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Characteristics of residual metals from phosphorus removal in sewage treatment plants around Paldang lake, Korea

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ABSTRACT

The abundant use of chemicals to remove phosphorus in water could pose a problem to the safety of drinking water. In this study, we investigated the amount of residual aluminum and iron remaining in river. Paldang lake consists of two major tributaries (North Han River and South Han River) and one minor tributary (Gyung-an Stream). As a result of a total inspection on 45 phosphorus removal treatment plants in Paldang watershed of Han River, it was found that 39 treatment plants used aluminum-related coagulants while six treatment plants used iron salts. We investigated aluminum and iron concentrations in influent and effluent from six representative phosphorus removal treatment plants (A–F) in three tributaries and found that iron concentrations in A and C and aluminum concentrations in B and D exceeded drinking water standards. The background concentrations of aluminum and iron not affected by treatment plants nearby were 0.04–0.20 and 0.09–0.11 mg/L, respectively. In sediments, the background concentrations of aluminum and iron were 70.9–86.3 and 37.2–51.3 g/kg, respectively. Aluminum and iron concentrations in six representative treatment plants in the three tributaries were 16.9–64.9 and 17.1–75.3 g/kg, respectively. Since the pH range in sediment was 6.8–7.8, the possibility to leach aluminum and iron was low. Among other water quality parameters, turbidity was significantly correlated to the concentration of aluminum and iron. Finally, the concentrations of aluminum and iron of this study in Korea are higher than those of Japan and Taiwan.

Keywords: Phosphorus removal; Alum; PAC; Iron salt; Coagulant; Sediment; Sewage treatment plants; Paldang lake

1. Introduction

A certain level of phosphorus exists in river water. Phosphorus plays an important role in the natural water system because it is a vital nutrient which is required for the growth of aquatic plants. However, the excessive amount of phosphorus in rivers could lead to algae bloom, which degrades the water quality and as a result, creates unpleasant taste and odors in drinking water supplies. Meanwhile, Paldang lake is the largest drinking water conservation area in Korea that provides drinking water for more than 24 million people in

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Seoul and its neighboring areas. Along this lake, three weirs were constructed as part of the Four Major Rivers project, which was aimed not only to prevent flood and drought but also to provide recreational facilities. After the weirs were built, the flow rate of water has decreased, which could be a cause of algae blooms. Factors contributing to algae bloom include increased nutrient inputs, the transport of cells or cysts via anthropogenic activities and increased flow rate of water [1,2]. Therefore, the discharge standard for phosphorus has become stricter in sewage treatment plants to prevent algae bloom. The special standard on phosphorus was introduced, restricting the phosphorus concentration in sewage discharge to 0.2 mg/L as total *P*. Consequently, more chemical coagulants are used to comply with the new effluent standard by modifying sewage treatment, for instance, establishing additional phosphorus removal processes in sewage treatment plants. However, residual metals such as aluminum and iron could pose a problem to aquatic ecosystems and human health in affected rivers. Aluminum sulfate ($Al_2(SO_4)_3$), known as alum, ferric sulfate ($Fe_2(SO_4)_3$), or poly-aluminum chloride (PAC) are commonly used as a chemical coagulant in sewage and wastewater treatment plants [3]. A number of studies have demonstrated that aluminum is a potent neurotoxicant, both in experimental animals and in humans [4–6]. According to [7], iron is also known that it may have a crucial effect on structures and functions of river ecosystems. He argued that iron contamination on an aquatic ecosystem affects to species diversity, the abundance of periphyton, and decreasing numbers of benthic invertebrates and fishes. Although the effect of these residual metals is evident, to our knowledge, there has been no investigation on residual concentrations of aluminum and iron in effluent and in affected rivers as well as sediments nearby when they flow into rivers. Simultaneously, this is the first study to examine the types of coagulants used in those plants in Korea. Additionally, due to a uniqueness of this study, few reference studies were found related to this paper. The purposes of the present study are: (a) To investigate what types of coagulants are used in 45 sewage treatment plants, (b) To examine the concentration of residual metals (aluminum and iron) in both water and sediment, and (c) To study the influence of water quality parameters as a function of distance variation.

