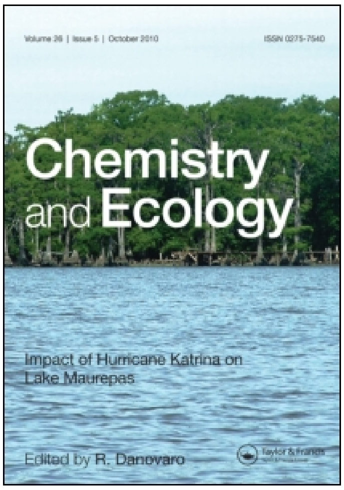

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Bahar, Md. Mezbaul and Yamamuro, Masumi(2008) 'Assessing the influence of watershed land use patterns on the major ion chemistry of river waters in the Shimousa Upland, Japan', Chemistry and Ecology, 24: 5, 341 — 355

To link to this Article: DOI: 10.1080/02757540802342291

URL: http://dx.doi.org/10.1080/02757540802342291

Chemistry and Ecology
Vol. 24, No. 5, October 2008, 341–355

Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

Assessing the influence of watershed land use patterns on the major ion chemistry of river waters in the Shimousa Upland, Japan

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(*Received 14 May 2008; final version received 14 July 2008*)

To assess the influence of land use pattern on the major ion chemistry of river water, seasonal changes in major ion concentrations were studied in the Shimousa Upland, Japan where urbanisation is still in progress. Water samples were collected from 24 sites from the Ohori River basin and analysed four times representing four seasons from August 2006 to April 2007 during baseflow or low flow conditions. The proportion of different land uses in the drainage area of each sampling site were estimated from a detailed digital land use map published by the Geographical Survey Institute of Japan by using Arcview/GIS. Electrical conductivity (EC) and the concentrations of Na^+, K^+, Cl^- and NO_3^- showed significant seasonal variation ($p \leq 0.05$). The correlation analysis results showed that forested areas had negative correlations with all ions. Farmland coverage was significantly associated with elevated levels of K^+, NO_3^- and SO_4^{2-} ($p \leq 0.05$). Urban land use appeared to have the greatest influence on the major ion chemistry. Residential areas showed significant positive correlations with K^+, Mg^{2+}, Ca^{2+}, NO_3^- and SO_4^{2-}, commercial areas with Mg^{2+}, Ca^{2+} and HCO_3^-, and urban developing areas with Ca^{2+} ($p \leq 0.05$). Cluster analysis (CA) on water quality parameters showed three different groups of similarity between the sampling sites and found them to be highly influenced by land use. It can be concluded that estimating the proportions of different land uses enables us to predict river water quality with respect to major ion concentrations.

Keywords: river water; major ion; land use; urbanisation; cluster analysis; GIS

1. Introduction

Rivers and their catchments are a very important part of our natural heritage. Rivers have been utilised by mankind over the centuries to the extent that very few, if any, are now in their natural condition [1]. River water chemistry is controlled by many natural and anthropogenic factors. These factors can either be spatially diffused or concentrated. Land use change is known to influence the biogeochemistry of watersheds [2–4]. 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

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ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540802342291
http://www.informaworld.com

increased [4–6]. Physical alteration of the landscape also occurs as a result of land use change, affecting the hydrogeologic dynamics of watersheds [7,8]. 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 watersheds and on 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 [9,10]. A focus at the watershed scale is possible due to the recent availability of GIS technology [4,11,12]. 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 [7,13].

The sampling of runoff and storm events is often used to examine the effects of land use on water quality [14,15]. Runoff is an important component of water quality investigations because runoff introduces sediment and mobilises chemical species directly off the landscape [14,15]. However, low or base flow in temperate streams is supplied predominately by shallow groundwater discharging to the stream channel [9,16]. Since shallow groundwater has moved through the landscape in the recent past, it provides a signal that is representative of surface geology, recent climate and land use [9,16]. Analytes associated with sediment may increase during storm events, while many solutes are most concentrated during base flow conditions [16]. 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.

