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Article

Utilization of Ion-Exclusion Chromatography for Water Quality Monitoring in a Suburban River in Jakarta, Indonesia

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Abstract: We evaluated the use of ion-exclusion chromatographic systems for analyzing the behavior of inorganic ions (e.g., bicarbonate, sulfate, chloride, nitrate, phosphate, dissolved silicate, sodium, ammonium, potassium, magnesium, and calcium ions) in a suburban river located in Jakarta, Indonesia. Carbonate, phosphate, and silicate ion concentrations were determined using ion-exclusion chromatography (IEC) on a weakly acidic cation-exchange resin column (WCX) in the H^+-form with water eluent. Other ions were identified by ion-exclusion/cation-exchange chromatography (IEC/CEC) on a WCX column with tartaric acid eluent. The use of IEC systems for water quality monitoring was advantageous for the following reasons: (1) the concentrations of analyte ions, except NO_3^- and silicate ions, increased from upstream to downstream; and (2) the speciation of inorganic nitrogen ions could be analyzed by single injection into the IEC/CEC. The IEC

approach provided beneficial information for the construction of sewage treatment facilities in our study area. Results showed that (1) the analyte concentrations for samples obtained in the downstream area were higher than those in the upstream area owing to contamination by domestic sewage; (2) the concentrations of NO_3^- and NH_4^+ correlated with the concentration of dissolved oxygen; and (3) bicarbonate concentrations increased downstream, likely due to respiration of bacteria and dissolution of concrete under low-oxygen conditions.

Keywords: ion-exclusion chromatography; inorganic ions; microbial reaction; suburban river; water in developing countries

1. Introduction

Water pollution and the eutrophication of lakes, rivers, and oceans have been caused by the influx of wastewater associated with rapid economic development, agriculture, and industry [1,2]. In particular, the manifestations of water pollution in developing countries are remarkable. Therefore, adequate water quality monitoring is required to secure water resources in a sustainable way.

The present study focuses on the Ciliwung River (Figure 1) in Jakarta, Indonesia. This river has become severely polluted by increasing urban populations (*i.e.*, increasing organic components in human sewage) and in response to agricultural (e.g., through fertilizer and pesticide use in agricultural fields of rice, vegetables, and fruit) and industrial development (e.g., through introduction of organic components, several heavy metals, and other products produced by the food, beverage, textile, and rubber industries) [3–10]. Such pollution is conducive to eutrophication, which occurs owing to the non-treated water discharged from human sewage contaminated with inorganic and organic components and several ionic nutrients [8–10]. To determine the degree of eutrophication of the river and secure its water resources, a sewage treatment system that can adequately treat wastewater should be developed; however, the development of such a system has been delayed, owing primarily to financial limitations. Under such circumstances, the necessity of water quality monitoring and management policies in Jakarta, where water environment problems are particularly serious, has been recognized prior to constructing the sewage treatment system.

Our research group collaborated with the Japan International Cooperation Agency (JICA) to analyze the present water quality characteristics of the Ciliwung River using several ion chromatographic methods. These methods included the following: ion-exclusion chromatography (IEC) with water eluent for bicarbonate, IEC with post-column derivatization for phosphate, and simultaneous IEC/cation-exchange chromatography (CEC) for common anions and cations. We developed these methods in a series of previous studies and demonstrated their usefulness for the monitoring of several environmental waters in terms of eutrophication, acidification, and other similar processes [11–21]. Additionally, these methods have been accepted as official analytical methods (e.g., EPA, JIS) [22–26].

Figure 1. Photographs showing (**a**) a panoramic view of the Ciliwung River; (**b**) sampling of the river water; and (**c**) the filtration of sampled water.
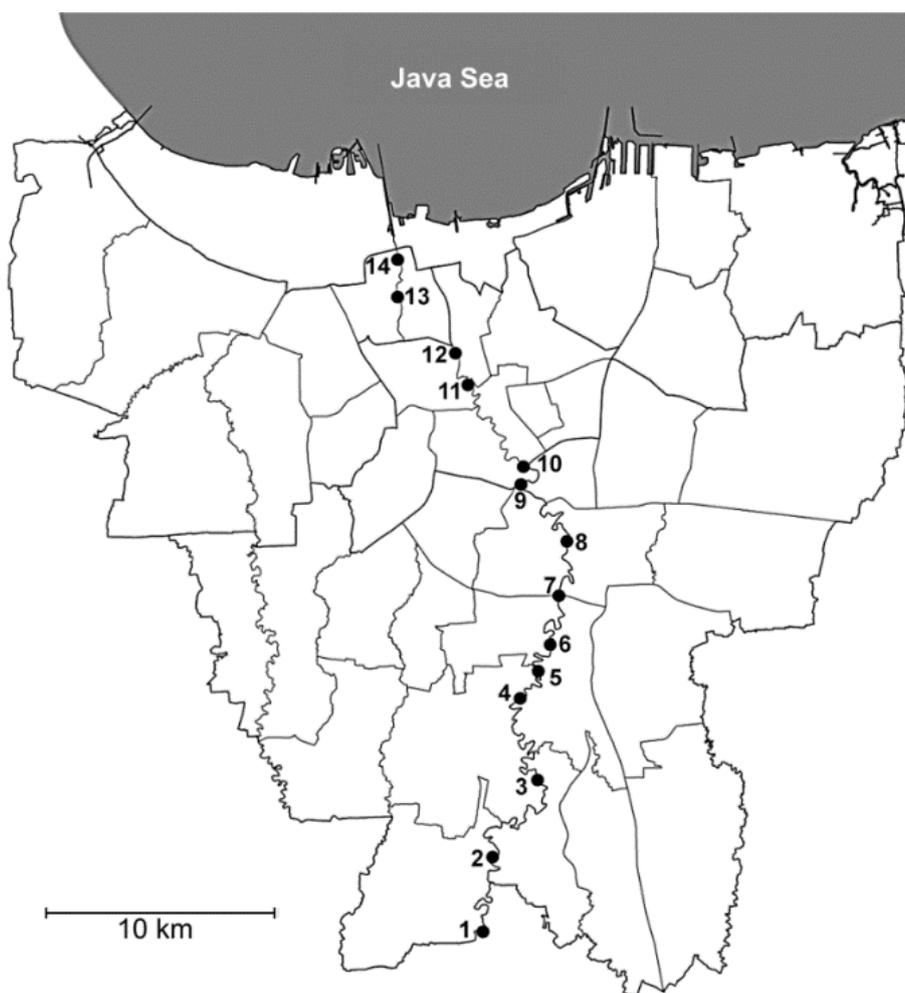