2. Experiment and analysis

2.1. Description of study area

Paldang lake is the largest drinking water reservoir in Korea whose water storage capacity is approximately 244×10^6 m^3 with a surface area of 20,085 km^2. This lake consists of two major tributaries, North Han River and South Han River, and one minor tributary Gyung-an Stream (Fig. 1). In terms of quantity of inflow into this lake, the portion of South Han River, North Han River, and Gyung-an Stream account for 55.0, 43.4, and 1.6%, respectively. Although Gyung-an Stream is a minor tributary and takes up a small amount of quantity of the inflow, it was selected for this study due to a significant load of nutrient and other pollutants.

2.2. Sampling collection

Totally, there are 45 sewage treatment plants to remove phosphorus around Paldang lake. After the analysis of aluminum and iron from those plants, two sampling places which showed the highest concentration of aluminum and iron from North Han River, South Han River, and Gyung-an Stream were selected. Fig. 1 shows that samples of river water were collected from six sampling places of sewage treatment plants (A, B, C, D, E, and F) in August–October. Based on a type of a coagulant, two groups were divided (A and C for iron *vs* B, D, E, and F for aluminum). Specifically speaking, A (iron) and B (aluminum) in North Han River, C (iron) and D (aluminum) in South Han River were selected as a sampling site. Since there is no treatment plant in Gyung-an Stream where iron salt was used, E and F were chosen to investigate the residual aluminum. Each sampling site had six sampling points; the influent, the effluent, 1 km upstream from the effluent, 1, 2, and 3 km downstream from the effluent in each treatment plant. River water samples were collected in 2 L polyethylene containers kept under 4˚C in a cool bag and then transferred to the laboratory of Han River environment research center.

Meanwhile, sediments near the effluents were collected to examine residual concentrations of aluminum and iron before and after the monsoon season.

The background concentration in water was determined selecting some places where there is no anthropogenic aluminum and iron source. Sediments were collected from six sampling places (A, B, C, D, E, and F) in August and October. Since many typhoons affect the Korean peninsula frequently and severely in September, sediments were not collected in that month. The details of sampling place in sediment are the same as those described in water. The background concentration in sediment was determined in four places where there is no source of aluminum and iron such as sewage treatment plants.

After sediments were collected by a polyethylene scoop, plastics, twigs, and stone with considerable size in sediments were removed. After that the sediment was transferred to a plate to be homogeneously