While water quality has improved remarkably during the past decades, Japanese rivers are still heavily impacted by canalisation, loss of most dynamic flood plains, flow regulation, invasion by exotic species, and intensive urbanisation [17]. Sudden development of Japanese industry and the increasing standard of living are extending the amount of water usage as well as polluting 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 chemical processes on surface water. Deterioration in the water quality of rivers in the valleys dissecting the urbanised uplands in and around big cities like Tokyo is one of the serious environmental issues. In a study of this upland area [18], it was found that the basic water quality of spring water is formed in the process of groundwater flow through geology by dissolution 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 urbanisation have resulted in the degradation of the water quality of rivers. The sampling and analytical design of this study, using dissolved chemistry and dominant land use, allows for the quantification of the specific contributions of land use on surface water quality. The objective of this study was to assess the individual effects of land use on major ion chemistry and to identify the dominant land uses which control water chemistry.

2. 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 the Tokyo Metropolitan Area (Figure 1). There are two major rivers in the basin, the Ohori and the Jiganehori. The Ohori River begins at Aota-shinden, Kashiwa-city, Chiba-prefecture, passes through Nagareyama city and Kashiwa city and drains into Teganuma Lake. The river length is 6.9 km. The other river, the Jiganehori River, is 6 km long and originates from two natural ponds near Kashiwanoha park and drains into the Ohori River near the Yabatsuka

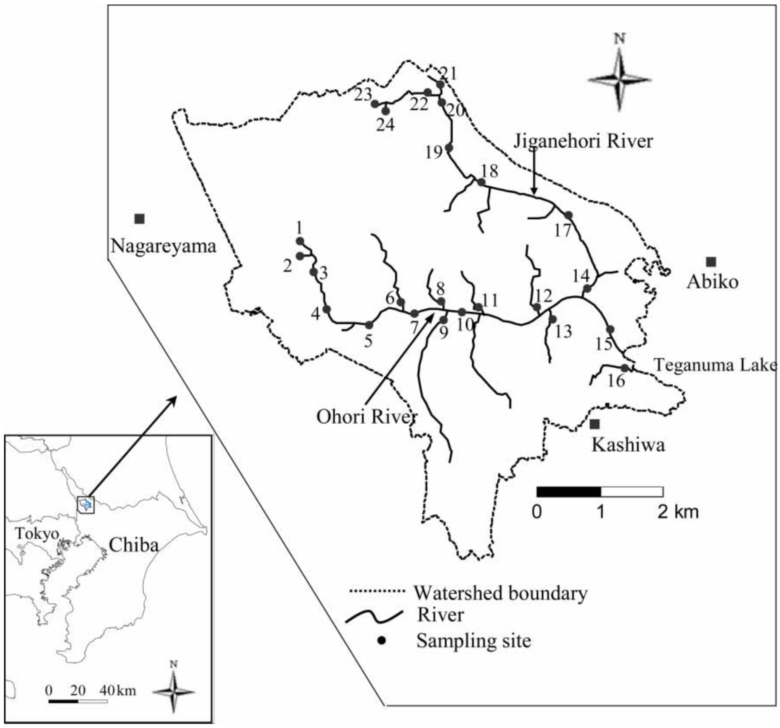

Figure 1. Study area and the location of sampling sites.

bridge. Many tributaries of the two rivers divide the upland in the basin. The total area of the drainage basin is 31 km^2. The urbanised ratio of this drainage basin at present is higher than 70% and it is a typical city river [19]. The mean annual temperature from 2001–2006 was 14.8 °C, the average for January is 3.7 °C (minimum) and for August 25.9 °C (maximum). The mean annual rainfall is 1461 mm, with minimum values in February and maximum values in August.

