	1.10	0.23	0.43	2.09	7.64
18	Kashiwa 7-chome	347.0	23.9	7.39	1.27	0.14	0.63	1.42	0.89	0.19	0.39	1.81	6.74
19	Okashiwa	321.0	24.0	7.66	1.15	0.12	0.60	1.37	0.83	0.13	0.36	1.77	6.34
20	Shorenji conflu.	379.0	23.0	6.91	1.55	0.09	0.63	1.39	1.65	0.05	0.22	1.92	7.51
21	Shorenji tributary	489.0	25.8	7.22	2.32	0.14	0.63	1.74	2.28	0.04	0.12	2.57	9.84
22	Shorenji main.	212.0	21.0	6.51	0.56	0.04	0.54	0.92	0.49	0.07	0.23	1.30	4.14
23	Kombukuro pond	142.3	20.5	5.77	0.39	0.01	0.47	0.46	0.27	0.07	0.31	0.69	2.67
24	Benten pond	84.5	17.8	5.71	0.30	0.00	0.24	0.17	0.33	0.10	0.06	0.24	1.44

Sampling date: Oct. 29 and 30, 2006

ID	Site name	EC [ $\mu$ S/cm]	Temp. °C	pH	Na <sup>+</sup> [meq/l]	K <sup>+</sup> [meq/l]	Mg <sup>2+</sup> [meq/l]	Ca <sup>2+</sup> [meq/l]	Cl <sup>-</sup> [meq/l]	NO <sub>3</sub> <sup>-</sup> [meq/l]	SO <sub>4</sub> <sup>2-</sup> [meq/l]	HCO <sub>3</sub> <sup>-</sup> [meq/l]	TMI [meq/l]
1	Mita east	250.0	18.5	7.04	0.54	0.06	0.52	1.31	0.39	0.26	0.50	1.24	4.83
2	Mita west	238.00	19.0	6.82	0.57	0.06	0.42	1.12	0.40	0.28	0.38	1.08	4.31
3	Komagi upper	250.00	18.7	7.14	0.56	0.06	0.51	1.27	0.40	0.26	0.48	1.25	4.80
4	Komagi	244.00	18.5	7.17	0.52	0.06	0.50	1.29	0.39	0.24	0.50	1.20	4.71
5	Shim komagi	250.30	19.5	6.61	0.47	0.07	0.53	1.39	0.36	0.24	0.50	1.15	4.71
6	Shim komagi trib.	308.0	19.5	6.87	0.83	0.06	0.66	1.42	0.52	0.26	0.67	1.48	5.90
7	Shimbashi	287.8	19.4	7.22	0.55	0.06	0.55	1.37	0.39	0.25	0.55	1.36	5.09
8	Nishimae	326.0	19.5	7.26	1.05	0.08	0.71	1.28	0.62	0.53	0.47	1.46	6.20
9	Uchino	261.0	19.2	7.59	0.42	0.05	0.57	1.54	0.31	0.32	0.46	1.42	5.08
10	Takadabashi	280.0	19.7	7.46	0.55	0.07	0.60	1.51	0.40	0.28	0.57	1.54	5.52
11	Yanaka ue	245.0	18.8	7.22	0.64	0.04	0.67	0.90	0.49	0.59	0.38	0.78	4.49
12	Hanaka	321.0	19.4	7.89	0.61	0.07	0.76	1.83	0.40	0.29	0.50	2.04	6.51
13	Matsugasaki	278.0	20.3	8.50	0.64	0.07	0.58	1.43	0.47	0.26	0.65	1.28	5.38
14	Jigane hori	344.0	20.1	7.66	0.86	0.10	0.77	1.70	0.62	0.25	0.59	1.88	6.78
15	Kita kashiwa	358.2	20.3	7.59	0.93	0.10	0.74	1.70	0.69	0.27	0.63	1.90	6.96
16	Kashiwa furusato	395.0	19.4	7.61	0.86	0.06	0.92	2.01	0.65	0.36	0.57	2.20	7.64
17	Matsuba chuo	347.0	19.7	7.57	0.98	0.10	0.73	1.63	0.72	0.23	0.58	1.85	6.81
18	Kashiwa 7-chome	350.0	19.5	7.43	0.98	0.11	0.66	1.59	0.73	0.18	0.56	1.85	6.67
19	Okashiwa	315.0	19.4	7.51	0.82	0.09	0.65	1.61	0.59	0.15	0.58	1.84	6.33
20	Shorenji conflu.	257.0	18.9	6.66	0.61	0.05	0.62	1.22	0.43	0.11	0.40	1.52	4.95
21	Shorenji tributary	394.0	18.6	6.65	1.05	0.12	0.81	2.12	0.54	0.05	0.59	2.78	8.07
22	Shorenji main.	192.9	17.9	6.67	0.46	0.03	0.53	0.84	0.39	0.13	0.28	1.06	3.73
23	Kombukuro pond	141.3	17.3	5.81	0.36	0.01	0.48	0.41	0.26	0.13	0.33	0.53	2.51
24	Benten pond	94.8	17.8	5.79	0.35	0.00	0.26	0.20	0.31	0.17	0.12	0.24	1.66