Here, we describe the following: (1) the behavior of the bicarbonate ion, which also demonstrates the alkalinity of water; (2) the behavior of SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}, which are indicators of water quality; (3) the influence of phosphate ($H_2PO_4^-$/HPO_4^{2-}) and silicate ions, which contribute to eutrophication; and (4) changes in the total quantity of ions in samples collected from the Ciliwung River. We also discuss the status of water pollution in the Ciliwung River, with specific reference to dissolve oxygen (DO), electrical conductivity (EC), and various biological reactions (e.g., aerobic oxidation, anaerobic decomposition, nitrification and denitrification reactions). Finally, we discuss the usefulness of the proposed IEC methods for analyzing ionic species for water quality monitoring.

2. Materials and Methods

2.1. Water Sampling in the Ciliwung River

The Ciliwung River flows through the 17 different blocks of Jakarta City, Indonesia. In the present study, river water samples were collected at 14 sites, with no samples collected in the coastal area (Figure 2), on 15 June 2010. Water samples were filtered through a membrane filter (pore size: 0.2 μm; DISMIC®-25$_{HP}$ PTFE, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) immediately following collection and then refrigerated at 4 ± 2 °C.

Figure 2. Sampling points along the Ciliwung River, Jakarta, Indonesia.

2.2. Reagents

All reagents used in this study were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), Pure water (18 MΩ·cm at 25 °C) obtained from a Sartorius Arium 611 reverse osmosis system was used for the dissolution and dilution of reagents. Stock solutions were prepared using the pure water. The standard solutions that were injected to the proposed ion chromatographic systems were prepared in the range 0.501–192 mg/L by diluting the stock solutions with pure water.

2.3. Ion-Exclusion Chromatography

2.3.1. Ion Chromatograph

We used a Tosoh IC-2001 ion chromatograph, which consisted of an eluent pump, sample injector, auto-sampler, column oven, and conductivity detector. We also used a Tosoh IC-WS work station for data analyses. In addition, the following chromatographic conditions and structures were used: (1) separation column; TSKgel Super IC–A/C packed with a polymethacrylate-supported weakly acidic cation-exchange resin in the H^+-form (150 mm × 6.0 mm i.d.; 4 μm-particle; and 0.2 meq./mL-capacity); (2) column temperature; 40 °C; and (3) injection volume; 30 μL.

2.3.2. IEC of Bicarbonate Ion

Bicarbonate ion concentrations in the river water samples were analyzed by IEC with water eluent. To sensitively detect the bicarbonate ion by IEC, a strongly acidic cation-exchange resin in the K^+-form (TSKgel SCX: 50 mm × 4.6 mm i.d.) was inserted as a conductimetric enhancement column between the separation column (TSKgel Super IC-A/C) and the conductivity detector. In practice, the calibration curve for carbonic acid (H_2CO_3) separated through weakly acidic cation-exchange resin column (WCX) in the H^+-form alone was nonlinear in the range 0.610–61.0 mg/L owing to the nature of conductometric detection for this weak electrolyte. Therefore, the bicarbonate ion was converted to a strong electrolyte (K_2CO_3) by the enhancement column [20]. Consequently, the use of the enhancement column allowed a linear relationship to be obtained over a wider concentration range (0.610–61.0 mg/L). The flow rate of the eluent was 0.5 mL/min. All other conditions are described in Section 2.3.1.

2.3.3. IEC/CEC of Inorganic Anions and Cations

Inorganic ions (*i.e.*, SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}) contained in the river water samples were analyzed using ICE/CEC. The optimized eluent used in this study was composed of a mixture of tartaric acid and 18-crown-6 [16–19]. The flow rate of the eluent was 0.6 mL/min. The separated ions were detected using a conductivity detector in the Tosoh IC-2001. All other experimental conditions are described in Section 2.3.1.

2.3.4. IEC-Post-Column Derivatization of Phosphate and Silicate Ions

Phosphate and silicate ions were analyzed by IEC with an all-automated post-column derivatization based on the molybdenum blue method to ensure high-sensitivity detection [13–15]. The coloring reagent and reducing agent for the separated phosphate and silicate ions were composed of 50 mM sulfuric acid plus 10 mM sodium molybdate, and 50 mM ascorbic acid, respectively. The reagent was transported to a reaction coil (Teflon tube, 600 mm × 0.25 mm i.d.) using a solution pump (Shimadzu LC-10AD) and mixed with the phosphate and silicate ions eluted from the separation column in automatic programmable flow. The reaction in the coil was performed at 40 °C. The detector used a Tosoh UV-8020 at a wavelength of 700 nm. The flow rates of the eluent and the reagent (using the post-column derivatization) were 1.0 mL/min and 0.5 mL/min, respectively. All other conditions are described in Section 2.3.1.