The landforms in the Ohori River basin consist of upland surfaces with an altitude of 15–30 m and alluvial lowland (2–9 m). 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. They are covered with volcanic ash layers with a maximum thickness of about 5 m. Five units define the geological setting of the site in descending order up to 43 m depth which is homogenous throughout the area: alluvial deposits, Kanto Loam, Joso Clay, the Kioroshi Formation and the Kamiiwashi Formation [20]. Quartz and plagioclase are the most abundant primary minerals throughout the layers. The 3 m thick Alluvial-floodplain-marine deposits formed during the Holocene period and the main sediments are gravel, sand, mud and peaty soils. After alluvial deposits all other formations were formed during the 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 m. Gravel, sand, mud, peaty soils and volcanic ash are the main sediments and quartz is the primary mineral. Clays of the Joso Formation occur beneath the Loam in the uplands. With a thickness of 3 m, the strata contain a high amount of plagioclase as the primary mineral. The Kioroshi Formation is underlain by an approximately 27 m thick layer, consisting of gravel, sand, mud and a fossil shell bearing mud. Both quartz and plagioclase are major in this formation with secondary minerals kaolinite, montmorrilonite and halloysite. Calcite and aragonite are found in the fossil shells. Sand is the major sediment of the Kamiiwashi Formation and is found beneath the Kioroshi Formation.

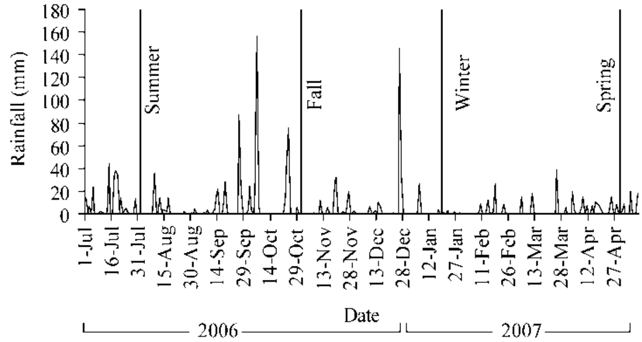

Figure 2. Sampling time and rainfall events.

3. Methods

3.1. *Water sampling and analytical methods*

Surface water grab samples were collected from 24 sites along the main river and tributaries (Figure 1) four times from August 2006 to April 2007 during low flow conditions, at least one week after a heavy rainfall event, if any (Figure 2). It is assumed that during low or base flow shallow ground water is the major source of water to the stream channel [16,21]. Base flow chemistry is desired as it represents the effects of regional characteristics and land use on stream quality. The sampling occasions were 1 and 2 August 2006 (summer), 29 and 30 October 2006 (fall), 19 and 20 January 2007 (winter) and 30 April 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 a 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 HCO_3^-, was quantified with a digital titrator (Hach) with 0.16 N HCl, and Bromcresol Green-Methyl Red as an indicator. One hundred millilitre water samples were collected separately at each sampling site into polyethylene bottles. The pre-washed bottles were rinsed with sample water three times 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 °C) until the analyses were completed. In the laboratory, the concentration of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and 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 HCO_3^-, measured in the field. The analytical data quality was ensured through careful standardisation, procedural blank measurements and duplicate samples.

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 images of watershed area and the drainage divides of sub-watersheds were collected from the city office. The divides of drainage basins were confirmed from contour maps and the raster images were digitised with the Ground Control Point technique using a 1:25,000 scaled topographic map. The resultant polygon data was then overlaid on the digital 10 m grid land use map published in 1994 by the Geographical Survey Institute of Japan, the latest officially published.