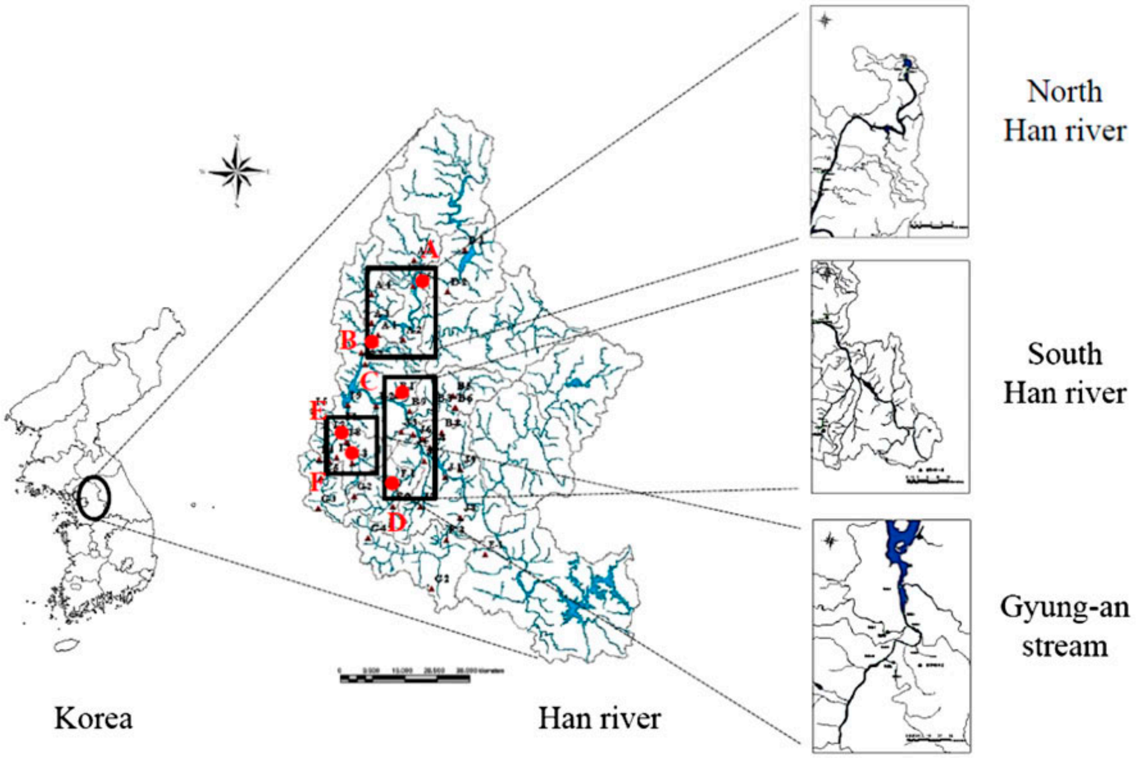

Fig. 1. Locations of the study area and rivers in accordance with a total inspection on 45 sewage treatment plants (▲) around Paldang lake and six representative sampling places (●) among the 45 treatment plants. The six representative sampling places were chosen from each tributary (South Han River, North Han River and Gyung-an Stream) in which two places were selected respectively, based on the highest concentration of aluminum and iron in the effluent of treatment plants.

mixed, sieved (pore diameter 2 mm), and collected in a 500 mL polyethylene container. After collection, the samples were stored in the refrigerator at approximately 4˚C prior to analysis.

2.3. Analytical methods

Temperature, electronic conductivity, pH, dissolved oxygen (DO), and salinity of river water samples were analyzed using 6920V2 (YSI, USA) on the spot. Alkalinity was determined by US. EPA method 310.2 using Smartchem 200 (Westco, USA). Total phosphorus was measured using AACS-V (BLtec, Korea) by Korean water standard method. Aluminum and iron were also determined by the Korean water standard method using inductively coupled plasma mass spectrometry (ICP-MS Bruker, Germany).

After the sediment was transferred to a 500 mL container, it was centrifuged with 2,000 rpm for 20 min and then the supernatant was discarded. After mixed for 10 min, the residue was used as a sample. Soil texture was measured using the soil texture analyzer (Microtrac S3500, USA).

For aluminum and iron analysis from sediment, it was dried by freeze dryer (FD.8512, Korea) and sieved through 0.063 mm mesh. Exactly 0.5 g of the sieved sediment was taken and then put in a collection container. After that, 5 mL of nitric acid, 2.5 mL of perchloric acid, and 5 mL of fluoric acid were added to it and the container was sealed. It was put on a hot plate and boiled with 80˚C for 1 h. The temperature was raised up to 220˚C until the sediment was dissolved completely. Then, 20 mL of 20% nitric acid was added at 80˚C to remove fluoric acid. Then again, 20 mL of 20% nitric acid was added to the container at the same temperature. After filtered with 0.45 μm filter paper (Whatman GD/XP PTFE), it was transferred to a 100 mL volumetric flask and massed up with 2% nitric acid. Finally, the sample was analyzed by inductively coupled plasma mass spectrometry (ICP-MS Bruker, Germany).

2.4. Statistical analysis

The SPSS statistical program (Version 14.0) was used. The data were analyzed using Pearson's correlation. It was used to analyze the relation between water quality and concentrations of aluminum and iron.

3. Results and discussion

3.1. Status of phosphorus removal treatment plants in Han River

Table 1 shows the types of coagulants used in phosphorus removal treatment plants in Han River. There were 45 treatment plants which had the capacity to treat sewage of more than 500 ton per day. Among coagulants, PAC accounted for 53.3%, followed by aluminum sulfate (alum), iron (III) chloride, and alternate use of PAC and alum. Consequently, coagulants related to aluminum took up as much as 86% of the sewage treatment plants. This result is in agreement with the previous research that aluminum is more effective precipitant than iron due to its chemical properties [8].

Table 1
Status of types of coagulants used for phosphorus removal in sewage treatment plants

Types of coagulants	Number of treatment plants	Percent (%)
PAC (Poly-aluminum chloride)	24	53.3
Alum (Aluminum sulfate)	11	24.5
Iron (III) chloride	6	13.3
Others*	4	8.9
Total	45	100.0

*Shows that one plant uses PAC and alum alternatively. Three plants use PAC, alum and polymer alternatively.