2.4. Analyses of Other Parameters

During the ion analyses using the IEC systems, we measured several parameters of the water samples relevant to water quality, including EC and DO. The EC values were determined using a Horiba conductivity meter (ES-12), while DO levels were determined by a HACH DO meter (HQ30d).
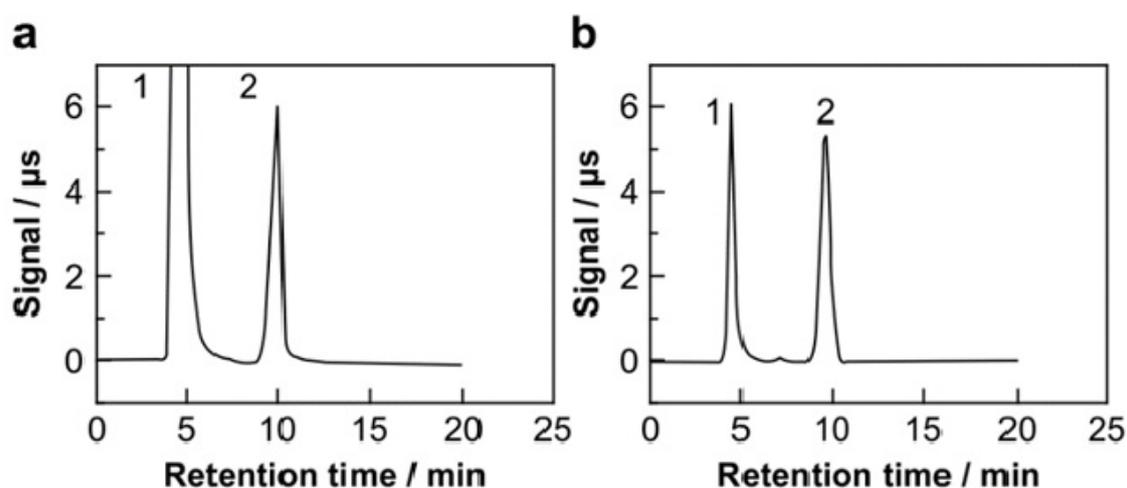
3. Results and Discussion

3.1. Analytical Performances of the IEC System

3.1.1. IEC for the Carbonate Ion

Bicarbonate ion concentration is an important indicator of alkalinity in river water and influences a variety of biological reactions [27,28]. The proposed IEC method can selectively separate and determine bicarbonate ion concentrations using a combination of WCX and water eluent; this is possible owing primarily to the complete penetration of the bicarbonate ion in the cation-exchange resin phase [15,20]. Furthermore, the connection of the enhancement column (TSKgel SCX in the K^+-form) allowed a wider concentration range to be obtained, because the post-column could convert from weak electrolyte (H_2CO_3) to strong electrolyte ($KHCO_3$). In the present study, we have demonstrated that IEC can successfully isolate the bicarbonate ion from salts of strong acids in approximately 10 min (Figure 3a). Figure 3b shows the ion chromatogram for the bicarbonate ion in a water sample collected from sampling point #6 in the Ciliwung River (Figure 2). The average concentration was found to be 83.0 mg/L, with maximum and minimum values of 164 mg/L (#14) and 40.9 mg/L (#2), respectively.

Figure 3. Ion-exclusion chromatogram of bicarbonate ion. Injected sample: (**a**) a mixture of 142 mg/L Na_2SO_4, 58.4 mg/L NaCl, 85.0 mg/L $NaNO_3$, and 84.0 mg/L $NaHCO_3$; and (**b**) river water sampled at point #6 in the Ciliwung River (Figure 2). Separation column: weakly acidic cation-exchange resin in the H^+-form, TSKgel Super IC-A/C (150 mm × 6.0 mm i.d.). Conductometric enhancement post-column: strongly acidic cation-exchange resin in the K^+-form, TSKgel SCX (50 mm × 4.6 mm i.d.). Eluent: pure water. Column temperature: 40 °C. Flow rate: 0.5 mL/min. Injection volume: 30 μL. Detector: conductivity. Peaks: 1 = strong acidic anions (SO_4^{2-}, Cl^-, and NO_3^-) and 2 = bicarbonate ion.

As summarized in Table 1, the calibration curves of the bicarbonate ion was found to be linear in the range 0.610–61.0 mg/L, with a correlation coefficient (r^2) of 0.9990. Moreover, the detection limit (S/N = 3) and RSD value (*n* = 10) in the peak area of the bicarbonate ion were found to be 31.1 μg/L and 0.5%, respectively.

Table 1. Analytical performances of three different IEC methods.

Analyte	Lineality range (mg/L)	Correlation coefficient	Detection limits (mg/L) *	Relative standard deviation (%)	Methodology
Sulfate ion	9.60–192	0.9993	0.874	0.330	
Chloride ion	3.55–70.9	0.9999	0.138	0.240	
Nitrate ion	6.20–124	0.9958	0.211	0.210	
Sodium ion	2.30–46.0	0.9999	0.177	0.400	IEC/CEC for common
Ammonium ion	1.80–18.0	0.9999	0.126	0.420	inorganic ions
Potassium ion	3.91–39.1	0.9928	0.403	0.620	
Magnesium ion	2.43–24.3	0.9995	0.102	0.250	
Calcium ion	4.01–40.1	0.9962	0.289	0.430	
Bicarbonate ion	0.610–6.10	0.9990	0.0311	0.500	IEC for bicarbonate ion
Phosphate ion	0.501–9.91	0.9900	0.0681	0.360	IEC for phosphate and
Silicate ion	0.510–10.1	0.9999	0.0955	1.10	silicate ions

Note: * signal-to-noise ratio of 3.