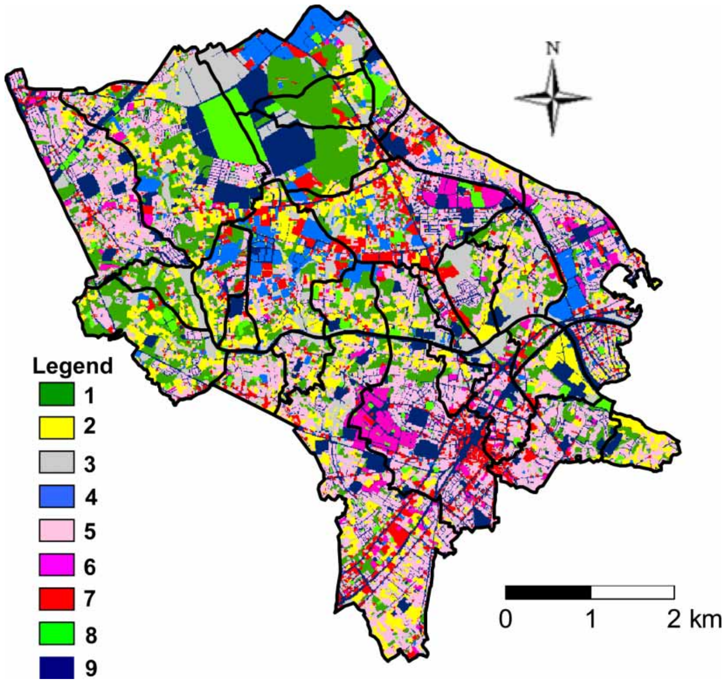

Figure 3. 1994 land use in the Ohori River basin. 1 = Forest, 2 = Farmland, 3 = Developing area, 4 = Industrial area, 5 = Low-rise residential, 6 = High-rise residential, 7 = Commercial area, 8 = Park, 9 = Others.

The total land use types in the original land use map produced by the Geographical Survey Institute of Japan included 15 which had been manipulated with similar characteristics and reduced to nine categories. Forest type includes all types of forest, farmland includes paddy fields and fields, 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 dense and tall buildings, commercial area includes all commercial and business centers, park is itself park area and others include roads, public facilities areas, and water bodies. The land use in the Ohori River basin is shown in Figure 3.

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 sourceshed of sampling sites, which was subsequently divided by the watershed area to derive the percentage of the watershed covered by each type. A sourceshed is defined as the total area that contributes to a selected drainage point or sampling site.

3.3. *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 $p > 0.05$ [22]. Analysis of variance (ANOVA) was used to determine whether there was a significant difference between seasonal concentrations at all sampling sites. Multiple comparisons among the seasonal means of each parameter were conducted using the 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 the 95% confidence level of the t-test and is classified as positive and negative according to the gradient of the regression relationship.

Multivariate statistics like cluster analysis (CA) were used to classify the water samples into different groups based on the relationships among them and later compared with the land use pattern. CA is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behaviour 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 [23]. Hierarchical CA was performed on the normalised 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 [24]. CA was applied to the water quality data set with a view to group the similar sampling sites.

4. Results

4.1. *Chemical characteristics*

The chemical composition of water in the Ohori River basin is variable with electrical conductivity ranging from 84.5 to 609 μS/cm in the summer; 94.5 to 395 μS/cm in the fall; 91 to 600 μS/cm in the winter and 82.2 to 678 μS/cm in the spring (Table 1). The highest EC value was measured at sampling station 21 in the fall and at 14 in the 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 μS/cm was always recorded at site 24 which is a spring and the headwater of the Jiganehori River. Ohori River water is moderately acidic to alkaline. The highest (9.33) and lowest (4.66) pH values were found during spring sampling.

There was no significant seasonal variation in the mean value of Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^-. The highest values of Mg^{2+} and HCO_3^- were recorded during winter, Ca^{2+} during fall and SO_4^{2-} during summer. Na^+ and Cl^- concentrations were highest during spring, reaching 4.17 and 3.38 meq/l respectively. Except Cl^- and NO_3^-, the lowest values of other ion concentration were recorded at site 24 in all seasons.

The chemical types of average (three seasons) water quality of each sampling point are plotted with hexadiagram (Figure 4). The water quality along the Ohori River mainstream is Ca-HCO_3 type except the most downstream point which is Na-HCO_3-Cl type. The concentration of ions increased in the downstream. The excess Na and Cl are added from the tributaries. The upper part of the Jiganehori River has Ca-HCO_3 type and it changes to Na-Cl-HCO_3 type. Tributaries have different water quality types like Na-Ca-HCO_3, Na-HCO_3, Na-Cl-HCO_3, Na-NO_3 and Ca-HCO_3. The water quality of 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 anthropogenic inputs are involved in controlling the chemical composition of the water in the Ohori River basin.

Significant correlations among water quality parameters suggest they have multiple sources (Table 2). Na^+ showed high correlation with K^+, Cl^- and HCO_3^-, K^+ with Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^-, Mg^{2+} with Ca^{2+} and HCO_3^-, Ca^{2+} with SO_4^{2-} and HCO_3^-, and NO_3^- with SO_4^{2-} indicating their common sources. There was significant correlation between TMI and all ions except NO_3^- and SO_4^{2-} which might have some specific sources.