3.2. Load of aluminum and iron

The aluminum concentration of treatment plants in South Han River ranges 0.00–3.36 mg/L and is higher than those in North Han River (0.01–1.85 mg/L) and Gyung-an Stream (0.00–0.52 mg/L). The load of aluminum in phosphorus removal treatment plants in Han River basin is presented in Table 2. Among three tributaries in our study, phosphorus removal treatment plants located in North Han River has the highest load of aluminum (0.1–37.7 kg/day), followed by Gyung-an Stream (0.0–21.0 kg/day) and South Han River (0.0–19.4 kg/day).

Table 2 shows the load of iron in phosphorus removal treatment plants in Han River basin. Sewage treatment plants in South Han River has the highest load of iron (0.0–53.5 kg/day), followed by North Han River (0.0–13.6 kg/day) and Gyung-an Stream (0.0–1.3 kg/day).

It is commonly known that pH plays a key role in determination of the solubility of metals in water solution. Since the pH range in three tributaries is similar, concentrations of aluminum and iron are not significantly different. However, turbidity may affect

Table 3
Relation analysis between water quality and aluminum/iron

		TP	Alkalinity	Salinity	Turbidity
Aluminum	*R*	0.185	0.109	0.114	0.687*
	P	0.06	0.28	0.33	0.00
Iron	*R*	0.384*	0.349*	0.503*	0.601*
	P	0.00	0.00	0.00	0.00

R: Pearson's correlation index, *P*: significance
*Correlation is significant at 0.01 level (two-tailed).

Table 2
Effluent characteristics of sewage treatment plants in North/South Han River and Gyung-an Stream

					Aluminum		Iron	
	pH	DO	EC	Turbidity	Concent-ration (mg/L)	Load of effluent (kg/day)	Concent-ration (mg/L)	Load of effluent (kg/day)
North Han River	6.4–7.2 (6.8)*	9.6–12.0 (11.1)	268–843 (426)	0.3–2.7 (1.4)	0.0–1.9 (0.8)	0.1–37.7 (5.5)	0.0–1.2 (0.2)	0.0–13.6 (2.2)
South Han River	6.4–7.6 (7.1)	3.8–11.9 (9.9)	231–724 (459)	0.3–5.2 (1.1)	0.0–3.4 (0.4)	0.0–19.4 (2.3)	0.0–3.3 (0.3)	0.0–53.5 (2.8)
Gyung-an Stream	6.8–8.1 (7.3)	6.5–11.8 (9.9)	330–731 (492)	0.0–1.4 (0.5)	0.0–0.5 (0.2)	0.0–21.0 (3.5)	0.0–0.0 (0.0)	0.0–1.3 (0.3)

*An average concentration.