3.1.2. Simultaneous IEC/CEC for Common Inorganic Ions

In the present study, we used IEC/CEC to simultaneously determine all major ionic compounds. IEC/CEC measured the speciation of inorganic nitrogen compounds (*i.e.*, NH_4^+ and NO_3^-) in water, which are important indicators of river eutrophication [1,29]. IEC/CEC is able to separate anions, based on ion-exclusion/penetration effects in the WCX phase, and cations, based on the cation-exchange effect by the functional groups (carboxylate groups) in the column.
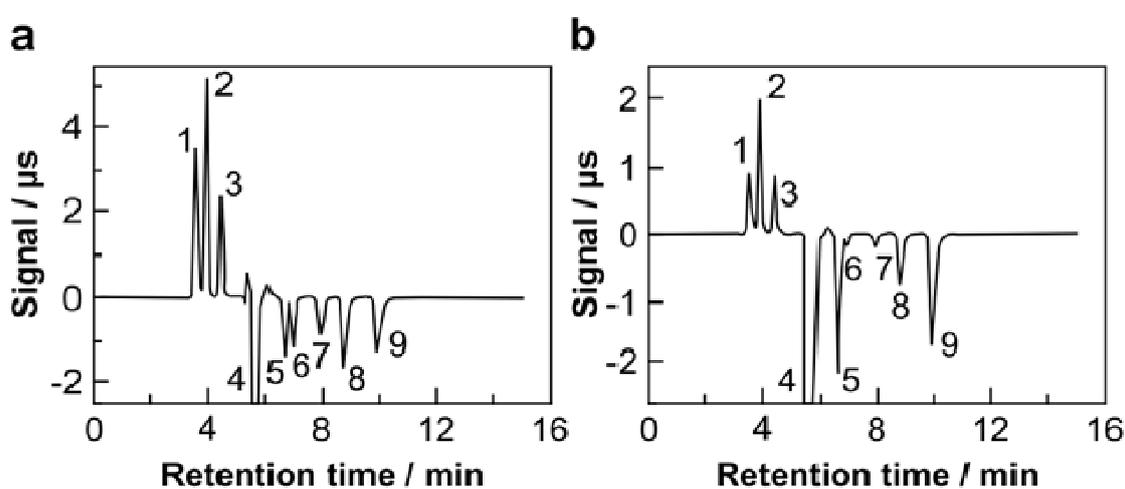
The concentration of tartaric acid affects the retention behavior of both anions and cations. For example, when increasing tartaric acid in the eluent, the retention times of anions increase owing to enhancement of the penetration effect for the weakly acidic cation-exchange resin phase; conversely, the retention times of cations decrease owing to the reduction of cation-exchange adsorption to the resin phase. In the latter case, the well-resolved separation of analyte ions (except NH_4^+ and K^+) was obtained by adding 15 mM tartaric acid in the elution. Next, in order to improve the resolution of NH_4^+ and K^+, we added 18-crown-6. The resolution was improved to various degrees, depending on the concentration of 18-crown-6 added to the eluent. Because K^+ was strongly bound to 18-crown-6 and the resulting complex was adsorbed to the resin phase, the retention time of K^+ was separated from that of NH_4^+ [16–19]. Consequently, the optimal elution was a mixture of 15 mM tartaric acid and 2.5 mM 18-crown-6. As shown in Figure 4a, the complete separation of the analyte anions and cations was obtained in approximately 10 min.

As summarized in Table 1, the calibration curves of the analytes were linear in each concentration range, and the correlation coefficients (r^2) were 0.9928–0.9999. Moreover, the detection limits (S/N = 3) and the RSD values in the peak areas of the analyte ions were 0.102–0.874 mg/L and 0.21%–0.62%, respectively.

Figure 4b shows the ion chromatogram for the anions and cations contained in the river water samples collected at sampling point #6 in the Ciliwung River. Based on IEC/CEC, the ion concentrations sampled at 14 points were found to be in the ranges 5.57–23.1 mg/L (SO_4^{2-}), 5.60–69.5 mg/L (Cl^-),

2.29–8.99 mg/L (NO_3^-), 6.44–59.5 mg/L (Na^+), 0.216–11.1 mg/L (NH_4^+), 2.27–6.92 mg/L (K^+), 3.82–9.92 mg/L (Mg^{2+}), and 22.6–52.5 mg/L (Ca^{2+}).

Figure 4. Ion-exclusion/cation-exchange chromatogram of inorganic anions and cations. Injected sample: (**a**) a mixture of 120 mg/L $MgSO_4$, 74.6 mg/L KCl, 85.0 mg/L $NaNO_3$, 53.5 mg/L NH_4Cl, and 101 mg/L KNO_3; and (**b**) river water sampled at point #6 in the Ciliwung River (Figure 2). Separation column: weakly acidic cation-exchange resin in the H^+-form, TSKgel Super IC-A/C (150 mm × 6.0 mm i.d.). Eluent: 15 mM tartaric acid and 2.5 mM 18-crown-6 ether. Column temperature: 40 °C. Flow rate: 1.0 mL/min. Injection volume: 30 μL. Detector: conductivity. Peaks: 1 = SO_4^{2-}, 2 = Cl^-, 3 = NO_3^-, 4 = elution dip, 5 = Na^+, 6 = NH_4^+, 7 = K^+, 8 = Mg^{2+}, and 9 = Ca^{2+}.