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 1). EC and the concentrations of Na^+, K^+, Cl^-, NO_3^- and

Table 1. Seasonal averages, coefficient of variation [CV(%)], minima and maxima for water quality parameters. The mean values indicate the averages of all sites. 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	Mean [CV(%)]	Min–Max	Mean [CV(%)]	Min–Max	Mean [CV(%)]	Min–Max	p-value*	p-value**
EC (μS/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	0.050	0.979
Na^{+}(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	0.002	0.784
K^{+}(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	0.004	0.530
Mg^{2+}(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	0.083	0.042
Ca^{2+}(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	0.893	0.732
Cl^{-}(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	0.006	0.938
NO_3^{-}(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	<0.0001	<0.0001
SO_4^{2-}(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	0.835	0.703
HCO_3^{-}(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	0.083	0.223
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	0.043	0.686
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	0.183	0.180
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	<0.0001	<0.0001

*All seasons.**Three seasons (except fall). EC, Electrical conductivity, TMI, Total major ion.

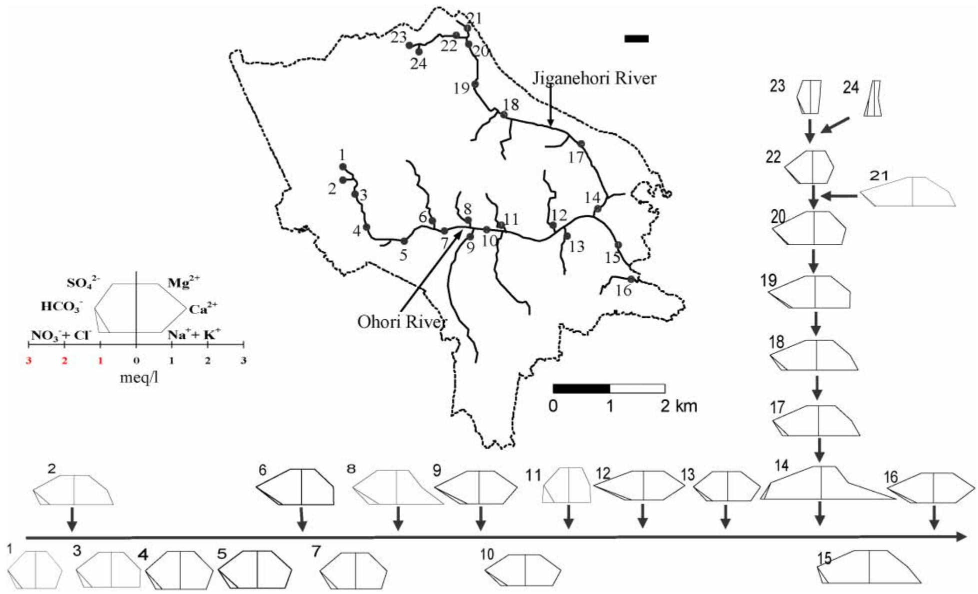

Figure 4. Hexadiagram of water quality on individual sampling point. The water quality data is the average of the summer, winter and spring seasons.

Table 2. Correlation matrix of water quality parameters.* The water quality data is the mean concentration of summer, winter and spring season ($n = 24$).

EC	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	TMI	
EC	1.00									
Na^+	**0.91**	1.00								
K^+	**0.84**	**0.74**	1.00							
Mg^{2+}	**0.66**	0.37	**0.43**	1.00						
Ca^{2+}	**0.71**	0.37	**0.63**	**0.84**	1.00					
Cl^-	**0.86**	**0.94**	**0.66**	0.37	0.36	1.00				
NO_3^-	0.20	0.05	0.30	0.24	0.23	−0.15	1.00			
SO_4^{2-}	0.39	0.21	**0.44**	0.39	**0.50**	−0.02	**0.64**	1.00		
HCO_3^-	**0.90**	**0.72**	**0.75**	**0.79**	**0.87**	**0.68**	0.09	0.36	1.00	
TMI	**0.99**	**0.89**	**0.83**	**0.69**	**0.74**	**0.84**	0.17	0.39	**0.94**	1.00

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

TMI showed significant seasonal variations ($p < 0.05$). Cl^- was highly variable among the sampling sites in the summer, winter and spring while NO_3^- was highly variable in the fall. Ca^{2+} and HCO_3^- did not vary significantly seasonally and there were tendency of higher values in the summer. Mg^{2+} and SO_4^{2-} also did not vary significantly over seasons and there were tendency of higher values in winter. pH did not vary significantly either among the sites or seasonally. Temperature varied significantly among seasons ($p < 0.001$) and there were less spatial variations.

