Chemical characterization of rainwater over Suwon region during farming and non-farming periods

Min-Kyeong Kim[1], Jong-Sik Lee[1], Goo-Bok Jung[1], Byong-Gu Ko[2], Soon-Ik Kwon[1], Min-Young Kim[1*], Kyu-Ho So[1], Sun-Gang Yun[1]

[1]Department of Agricultural Environment, National Academy of Agricultural Science, Rural Development Administration (RDA), Suwon, Republic of Korea; *Corresponding Author: mykim75@korea.kr
[2]Dresearch Planning Division, Rural Development Administration, Suwon, Republic of Korea

ABSTRACT

Recently, special attention has been given to acid rain and its problem to environment such as acid precipitation and air pollution in East Asia. In the present study, rainwater samples were collected from Apr to Oct (farming period) and from Nov to Mar (non-farming period) in 2009 ~ 2011. The samples were chemically characterized for the assessment of emission sources. Suwon region, a typical agricultural area in Gyeonggi province (South Korea) was chosen as a study site. The content of ionic species and their temporal variation were used for factor analysis, which was used to presume the natural and anthropogenic sources depending upon the farming and non-farming periods. The cations observed during farming and non-farming periods were $NH_4^+ > Na^+ > Ca^{2+} > K^+ > H^+ > Mg^{2+}$ and $Na^+ > N NH_4^+ > Ca^{2+} > H^+ = Mg^{2+} > K^+$, respectively. The anions during farming and non-farming periods were $SO_4^{2-} > NO_3^- > Cl^-$ and $NO_3^- > SO_4^{2-} > Cl^-$, respectively. While the amounts of sulfate, one of the major dissolved components of rainwater were 113.5 and 177.0 $ueq \cdot L^{-1}$, the ones of $NSS\text{-}SO_4^{2-}$ (Non-Sea Salt sulfate) were 93.7 and 87.1% during farming and non-farming periods, respectively. The comparison of observed pH values (pH_{obs}) with the theoretical pH values (pH_{the}) showed that the neutralization of rainwater considerably went along during farming and non-farming periods. The highest amount of rainfall throughout the year was 310.5 mm in August and its corre sponding nitrogen loading was 5.03 $kg \cdot ha^{-1}$. The major ion contents for crop growth, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, were 49.4, 5.5, 18.1, 1.4 $kg \cdot ha^{-1}$ from April to October. The major contributions to the existing chemical ions in rainwaters during farming and non-farming periods were from the natural sources (sea and soil) and the anthropogenic sources (human and animal waste, vehicular emission + fossil fuels combustion), respectively.

Keywords: Acidity; Discharge; Nutrient; Rainwater

1. INTRODUCTION

As rapid industrialization has substantially increased environmental pollution and public concern, much attention has been given to the evaluation of the pollution level which caused by atmospheric deposition and acid rain [1,2].

Rainwater, although purifies pollutants in the air, it is becoming a sources of pollution, for example, from wildfire, geological activity, dust storm [3] and human and industrial activities [1,4] to the environment. The effect of acid rain depends upon the direction and speed of wind, therefore, the widespread damage to the neighboring countries is both directly and indirectly massive [5]. Crop, soil and surface water are easily exposed to chemical wet (rain, snow, fog, etc.) and dry precipitates (gas, fine particles, etc.). The chemical and physical damages by rainwater to forest and agricultural products [6], soils and microorganisms [7], streams and lakes [8], buildingv [9,10] and humans [11] were monitored by previous studies.

In the past, only few studies concerning chemical investigation of rainwater and assessment of its emission sources (natural vs. anthropogenic) to reduce the consequences of pollution on ecosystems were investigated [12-15]. They defined the emission sources, dust from sea salt and soil dust (i.e., Ca^{2+}, Mg^{2+}, HCO_3^-/CO_3^{2-}) as natural sources and intensive coal burning, gases and particles emitted from industries and vehicles (i.e., SO_4^{2-}) as anthropogenic sources. Their findings of rainwater

chemistry correlated with spatial-temporal and meteorological conditions indicated that the impact of pollution transport from distant emission sources may play an important role at the study site, as local pollution alone cannot account for the high levels of ion concentrations in the analyzed rainwater [12].