3.1.3. IEC for Phosphate and Silicate Ions

Phosphorus (*i.e.*, the phosphate ion in the aqueous phase) is a limiting factor related to eutrophication, in conjunction with nitrogen. Generally, the total concentration of phosphorus in environmental water is one to two orders of magnitude lower than that of total nitrogen [30–33], and eutrophication can be caused by even lower concentrations of the phosphate ion. Therefore, highly sensitive detection methods are needed to determine phosphate ion concentration. In practice, when injecting the river water samples into ICE/CEC (described in Section 3.1.2), the phosphate ion could not be detected for all river samples owing to its much lower concentrations compared to other common ions.
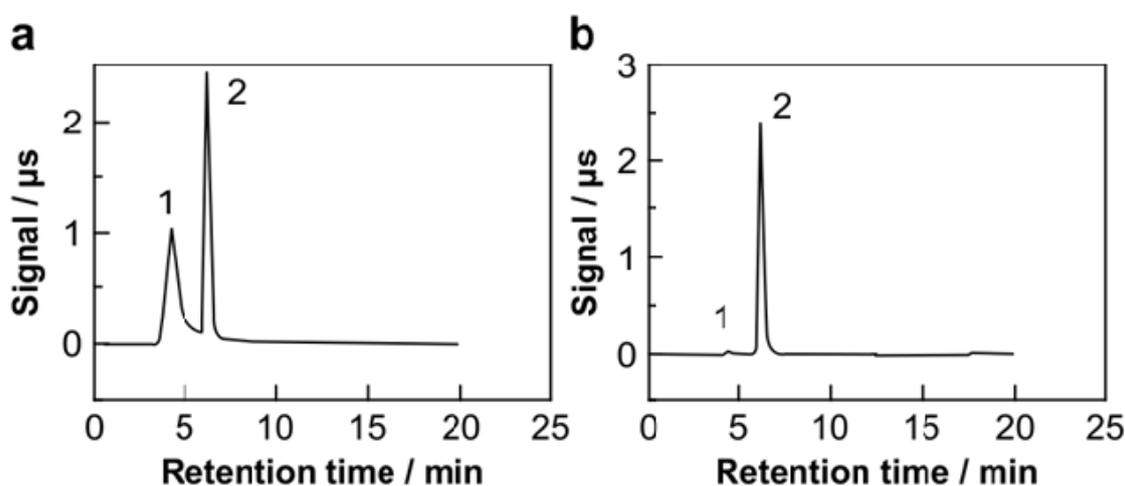
We introduced the post-column derivatization method, which applied the molybdenum blue method for detecting the phosphate ion after IEC with water eluent [14,15]. IEC-post-column derivatization could simultaneously detect phosphate and silicate ions at 700 nm (Figure 5a).

As summarized in Table 1, the calibration curves for both phosphate and silicate ions were linear in each concentration range, with correlation coefficients (r^2) of 0.9900 and 0.9999 for phosphate and silicate ions, respectively. Moreover, the detection limits (S/N = 3) were 0.0681 mg/L and 0.0955 mg/L and the RSDs in the peak areas were 0.36% and 1.1% for phosphate and silicate ions, respectively.

Figure 5b presents the ion chromatogram of the phosphate and dissolved silicate ions contained in the river water samples collected at sampling point #6 in the Ciliwung River. Based on IEC, the ion

concentrations sampled at 14 points were found to be in the ranges of 0.0681–0.681 mg/L (phosphate) and 3.46–12.1 mg/L (dissolved silicate ion).
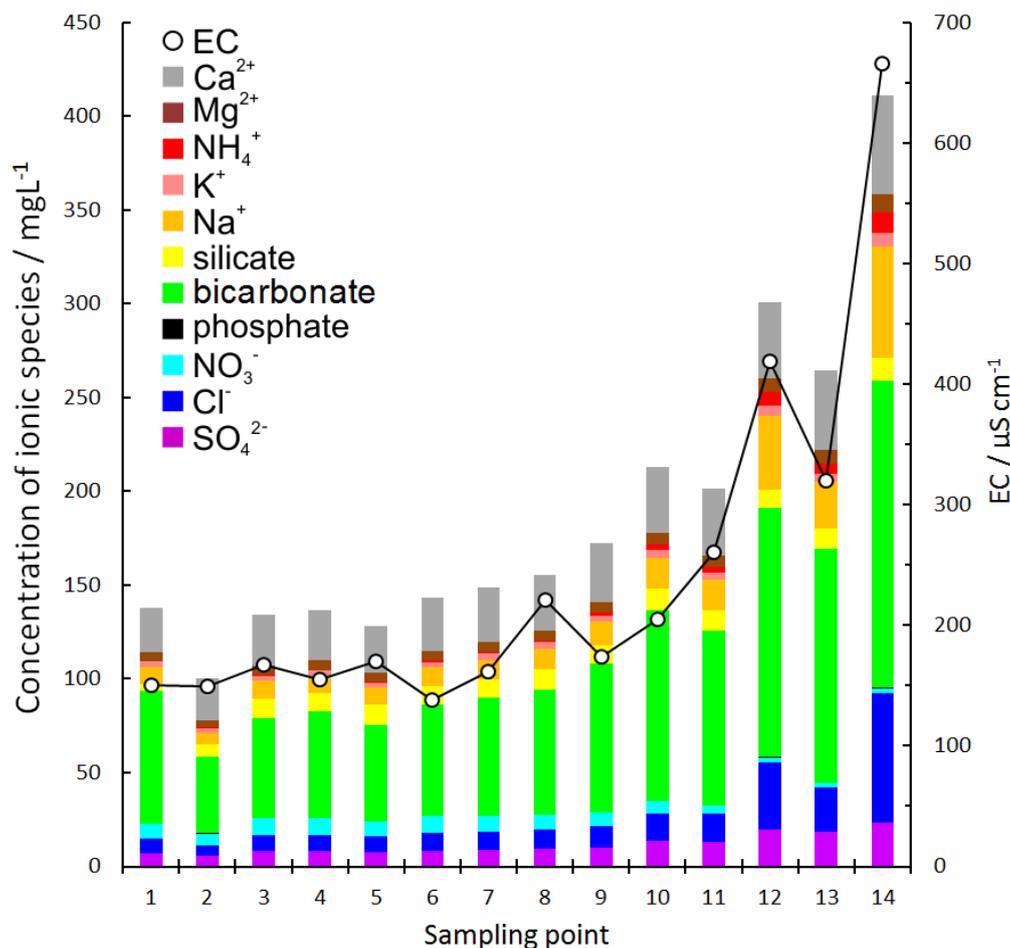
Figure 5. Ion-exclusion chromatogram of phosphate and silicate ions. Injected sample: (**a**) a mixture of 47.6 mg/L KH_2PO_4 and 39.1 mg/L Na_2SiO_3; and (**b**) river water sampled at point #6 in the Ciliwung River (Figure 2). Separation column: weakly acidic cation-exchange resin in the H^+-form, TSKgel Super IC-A/C (150 mm × 6.0 mm i.d.). Eluent: pure water. Coloring reagent: a mixture of 50 mM sulfuric acid and 10 mM sodium molybdate. Reducing agent: 50 mM ascorbic acid. Column temperature: 40 °C. Flow rate: 1.0 mL/min (eluent) and 0.5 mL/min (coloring reagent). Injection volume: 30 μL. Detector: visible at 700 nm. Peaks: 1 = phosphate ion and 2 = silicate ion.