Sampling date: Jan. 19 and 20, 2007

ID	Site name	EC [ $\mu$ S/cm]	Temp. °C	pH	Na <sup>+</sup> [meq/l]	K <sup>+</sup> [meq/l]	Mg <sup>2+</sup> [meq/l]	Ca <sup>2+</sup> [meq/l]	Cl <sup>-</sup> [meq/l]	NO <sub>3</sub> <sup>-</sup> [meq/l]	SO <sub>4</sub> <sup>2-</sup> [meq/l]	HCO <sub>3</sub> <sup>-</sup> [meq/l]	TMI [meq/l]
1	Mita east	303.0	9.0	7.06	0.81	0.09	0.60	1.27	0.61	0.34	0.53	1.29	5.54
2	Mita west	361.0	10.8	6.93	1.21	0.12	0.60	1.24	0.87	0.54	0.56	1.42	6.55
3	Komagi upper	340.0	10.0	7.10	1.08	0.11	0.60	1.27	0.76	0.46	0.56	1.38	6.23
4	Komagi	327.0	9.6	7.17	0.89	0.09	0.64	1.37	0.69	0.39	0.57	1.36	5.99
5	Shim komagi	372.0	8.0	7.35	0.96	0.10	0.68	1.46	0.72	0.41	0.60	1.98	6.90
6	Shim komagi trib.	354.0	13.3	7.17	1.36	0.14	0.65	1.21	0.86	0.29	0.47	1.96	6.94
7	Shimbashi	342.0	8.5	7.50	0.94	0.10	0.65	1.38	0.73	0.39	0.62	1.67	6.49
8	Nishimae	376.0	13.7	7.33	1.70	0.13	0.64	1.10	0.81	0.59	0.47	1.98	7.42
9	Uchino	333.0	12.1	7.45	0.70	0.07	0.80	1.72	0.52	0.40	0.55	1.74	6.51
10	Takadabashi	349.0	9.4	7.49	0.94	0.09	0.68	1.50	0.69	0.37	0.66	1.57	6.51
11	Yanaka ue	355.0	11.8	7.23	1.08	0.12	0.68	1.23	0.81	0.85	0.51	1.25	6.53
12	Hanaka	367.0	11.4	7.75	0.79	0.08	0.99	1.95	0.53	0.37	0.55	2.27	7.52
13	Matsugasaki	284.0	10.9	8.44	0.76	0.08	0.57	1.33	0.59	0.28	0.68	1.14	5.43
14	Jigane hori	600.0	11.4	7.34	3.39	0.16	0.80	1.48	2.60	0.30	0.52	2.60	11.85
15	Kita kashiwa	500.2	8.5	7.40	2.11	0.15	0.88	1.74	1.77	0.32	0.69	2.18	9.83
16	Kashiwa furusato	375.0	11.5	7.20	0.95	0.07	0.93	1.90	0.75	0.32	0.59	2.10	7.60
17	Matsuba chuo	444.0	8.7	7.36	1.80	0.16	0.83	1.44	1.56	0.41	0.56	1.92	8.67
18	Kashiwa 7-chome	464.0	8.6	7.31	1.98	0.17	0.78	1.41	1.74	0.36	0.53	1.98	8.96
19	Okashiwa	340.0	7.8	7.57	1.13	0.11	0.68	1.42	0.89	0.23	0.44	1.80	6.70
20	Shorenji conflu.	253.0	7.9	6.67	0.72	0.06	0.60	1.06	0.57	0.11	0.33	1.50	4.95
21	Shorenji tributary	474.0	6.6	6.53	1.77	0.13	0.78	1.93	1.32	0.20	0.43	2.90	9.47
22	Shorenji main.	206.0	8.5	6.41	0.55	0.04	0.55	0.83	0.50	0.11	0.27	1.07	3.92
23	Kombukuro pond	143.7	7.4	5.75	0.35	0.01	0.51	0.42	0.27	0.12	0.36	0.54	2.57
24	Benten pond	91.0	12.5	5.71	0.33	0.01	0.27	0.20	0.34	0.14	0.10	0.22	1.59