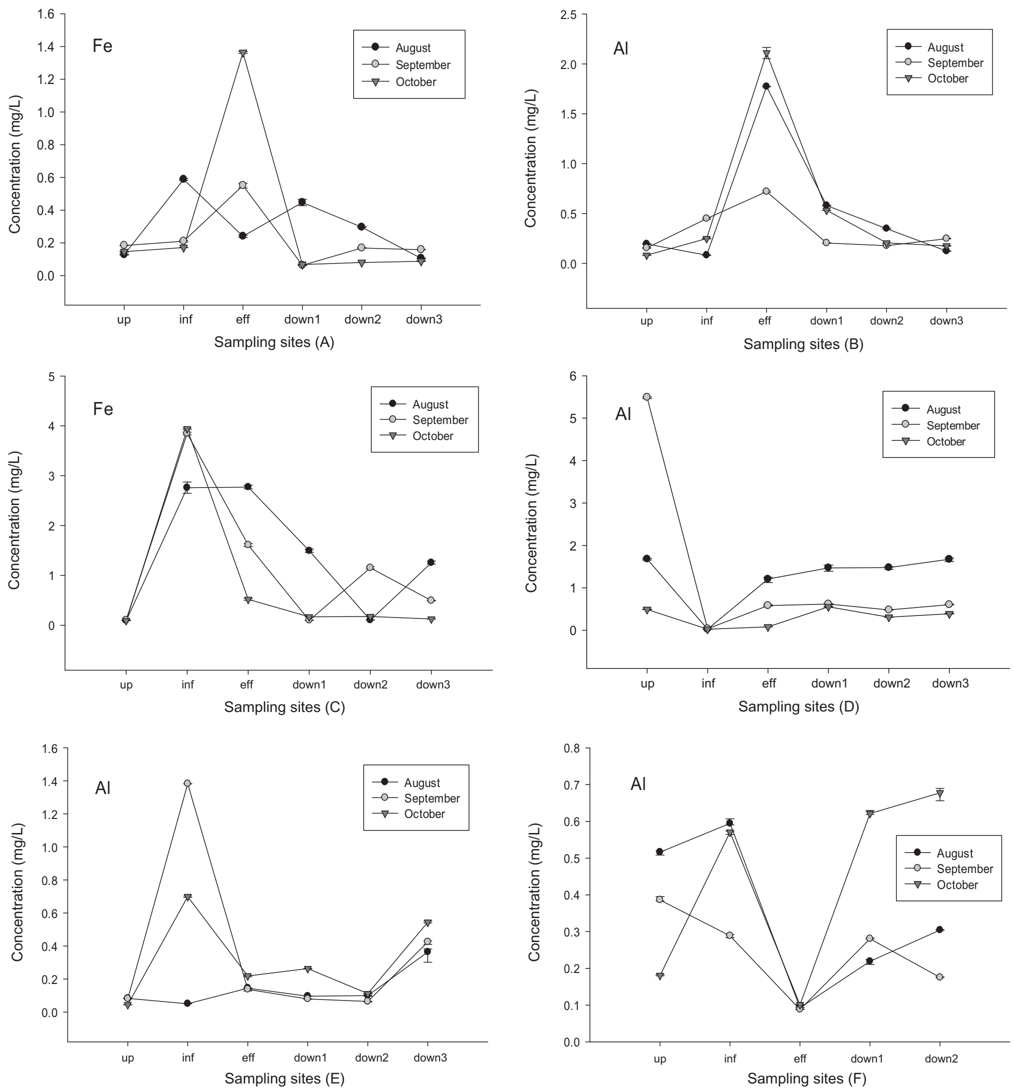

Fig. 2. Distribution of aluminum and iron concentration as a function of sampling sites.

aluminum and iron concentration (Table 3). When turbidity is higher, those concentrations are also higher. This result is in agreement with [9] whose result shows the turbidity was correlated with aluminum and iron concentration. The most likely explanation of this phenomenon is that aluminum and iron are adsorbed on the surface of particles which cause turbidity.

3.3. Distribution characteristics of residual aluminum and iron concentrations

3.3.1. Distribution of aluminum and iron concentration in water in accordance with distance

Fig. 2 is presented in order to understand how aluminum and iron are distributed from 1 km downstream (down1) to 3 km downstream (down3). After the effluent iron concentrations of A and C in water from August through October ranged 0.07–0.45 and 0.10–1.49 mg/L, respectively. The Korean drinking water standard for iron is 0.3 mg/L. After the effluent aluminum concentrations of B, D, E, and F from August to October ranged 0.12–0.58, 0.31–1.66, 0.06–0.55, and 0.09–0.67 mg/L, respectively. The Korean drinking water standard for aluminum is 0.20 mg/L. Since there is no standard regulating the concentration of aluminum in rivers and streams, the standard for drinking water was used in this paper to compare with the concentration of effluent from sewage treatment plants. As can be seen in Fig. 2, the background concentration of aluminum and iron played an important role in determination of those concentrations in accordance with distance. Although an effluent concentration is low, when a background concentration is higher than that of the effluent, the effluent concentration eventually will be equal to the background concentration. However, we found it interesting that the concentration of aluminum in E suddenly became higher at 3 km from the effluent. It can be explained by the fact that the concentration at down 3 (3 km downstream from the effluent) may be affected by the background concentration. This was compared with other results. For example, except for A and B, ours is in contrast to [10] whose result showed that aluminum concentration decreased as a function of distance with 7 μg L^{-1} km^{-1}. The result by [9] is also in disagreement with ours. According to their result, aluminum concentration declines notably with an average of 36 μg L^{-1} km^{-1} as distance increases from sewage treatment plants. It may be assumed that compared to study areas of [9] and [10], our study has no industrial area or no other sources for aluminum and iron because Paldang lake is a conservative area for drinking water.