South Korea is located in East Asia, on the southern half of Korean Peninsula jutting out from the far east of the Asian land mass. There were no noticeable damages by atmospheric acid rain until now. In addition, the previous studies simply characterized the rainwater (and acid rain) properties [16-20]. Different from Western Europe, South Korea has the unique characteristics including the considerable change of monthly precipitation and the neutralization of acid rain by alkali components in the air. However, public awareness of environmental pollution and geological circumstance of South Korea that locates on the east side of China where sulfurous acid gas emission was originated by rapid industrialization has increased and demanded the continuous monitoring on physiochemical properties of yellow dust and acid rain.

In this study, rainwater samples were collected from April to October (farming period) and November to March (non-farming period), 2009-2011 in Suwon region, Gyeonggi province, South Korea. The rainwater chemistry including the contents of ionic species and their temporal variation was used for factor analysis, which was then used to presume the natural and anthropogenic sources depending upon the farming and non-farming periods.

2. MATERIALS AND METHODS

2.1. Study Site and Sample Collection

The present study was conducted at an experimental station at the National Academy of Agricultural Science, Rural Development Administration (37$^{\bullet}$16'28.72"N,

126$^{\bullet}$59'10.53"E, Suwon city, Gyeonggi province, South Korea) (**Figure 1**). An automatic rainfall collector was installed and a total of 66 rainwater samples, 40 samples for farming (April to October) and 22 samples for non-farming (November to March) periods, were collected from November, 2009 to October, 2011. Hourly wet sampling was carried out using an automatic sampler (AQUA Control Co., Japan).

2.2. Sample Analyses

Rainwater samples were analyzed using the APHA method [21] and standard methods for the examination of environmental pollution [22]. The measurement of pH and EC were done using EA 940 ion analyzer (Orion, USA) and Model 162 conductivity meter (Orion, USA), respectively. Other chemical properties (NH_4-N, SO_4^{2-}, NO_3-N, Cl^-) and cations (Ca^{2+}, K^+, Mg^{2+}, Na^+) were analyzed by indophenol blue method, nephelometry method, ultraviolet spectrophotometry, Mercury (II) Thiocyanate and ICP (GBC Intergra XMP, Australia) methods, respectively.

2.3. Statistical Analysis

Statistical package (PASW Statistics 18) was used for calculations. Principal component analysis (PCA) allowed to find out associations between variables, thus reducing the dimensionality of the data table. This is accomplished by diagonalization of the correlation matrix of the data, which transforms the 10 original variables into 10 uncorrelated (orthogonal) ones (weighed linear combinations of the original variables) called principal components (PCs). The eigenvalues of the PCs are a measure of their associated variance; the participation of the original variables in the PCs is given by the loadings, and the individual transformed observations are called scores. A Varimax rotation allows to "clean up" the PCs
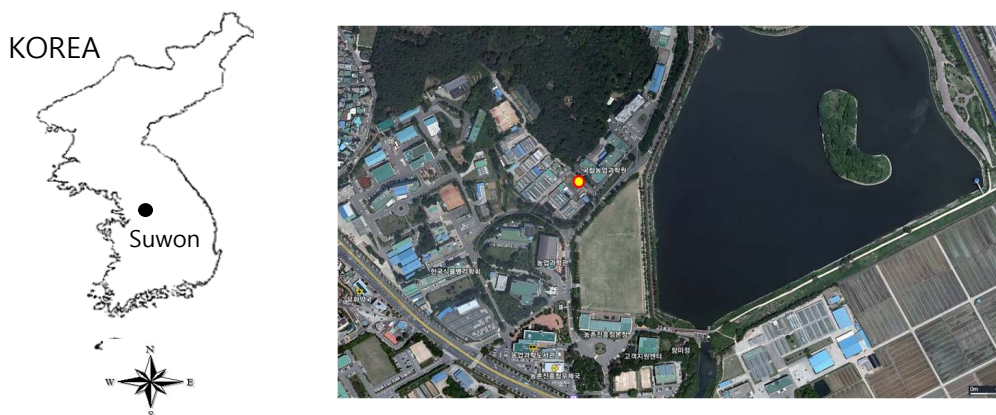
KOREA

Suwon

Figure 1. Study site and sampling location (National Academy of Agricultural Science, Rural development administration, Suwon, Gyeonggi, South Korea).

by increasing the participation of the variables with higher contribution., and simultaneously reducing that of the variables with lesser contribution. In that way, the number of original variables contributing to each VF is reduced at the cost of a loss of orthogonality.