Sampling date: April 30, 2007

ID	Site name	EC [μS/cm]	Temp. °C	pH	Na <sup>+</sup> [meq/l]	K <sup>+</sup> [meq/l]	Mg <sup>2+</sup> [meq/l]	Ca <sup>2+</sup> [meq/l]	Cl <sup>-</sup> [meq/l]	NO <sub>3</sub> <sup>-</sup> [meq/l]	SO <sub>4</sub> <sup>2-</sup> [meq/l]	HCO <sub>3</sub> <sup>-</sup> [meq/l]	TMI [meq/l]
1	Mita east	308.0	13.8	7.20	0.98	0.11	0.53	1.34	0.68	0.14	0.46	1.42	5.67
2	Mita west	393.0	16.8	7.17	1.58	0.17	0.51	1.28	1.00	0.11	0.49	1.80	6.94
3	Komagi upper	364.0	16.8	7.45	1.39	0.13	0.53	1.33	0.93	0.25	0.47	1.62	6.65
4	Komagi	343.0	17.2	7.40	1.09	0.13	0.57	1.43	0.81	0.14	0.51	1.44	6.11
5	Shim komagi	373.5	16.0	7.40	1.19	0.14	0.53	1.50	0.82	0.34	0.59	1.23	6.34
6	Shim komagi trib.	342.0	19.2	7.22	1.24	0.11	0.63	1.33	0.77	0.02	0.63	1.73	6.46
7	Shimbashi	314.0	17.2	7.41	1.10	0.11	0.52	1.32	0.80	0.18	0.65	1.02	5.71
8	Nishimae	387.0	17.7	7.49	2.07	0.11	0.50	1.07	0.79	0.26	0.49	1.99	7.30
9	Uchino	313.0	18.1	7.85	0.72	0.07	0.66	1.70	0.50	0.33	0.47	1.71	6.16
10	Takadabashi	332.0	17.5	7.50	1.09	0.10	0.56	1.52	0.76	0.24	0.69	1.38	6.35
11	Yanaka ue	301.0	17.6	7.53	1.03	0.09	0.57	0.93	0.68	0.31	0.42	1.36	5.38
12	Hanaka	337.0	16.8	7.97	0.85	0.08	0.80	1.74	0.53	0.27	0.44	2.06	6.77
13	Matsugasaki	286.0	20.1	9.33	0.92	0.09	0.47	1.32	0.70	0.20	0.67	1.13	5.50
14	Jigane hori	678.0	21.7	8.33	4.17	0.24	0.64	1.33	3.38	0.13	0.30	2.40	12.59
15	Kita kashiwa	504.5	20.7	7.70	2.28	0.18	0.76	1.74	1.99	0.19	0.63	2.07	9.84
16	Kashiwa furusato	370.0	15.2	7.48	0.95	0.07	0.89	1.90	0.67	0.24	0.57	2.12	7.39
17	Matsuba chuo	367.0	23.0	9.09	1.57	0.17	0.60	1.36	1.12	0.16	0.42	1.86	7.26
18	Kashiwa 7-chome	360.0	21.2	8.39	1.49	0.15	0.54	1.35	1.01	0.19	0.37	2.03	7.14
19	Okashiwa	358.0	22.1	8.57	1.39	0.14	0.53	1.38	0.97	0.08	0.37	2.00	6.85
20	Shorenji conflu.	273.0	18.7	7.49	0.78	0.05	0.56	1.27	0.69	0.05	0.35	1.48	5.23
21	Shorenji tributary	502.0	18.5	7.10	2.22	0.13	0.67	1.93	2.01	0.00	0.24	2.60	9.80
22	Shorenji main.	252.0	17.3	7.05	0.67	0.04	0.57	1.12	0.63	0.10	0.36	1.42	4.91
23	Kombukuro pond	142.8	17.5	6.07	0.33	0.01	0.50	0.48	0.23	0.09	0.33	0.58	2.56
24	Benten pond	82.2	14.1	4.66	0.30	0.00	0.23	0.16	0.31	0.10	0.07	0.22	1.40