Comparison of means of different seasons showed that the EC value in the fall was lower and significantly different from other seasons. Concentrations of Na^+ and Cl^- were about half what they were during the other three seasons. Due to having similarity, the water quality data of summer, winter and spring were again subjected to an ANOVA test to determine the variability. The results showed that only Mg^{2+}, NO_3^- and temperature had significant seasonal differences. As most of the parameters did not show significant differences among those three seasons therefore the data sets were divided into two. One is fall data itself and the average of the other three seasons for correlation analysis with land use variables.

4.3. *Land use characteristics*

According to the land use of 1994, approximately 61% of the Ohori River watershed was covered with urban land use. 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. 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.

4.4. *Land use-water quality relationship*

The correlation coefficients between ion concentrations (in milliequivalent unit) and land use characteristics (in percent) are shown in Tables 3 and 4. 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 development area was positively correlated with Ca^{2+} and HCO_3^-. The 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 the case of average water quality data and the fall data showed significant correlations with Ca^{2+} and SO_4^{2-}.

4.5. *Groupings of water quality*

Results of cluster analysis for the 24 water samples using their chemical components were illustrated with a tree dendrogram (Figure 5). The optimum number of clusters was identified based

Table 3. Correlation matrix of major ion concentrations and land use characteristics.* The water quality data is the mean concentration of summer, winter and spring seasons ($n = 24$).

	EC	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	TMI
Forest	**−0.67**	−0.37	**−0.66**	**−0.68**	**−0.85**	−0.30	−0.36	**−0.61**	**−0.73**	**−0.67**
Farmland	0.37	0.24	**0.52**	0.25	0.38	−0.04	**0.60**	**0.61**	0.36	0.36
Developing area	0.22	0.07	0.09	0.37	**0.41**	0.15	−0.30	−0.05	0.39	0.25
Industrial area	0.14	0.26	0.06	−0.12	−0.01	0.30	**−0.57**	−0.38	0.25	0.16
Low-rise residential area	0.34	0.08	0.35	**0.48**	**0.54**	−0.01	**0.70**	**0.62**	0.29	0.32
High-rise residential area	**0.46**	0.35	**0.60**	0.32	**0.44**	0.36	0.26	0.35	0.37	**0.46**
Commercial area	0.27	0.14	0.33	**0.41**	**0.48**	0.12	−0.03	0.31	**0.43**	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	**0.44**	**0.42**	0.15	0.19	0.33	0.25	0.28

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

Table 4. Correlation matrix of major ion concentrations (fall season data) and land use characteristics* ($n = 24$).

	EC	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	TMI
Forest	**−0.70**	**−0.40**	**−0.62**	**−0.56**	**−0.79**	−0.30	−0.26	**−0.77**	**−0.63**	**−0.69**
Farmland	0.28	0.16	0.22	0.21	0.27	0.09	**0.59**	0.36	0.11	0.25
Developing area	0.30	0.14	0.36	0.31	**0.41**	0.09	−0.38	0.32	**0.45**	0.35
Industrial area	0.23	**0.44**	0.27	0.24	0.13	0.24	**−0.46**	0.15	0.35	0.25
Low-rise residential area	0.29	−0.02	0.13	0.20	0.39	−0.01	**0.58**	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	**0.42**	0.27	0.23	0.38	**0.45**	0.29	0.07	**0.60**	0.34	**0.42**
Park	0.36	0.38	**0.54**	0.18	0.37	0.26	−0.18	0.26	**0.41**	0.37
Others	0.28	0.04	0.31	0.23	0.36	0.12	0.02	**0.45**	0.23	0.27