3. RESULTS AND DISCUSSION

The average monthly rainfalls during farming and non-farming periods were 1050 mm and 286 mm, respectively. Seventy-eight percentage of the total rainfall was concentrated during farming period and the highest amount of rainfall was observed in August in 2010 (**Figure 2**).

The chemical properties of rainwater are essential to determine the causative agent of acidity and neutralization. **Table 1** lists the component ratio of each ion. The cations observed during farming and non-farming periods were $NH_4^+ > Na^+ > Ca^{2+} > K^+ > H^+ > Mg^{2+}$ and $Na^+ > NH_4^+ > Ca^{2+} > H^+ = Mg^{2+} > K^+$, respectively. The anions during farming and non-farming periods were $SO_4^{2-} > NO_3^- > Cl^-$ and $NO_3^- > SO_4^{2-} > Cl^-$, respecttively. During both farming and non-farming periods, Na^+ and NH_4^+ were occupied by 60% among other cations, and SO_4^{2-} and NO_3^- were occupied by more than 80% among other anions. This is consistent to previous studies [17,19,20]. The high values of SO_4^{2-} and NO_3^- reflect a more important influence from local pollution sources such car and plant and NH_4^+ may be a good indicator of common agricultural practices. The elements of natural sources (e.g., Ca^{2+}, Mg^{2+}, HCO_3^-/CO_3^{2-}) have lower concentrations during farming period, which was caused by more frequent rain events. Arsene *et al.* [12] also mentioned that the amount of rainfall can influence the levels of the main ions in rainwater, which indicated that the smaller level of ion is caused by the higher amount of rainfall due to dilution effect.

Figure 3 shows the monthly changes of SS-SO42- (Sea-Salt sulfate) and NSS-SO_4^{2-} (Non-Sea salt sulfate) in rainwater. The concentration of NSS-SO_4^{2-} discharged from an anthropogenic source was calculated using NSS-$SO_4^{2-} = [SO_4^{2-}] - [Na^+] \times 0.121$ and the sea-salt sulfate was excluded in the calculation. In case of Na^+, there was no anthropogenic source except for sea salt; therefore, it was assumed that the component of sea water is consistent with the one of sea salt particles [23,24]. The coefficient of 0.121 was used as an equivalence ratio of $[Na^+]/[SO_4^{2-}]$ in sea water. During farming and non-farming periods, the total amounts of sulfate dissolved in rainwater were 113.5 and 177.0 ueq·L^{-1}, respectively. The sulfate content in December was particularly highest. The content of NSS-SO_4^{2-} in sulfate during farming and non-farming periods were 93.7 and 87.1%, respectively [17,19,20].

The observed pH values (pH$_{obs}$) were measured to assess the neutralization of rainwater acidity and **Figure 4** shows the comparison of pH values measured from the
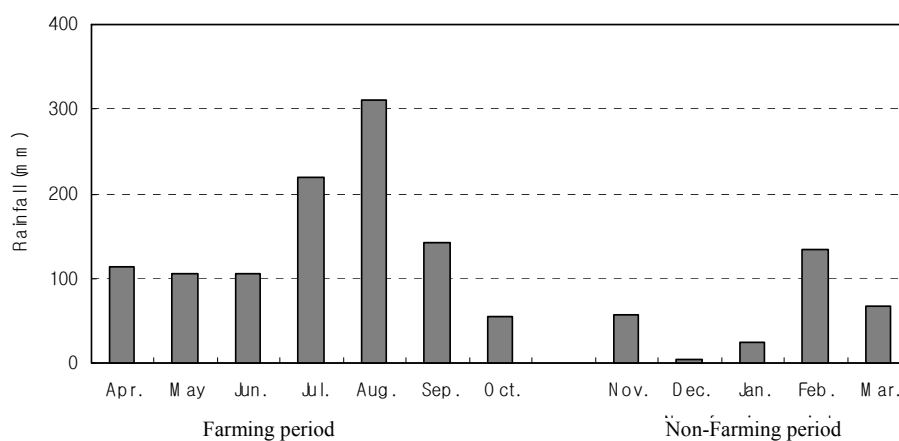

Figure 2. Monthly rainfall in Suwon during farming (April to October in 2010 and 2011) and non-farming (November to March in 2009 and 2010) periods.