3.2. Transition of Ionic Composition in the Ciliwung River

In this section, we discuss the transition of ionic composition in river water samples collected at 14 points along the Ciliwung River (Figure 2). Figure 6 shows the classifications of the ion concentrations obtained through the three types of IEC systems. The concentrations of analyte ions, with the exception of NO_3^- and silicate ions, increased from upstream to downstream. Moreover, EC values changed from 150 to 666 μs/cm, which is a parameter of total ionic species in a water sample and also increased from sampling points #1 to #14 (Figure 6). The average concentrations were as follows (from highest to lowest): bicarbonate ion (83.0 mg/L) > Cl^- (17.0 mg/L) > SO_4^{2-} (11.5 mg/L) > dissolved silicate (9.55 mg/L) > NO_3^- (6.20 mg/L) > phosphate (0.155 mg/L) for the anionic components, and Ca^{2+} (32.1 mg/L) > Na^+ (17.5 mg/L) > Mg^{2+} (5.83 mg/L) > K^+ (3.52 mg/L) > NH_4^+ (2.52 mg/L) for the cationic components. Conversely, the average concentrations of the most abundant ions found in samples of unpolluted river water worldwide are as follows: bicarbonate ion (56.1 mg/L) > SO_4^{2-} (10.6 mg/L) > Cl^- (8.13 mg/L) > NO_3^- (0.869 mg/L) for the anionic components, and Ca^{2+} (15.2 mg/L) > Na^+ (6.90 mg/L) > Mg^{2+} (3.89 mg/L) > K^+ (2.11 mg/L) for the cationic components [34–36]. Based on these data, it is clear that the concentrations of the bicarbonate ion, Cl^-, NO_3^-, NH_4^+, the phosphate ion, and the silicate ion in the Ciliwung River are higher than the global average values for these ions.

Figure 6. Changes in ionic components and electrical conductivity (EC) in river water samples between sampling points.
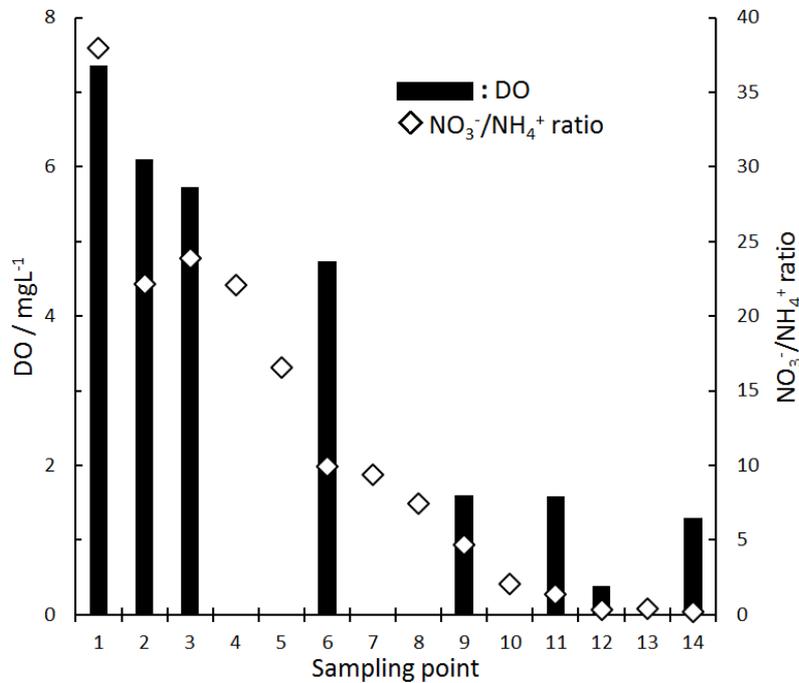

In the eutrophicated river water, the high concentration of the bicarbonate ion may have been derived from organic compounds in human sewage and related to photosynthesis, respiration, and other biological and non-biological reactions and exchanges with the atmosphere; such processes can create a buffering effect. Bicarbonate ion concentrations may also reflect some contribution from the dissolution of concrete under low DO concentrations. In contrast, the concentration of Cl^- was likely derived primarily from human sewage, raw sewage, and sea water.