3.3.2. *Distribution of aluminum and iron concentrations in sediments in accordance with distance*

Soil texture was determined in pre-monsoon and post-monsoon seasons. In six phosphorus removal treatment plants, sand accounted for 82.8–98.5% before the monsoon season, which demonstrates that regardless of sites the main composition of soil was sand. It is in agreement with the result by [11]. They proposed that continuous deposition of alluvium on the riverbed of Paldang lake may be an attribution to the fact that sand was a main composition. However, after the monsoon season, the composition in some places (B and D) changed dramatically. This indicates that after the monsoon season, the significant accumulation of suspended particles occurred. Due to a geographical reason, a torrential rain during the monsoon season led to the increase of silt coming from agricultural area or other areas neighboring Paldang lake. As a result, the portion of sand, silt, and clay was 56, 44, and 0%, respectively in B. In D, the portion of sand, silt, and clay was 63, 36, and 1%, respectively (Table 4). In all of the sites except B and D in October, soil texture showed a similar classification. According to US Department of Agriculture soil texture triangle, all the sites except B and D in October are categorized as sand. Soil texture of B in October is classified as sandy loam while that of D in October is categorized as silt loam. Soil texture in sediment of background sites was that the contents of sand, silt, and clay were 63–100, 0–36, and 0–1%, respectively. Soil texture in sediment near sewage treatment plants shows a similar pattern with those of background sites, which is classified as sand, sandy loam, or silt loam. A few previous studies have shown that the grain size played a key role in controlling sedimentary heavy metal concentrations [12,13]. During the monsoon season, the volume of water and flow rate increases dramatically and consequently sediment may be washed away. After the monsoon season, however, the flow rate decreases and the settlement of the suspended particle occurs. Due to this reason, soil composition of B and D is different from other sites.

The pH plays an important role in determination of leaching heavy metals from sediments and depends on the buffering capacity of the sediments [11]. At the

Table 4
Soil texture and aluminum/iron concentration in sediments near six sewage treatment plants

Month		Soil texture (%)			Concentration (g/kg)		
		Sand	Silt	Clay	Al	Fe	pH
Monsoon season (August)	A (Fe)	82.8	16.5	0.8	21.2	39.8	6.8
	B (Al)	98.5	1.5	0.0	35.3	37.9	7.3
	C (Fe)	97.6	2.4	0.0	19.3	75.3	7.5
	D (Al)	96.9	3.1	0.0	32.4	35.0	7.4
	E (Al)	87.9	12.1	0.0	16.9	17.1	7.5
	F (Al)	96.7	3.3	0.0	64.9	20.2	7.8
Post-monsoon season (October)	A (Fe)	89.0	11.0	0.0	33.1	40.9	7.1
	B (Al)	56.0	44.0	0.0	24.8	36.7	7.6
	C (Fe)	89.6	10.4	0.0	26.8	40.8	7.3
	D (Al)	36.2	62.9	0.8	41.6	38.5	7.3
	E (Al)	98.6	1.4	0.0	28.1	32.2	7.4
	F (Al)	97.5	2.5	0.0	23.2	33.4	7.4

certain level of pH, metals will start being released from the sediments [14]. Since the pH of sediment ranged 6.8–7.8 in this study, it had a low possibility that aluminum and iron were released.

Before the monsoon season, concentrations of aluminum and iron near six sewage treatment plants ranged 16.9–64.9 g/kg (mean: 31.7 g/kg) and 17.1–75.3 g/kg dry weight (mean: 37.6 g/kg), respectively. After the monsoon season, those of aluminum and iron were 23.2–41.6 (mean: 29.6 g/kg) and 32.2–40.9 g/kg dry weight (mean: 37.1 g/kg), respectively (Table 4).

Background concentrations of aluminum and iron which refer to the place without sewage treatment plants upstream were 70.9–86.3 g/kg (mean: 79.8 g/kg) and 37.2–51.3 g/kg (mean: 44.5 g/kg), respectively. This result shows that overall concentrations of aluminum and iron in sediments near treatment plant discharge were lower than those of the background sites. It was found that the concentrations of aluminum and iron of Beppu Bay in Japan ranged 44.1–71.8 and 29.1–39.2 g/kg, respectively [15]. In Taiwan, the concentration of iron in Keelung River was 27.0–59.0 and 29.0–40.0 g/kg, respectively [13]. Overall, background concentrations of aluminum and iron in Korea are higher than those in Japan and Taiwan.