**Land use data**

ID	Site name	Forest (%)	Farmland (%)	Developing (%)	Industrial (%)	Low-rise residential (%)	High-rise residential (%)	Commercial (%)	Park (%)	Others (%)
1	Mita east	15.28	12.36	16.94	3.58	17.35	1.26	4.47	11.69	17.07
2	Mita west	9.87	5.81	9.19	0.97	41.39	3.33	6.10	3.03	20.30
3	Komagi upper	13.13	9.75	13.85	2.54	26.94	2.09	5.12	8.24	18.36
4	Komagi	15.57	10.77	14.35	3.87	24.90	1.74	5.48	7.09	16.24
5	Shim komagi	18.35	12.69	14.06	3.56	23.03	1.43	5.14	6.65	15.09
6	Shim komagi trib.	8.88	18.47	13.24	25.00	9.21	0.01	15.75	0.41	9.03
7	Shimbashi	16.57	13.70	13.99	6.49	22.28	1.16	6.70	5.32	13.78
8	Nishimae	20.68	18.30	10.28	11.02	18.36	0.32	4.96	8.15	7.93
9	Uchino	7.43	16.73	9.92	0.82	33.39	4.92	8.66	1.58	16.56
10	Takadabashi	14.41	14.54	12.86	5.25	24.92	2.10	7.12	4.52	14.26
11	Yanaka ue	20.87	14.35	10.42	3.69	27.64	0.80	3.60	3.18	15.45
12	Hanaka	10.97	10.65	23.89	0.09	24.33	1.29	10.10	1.34	17.34
13	Matsugasaki	2.47	2.19	16.72	0.04	27.93	4.38	14.95	2.82	28.51
14	Jigane hori	15.46	9.28	14.61	8.89	16.94	3.81	8.70	4.38	17.93
15	Kita kashiwa	12.85	12.60	13.35	3.97	25.90	3.35	7.98	3.71	16.30
16	Kashiwa furusato	11.69	4.23	8.91	0.37	41.82	1.51	10.50	3.10	17.88
17	Matsuba chuo	18.46	9.12	13.68	9.06	12.88	3.24	9.99	5.56	18.01
18	Kashiwa 7-chome	28.92	6.39	15.56	11.51	4.78	0.44	5.87	7.60	18.93
19	Okashiwa	27.23	6.38	19.15	15.02	4.55	0.64	5.54	8.18	13.32
20	Shorenji conflu.	22.16	3.79	22.86	23.66	1.79	0.59	6.26	4.98	13.91
21	Shorenji tributary	4.99	4.64	17.16	29.05	12.12	1.18	4.66	12.79	13.40
22	Shorenji main.	35.55	6.95	20.00	9.86	1.63	0.44	5.93	6.41	13.23
23	Kombukuro pond	58.21	0.00	10.12	8.90	2.00	0.00	2.80	0.00	17.98
24	Benten pond	86.20	0.00	3.41	5.79	0.00	0.00	3.92	0.00	0.68

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Land use control on water chemistry of Ohori River, Chiba, Japan