The concentrations of NO_3^- and NH_4^+ decreased and increased, respectively, between sampling points #1 to #14. We also observed a strong relationship between DO and the concentration ratio of NO_3^- to NH_4^+ at each sampling point (Figure 7). These results suggest that the water at sampling points #7 to #14 was altered to form a reducing environment.

The concentration of the phosphate ion increased between sampling points #1 and #14, likely owing to organic phosphorus compounds in components such as human sewage and raw sewage, among others. Conversely, the concentration of the silicate ion remained relatively constant between sampling points. This can likely be attributed to the fact that the ion originated from natural sources (e.g., soil or sediment) within the research area and not from domestic wastewater. However, further investigation of this result will be required in future research.

Figure 7. Changes in NO_3^-/NH_4^+ ratios and dissolved oxygen (DO) [1] in the river water samples taken from each sampling point.[1]: Following data collection, DO concentrations were available for only 8 of the 14 sampling points, because the cable of the DO meter used was 5 m long; thus, the meter could not be used at sampling points with depths shallower than 5 m.
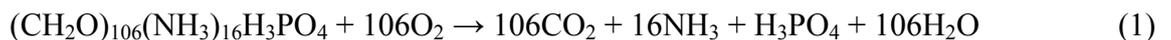

3.3. Changes in the Ionic Concentrations for Various Biological and Chemical Reactions

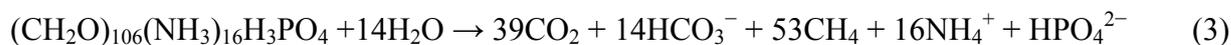3.3.1. Inorganic Nitrogen Species and DO

In reference to the eutrophication of the Ciliwung River, we discuss the influences of inorganic nitrogen and carbonate ions on DO based on biological reactions, because these parameters are closely related to eutrophication in closed aquatic environments. We focused on the differences between NO_3^- and NH_4^+ concentrations between sampling points #1 to #6 and #7 to #14.

Between sampling points #1 to #6, DO concentrations decreased from 7.36 mg/L (#1) to 4.73 mg/L (#6). Water quality in this area was in a relatively aerobic state. Such aerobic conditions have been predicted to cause aerobic oxidation of organic nitrogen and phosphorus compounds by microorganisms (Equation (1)) and a nitrification reaction by nitrifying bacteria (Equation (2)) [37–39].

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 106O_2 \rightarrow 106CO_2 + 16NH_3 + H_3PO_4 + 106H_2O \qquad (1)$$

$$NH_4^+ + 1.83O_2 + 1.98HCO_3^- \rightarrow 0.0210C_5H_7NO_2 + 0.979NO_3^- + 1.04H_2O + 1.88H_2CO_3 \qquad (2)$$

The organic nitrogen and phosphorus compounds in the river water were decomposed to NH_3, and NH_3 was dissolved as the ionic form (NH_4^+) in the aqueous solution. DO was converted to dissolved CO_2 (bicarbonate ion). In contrast, NH_4^+ was oxidized to NO_3^- through nitrification, and HCO_3^- was converted to H_2CO_3 ($H_2O + CO_2$). Accordingly, NO_3^- concentrations at sampling points #1 to #6 were slightly higher than NH_4^+ concentrations.
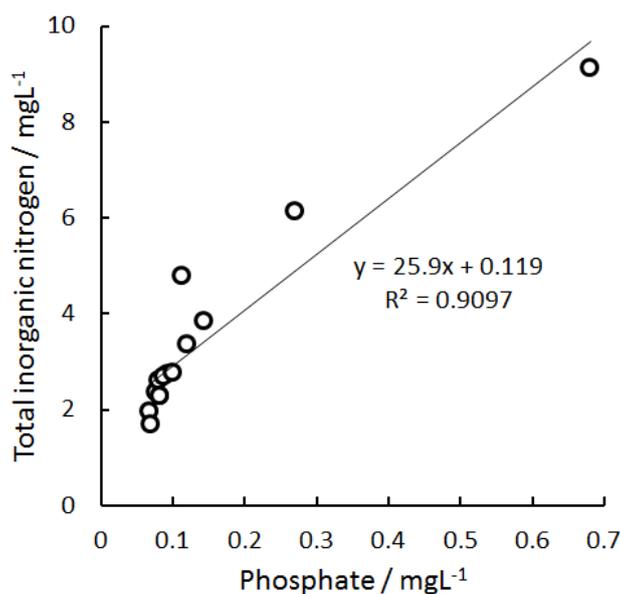
Between sample points #7 and #14, DO concentrations further decreased from 1.60 mg/L (#7) to 0.39 mg/L (#13). This likely caused the decomposition of organic nitrogen compounds by microorganisms (Equation (3)) and a denitrification reaction by denitrifying bacteria (Equation (4)) under low-DO conditions [40–42].

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 14H_2O \rightarrow 39CO_2 + 14HCO_3^- + 53CH_4 + 16NH_4^+ + HPO_4^{2-} \quad (3)$$

$$NO_3^- + 1.08\ CH_3OH + 0.24\ H_2CO_3 \rightarrow 0.056\ C_5H_7O_2N + 0.47\ N_2\uparrow + 1.68H_2O + HCO_3^- \quad (4)$$

The organic nitrogen and phosphorus compounds in the river water were decomposed to NH_4^+. In addition, this decomposition generated gases, such as CO_2 and CH_4. NO_3^- was also reduced to N_2 gas through denitrification at the same moment that HCO_3^- was produced. Therefore, at lower DO conditions, the formation of NH_4^+ and HCO_3^- and the reduction of NO_3^- occurred simultaneously. These reactions were likely caused by the inflow of domestic wastewater. In addition, because of the eutrophication of the estuary, the pollution of seawater as well as river water is expected.