4. Conclusions

Recently, due to the strict regulation, sewage treatment plants around Paldang lake are using alum, PAC, and iron salts to remove phosphorus. A significant number of sewage treatment plants used alum or aluminum-related coagulants (83%) to remove phosphorus around Paldang lake. In some representative places, concentrations of aluminum and iron in final effluent exceeded the Korean drinking water standard (A and C for iron, B and D for aluminum). Due to dilution, excessive concentration in final effluents in sewage treatment plants became below the Korean drinking water standard in accordance with distance in North Han River. Due to seasonal reasons, concentrations of aluminum and iron in sediment did not have significant correlation with the particle size. Turbidity played an important role in determination of concentrations of aluminum and iron in water. Since this research was conducted for the first time in Korea, to our knowledge, to investigate the effect of chemical coagulants in sewage treatment plants on Paldang lake, the largest drinking water reservoir, the findings of this study could be used for fundamental data to establish environmental policy to minimize the adverse impact on the aquatic ecosystem and to provide measures for water utilization.

References

[1] H.R. Maier, G.C. Dandy, Modelling cyanobacteria (blue-green algae) in the River Murray using artificial neural networks, Math. Comput. Simul. 43 (1997) 377–386.
[2] J.M. O'Neil, T.W. Davis, M.A. Burford, C.J. Gobler, The rise of harmful cyanobacteria blooms: The potential roles of eutrification and climate change, Harmful Algae 14 (2012) 313–334.
[3] N. Muisa, Z. Hoko, P. Chifamba, Impacts of alum residues from Morton Jaffray water works on water quality, Phys. Chem. Earth 36 (2011) 853–864.
[4] T.P. Flaten, A.C. Alfrey, J.D. Birchall, J. Savory, R.A. Yokel, Status and future concerns of clinical and environmental aluminum toxicology, J. Toxicol. Environ. Health 48 (1996) 527–541.
[5] T.P. Flaten, Aluminium as a risk factor in Alzheimer's disease with emphasis on drinking water, Brain Res. Bull. 55 (2001) 187–196.
[6] A. Alonso-Mateos, M.J. Almendral-Parra, Y. Curto-Serrano, F.J. Rodríguez-Martín, Online monitoring of aluminium in drinking water with Fluorimetric detection, z J. Fluoresc. 18 (2008) 183–192.
[7] K.M. Vuori, Direct and indirect effects of iron on river ecosystems, Finn. Zool. Bot. Publ. Board 32 (1995) 317–329.
[8] T. Clark, T. Stephenson, P.A. Pearce, Phosphorus removal by chemical precipitation in a biological aerated filter, Water Res. 31 (1997) 2557–2563.
[9] W. Wang, H. Li, X. Wang, Y. Liu, Spatial variations of total aluminum species in drinking water supplies in Xi'an studied applying geographic information system, J. Environ. Sci. 22 (2010) 519–525.
[10] I. Cech, J. Montera, Spatial variations in total aluminum concentrations in drinking water supplies studied by geographic information system (GIS) methods, Water Res. 34 (2000) 2703–2712.
[11] G. Bartoli, E. Sagnella, A. Fioretto, Heavy metal content in sediments along the Calore river: Relationships with physical-chemical characteristics, J. Environ. Manage. 95 (2012) S9–S14.
[12] S. Lin, I.J. Hsieh, K.M. Huang, C.H. Wang, Influence of Yangtze river and grain size on the spatial variations of heavy metals and organic carbon in the East China Sea continental shelf sediments, Chem. Geol. 182 (2002) 377–394.
[13] K.M. Huang, S. Lin, Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan, Chemosphere 53 (2003) 1113–1121.
[14] S.Y. Chen, J.G. Lin, Bioleaching of heavy metals from sediment: Significance of pH, Chemosphere 44 (2001) 1093–1102.
[15] A. Amano, M. Kuwae, T. Agusa, K. Omori, H. Takeoka, S. Tanabe, T. Sugimoto, Spatial distribution and corresponding factors of metal concentrations in urface sediments of Beppu Bay, Southwest Japan, Mar. Environ. Res. 71 (2011) 247–256.