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

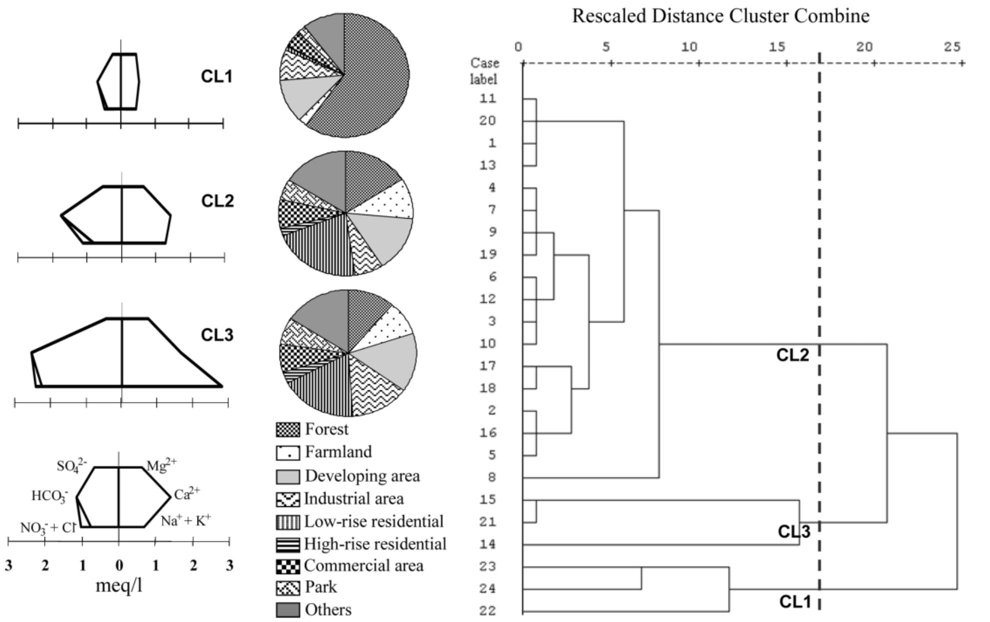

Figure 5. Dendrogram from cluster analysis, hexadiagram of each cluster of water quality and average land use patterns.

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 parameter 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 parameters of each clusters and their speciation with water quality description are presented in Table 5. Cluster 1 showed low concentrations of all chemical constituents among the clusters. The sampling sites under this group were upstream points of the Jiganehori River and two of them were springs. The average land use of these sites indicated that most of the watersheds were covered by forest and less urbanisation (Figure 5). Cluster 2

Table 5. Description and interpretation of cluster analysis.

Clusters	Sampling sites	Water quality parameters										Water quality description
		EC	TMI	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Cl^{-}	NO_3^{-}	SO_4^{2-}	HCO_3^{-}	
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_3^{-} and SO_4^{2-} 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_3^{-} at lowest range, SO_4^{2-} 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 $\mu S/cm$.

included most of the sampling sites and the water quality was characterised by high concentrations of NO_3^- and SO_4^{2-} and moderate concentrations of other parameters. More urbanised land use with less forest coverage characterised 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 the highest industrial area among clusters. The high EC in this cluster was due to the excess Na^+ and Cl^-concentrations. Sampling site 14 and 21 under this cluster had distinct industrial land use background in the watershed.

5. Discussion

Most seasonal variations in river water chemistry are driven by climatic and biotic factors and are therefore largely governed by processes occuring in the terrestrial part of the watershed [25]. In this study, water quality showed slight seasonal differences in concentrations 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 EC values resulted from the low concentration of Na^+ and Cl^- while other ion concentrations remained close to the value during other seasons value. Na^+ and Cl^- tend to vary with season and usually decline with increasing discharge [26]. Tributaries in the Ohori River basin have high EC compared to the value measured along the mainstream. Like many other major river studies [27–29], EC in the Ohori River basin increases from the headwaters to the river mouth. This is because the number of tributaries and the intensity of anthropogenic activity increases downstream.