The concentrations of the phosphate ion (0.0619–0.681 mg/L) determined by IEC-post-column derivatization were much lower than those of common analyte ions, but the concentrations of phosphate and other ions increased from sampling points #1 to #14. The increase of phosphate ion concentration was caused by the draining of synthetic detergents and household wastewater into the river water. Furthermore, as shown in Figure 8, the concentration of phosphorus was related to the concentration of total nitrogen ($NO_3^- + NH_4^+$) ($r^2 = 0.9097$). Therefore, the phosphate ion was likely related to the formation of NO_3^- under aerobic conditions (Equation (1)) and the formation of NH_4^+ under low-DO conditions (Equation (3)) [37,40].

Figure 8. Relationship between total inorganic nitrogen ($NO_3^- + NH_4^+$) and the phosphate ion in river water samples.
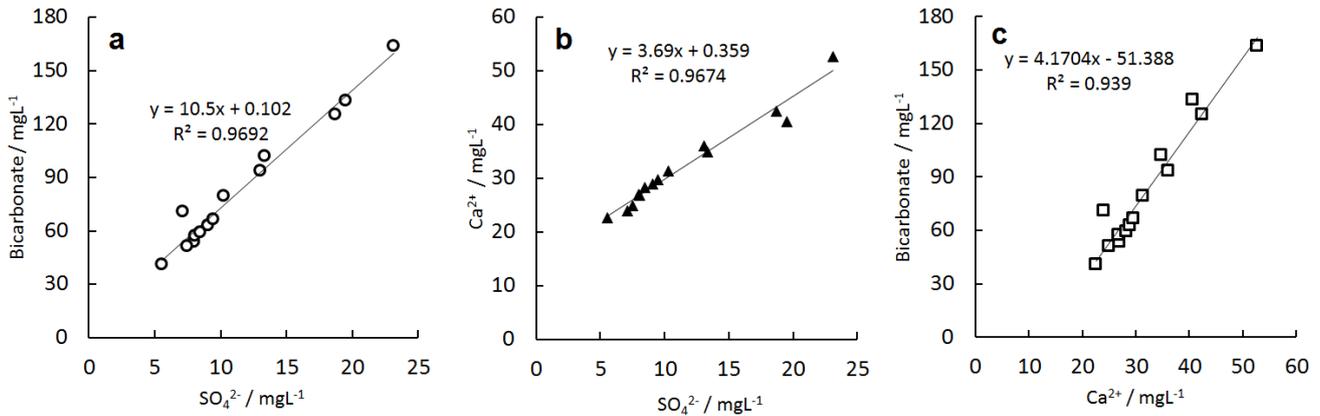

3.3.3. Bicarbonate, Sulfate, and Calcium Ions

When we investigated the correlations between all ion species obtained from the IEC systems, we found strong correlations between the bicarbonate ion, SO_4^{2-}, and Ca^{2+}. As shown in Figure 9, the

correlation coefficients (r^2) were 0.9692 for both bicarbonate and SO_4^{2-} (Figure 9a), 0.9674 for Ca^{2+} and SO_4^{2-} (Figure 9b), and 0.9390 for bicarbonate and Ca^{2+} (Figure 9c).

Figure 9. Relationship between SO_4^{2-}, bicarbonate, and Ca^{2+} ions in river water samples: (**a**) bicarbonate *vs.* SO_4^{2-}; (**b**) Ca^{2+} *vs.* SO_4^{2-}; and (**c**) bicarbonate *vs.* Ca^{2+}.

These results relate to SO_4^{2-} levels contained in urban sewage, detergents, and human waste. SO_4^{2-} is also generated from the decomposition of organic sulfur compounds by sulfur-oxidizing and sulfate-reducing bacteria. During the decomposition process, the bicarbonate ion was also generated through the reduction process that occurs in the following reaction (Equation (5)) [43,44]:

$$SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + H_2S\uparrow \tag{5}$$

Additionally, the strong correlation between Ca^{2+} and SO_4^{2-} can likely be attributed to the fact that SO_4^{2-} converted from H_2S by sulfur-oxidizing bacteria reacted with calcium hydroxide ($Ca(OH)_2$) leached from concrete, thus forming $CaSO_4$. The free Ca^{2+} and the bicarbonate ion in the water solutions generated insoluble $CaCO_3$. When Ca^{2+} concentration is higher than that of other analyte cations, the deterioration of concrete supports in the drainage system may occur.

4. Conclusions

In the present study, water quality in the Ciliwung River basin, which is affected by typical influxes of domestic wastewater, was analyzed by three advanced IEC modes. Our results indicate the severe eutrophication state of the river water, including increases in ammonium and phosphate ion, and the deterioration of the drainage system's concrete with elution of Ca^{2+} and SO_4^{2-} in the downstream region.

Accordingly, the construction of a sewage treatment system that can successfully treat the organic components and nutrients present is required in the Ciliwung River basin area.

and Shin-ichi Onodera at the Graduate School of Integrated Arts and Sciences (Hiroshima University) for help with field research and sample collection.

Author Contributions

Sample analysis, data evaluation and drafting the manuscript was done by Daisuke Kozaki with contributions by Takashi Ozaki, Masanobu Mori, Nobutake Nakatani and Kazuhiko Tanaka. Water sample was collected by Kazuhiko Tanaka supported with Daisuke Kozaki. Kazuhiko Tanaka headed the water quality monitoring section of this project. All authors read and approved the final manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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