The correlation analysis results of this study suggest that, using 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 sources (which later mix with the river and are diluted) as well as non-point source pollution that is commonly associated with urbanised 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 a positive correlation with Ca^{2+}, Mg^{2+} and NO_3^- was found [30]. Forests take up nutrients for their growth and function and in forested land use chemical weathering and throughfall are the available sources of ions. Na^+ and 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 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 concentrations of ions while some big industries do not. This point source nature of industrial land use might not result in good correlations. Na^+ and Cl^- likely come from domestic effluents, industries and roads. 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 [31].

In manure and commercial fertilisers, K^+ is an essential nutrient, while Ca^{2+} and Mg^{2+} are less important constituents [32]. The possible sources of K^+ are domestic effluents and fertilisers used in agricultural land and home gardens. Mg^{2+} and Ca^{2+} might come from salts in domestic wastewater, concrete structure and fertilisers used in agricultural land. Relatively small temporal and spatial variations of these ions also indicated their natural origin which resulted from weathering of carbonate and silicate minerals.

NO_3^- and SO_4^{2-} showed significant positive correlations with farmland and low-rise residential area. NO_3^--N and agricultural land use relationship has been frequently reported in previous studies [33–35]. It likely comes from fertilisers used on agricultural land and in home gardens, biological activity of plants and domestic effluents. Sources of SO_4^{2-} include sulfuric salts in domestic wastewater and fertiliser. Natural processes such as the chemical weathering of rocks and dissolution of atmospheric and soil CO_2 gas could be the mechanism which supplies HCO_3^- to surface and groundwater. In the present study HCO_3^- shows weak positive correlations with all land uses except forest. So, the potential anthropogenic sources of CO_2 are (a) CO_2 gas originating from municipal wastes and (b) CO_2 gas due to the oxidation organic materials leaked from sewage systems.

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 a big difference in the water quality of cluster 2 and cluster 3 but the land use was almost similar. The difference in water quality was due to industrial land use.

There was no evidence that the concentration of major ions 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 [36]. Many species from rivers that show a strong seasonal variation in discharge show synchronised reproduction at the onset of the rainy season [37–39], for instance due to a strong drop in conductivity [40,41]. The present results show that the conductivity as well as the concentration of some ions dropped during the 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 the rainy season. High concentrations of dissolved ions may also affect the speciation of toxic metals and the toxicity of these metals [36]. Complexation of metals by inorganic ligands such as CO_3^{2-} and Cl^- may strongly limit the bioavailability and toxicity of metals [42–44]. Cations such as Ca^{2+} and Mg^{2+} reduce the toxic effects of metals for fish by competition for metal binding sides at negatively charged fish gills [42,45]. Presence of excess nutrients like NO_3^- can cause health problems in infants and animals, as well as the eutrophication of water bodies [46]. Nitrate has been linked to agricultural activities due to the use of fertilisers. However, there are other nitrate sources related to urban development that can increase nitrate concentrations in river water.

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. It was found that 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 K^+, NO_3^- and SO_4^{2-} concentrations. Residential areas were associated with higher concentrations of K^+, Mg^{2+}, Ca^{2+}, NO_3^- and HCO_3^-, commercial areas with Mg^{2+}, Ca^{2+} and HCO_3^-, and urban developing areas with Ca^{2+}. Although weak positive correlations were found between the proportion of industrial area and Na^+ and Cl^-, their excess concentrations were found in the sampling sites near the industrial area. Water quality clusters were also found to be highly influenced by land use. It is becoming clear that there are distinctive and consistent patterns to the impacts of land use on water quality.

Future work to incorporate the effects of changing land use on water chemistry and to characterise the base flow chemistry of urban streams and to 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 in land use patterns in future, the levels of major ions will be changed accordingly. Hence future land development and management should be considered with care. With better land use planning, we may be able to curtail some of the water quality problems in future.

Acknowledgements

The authors would like to thank the Environment Section of Kashiwa City Hall, Chiba Prefecture, Japan for providing the drainage area map of the Ohori River and its tributaries. The authors are grateful to Dr Yasushi Agata for his help during field survey and GIS analysis. This study was carried out while M. M. Bahar was receiving a postgraduate scholarship from the ADB-Japan Scholarship Program.

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