Table 1. Cationic and anionic composition ratios of rainwater collected in Suwon during farming (April to October in 2010 and 2011) and non-farming (November to March in 2009 and 2010) periods.

Periods	Cation (%)						Anion (%)		
	NH_4^+	Ca^{2+}	K^+	Mg^{2+}	Na^+	H^+	NO_3^-	SO_4^{2-}	Cl^-
Farming	30.2	17.3	12.8	8.5	20.8	10.4	36.1	51.2	12.6
Non-farming	22.1	21.5	2.5	7.3	39.3	7.3	40.0	38.0	22.0
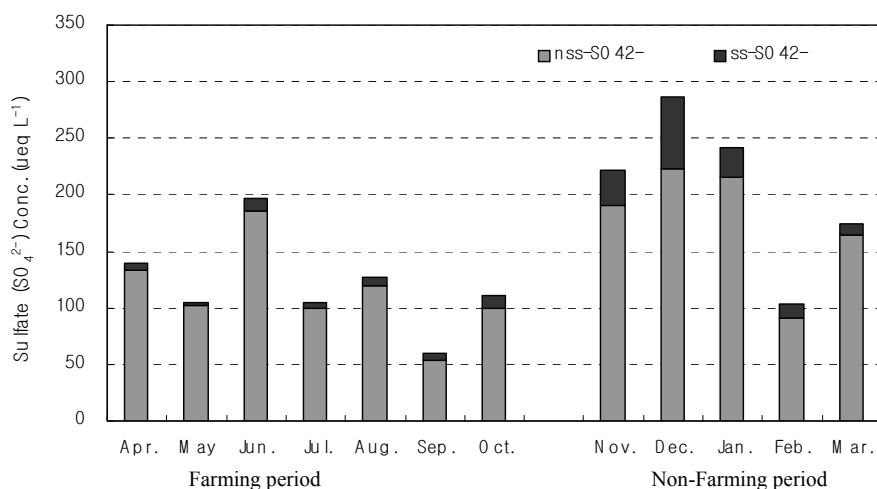
Figure 3. Monthly variation of sulfate contents in rainwater during farming (April to October in 2010 and 2011) and non-farming (November to March in 2009 and 2010) periods.
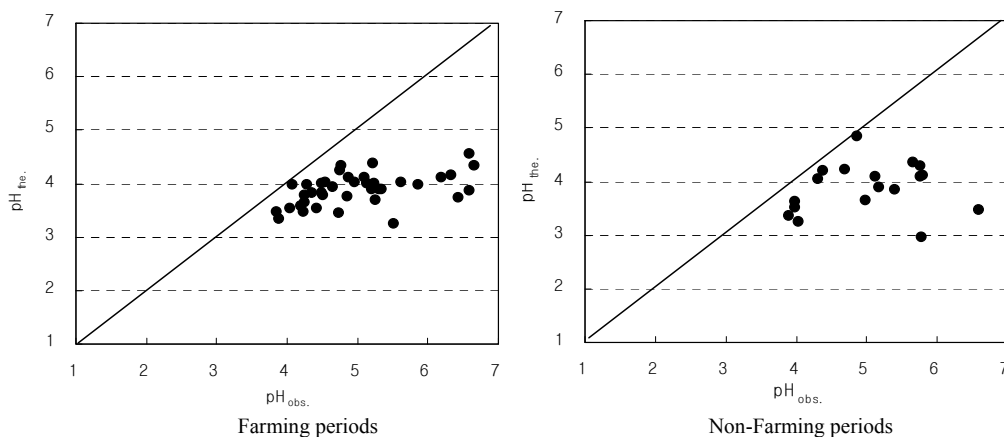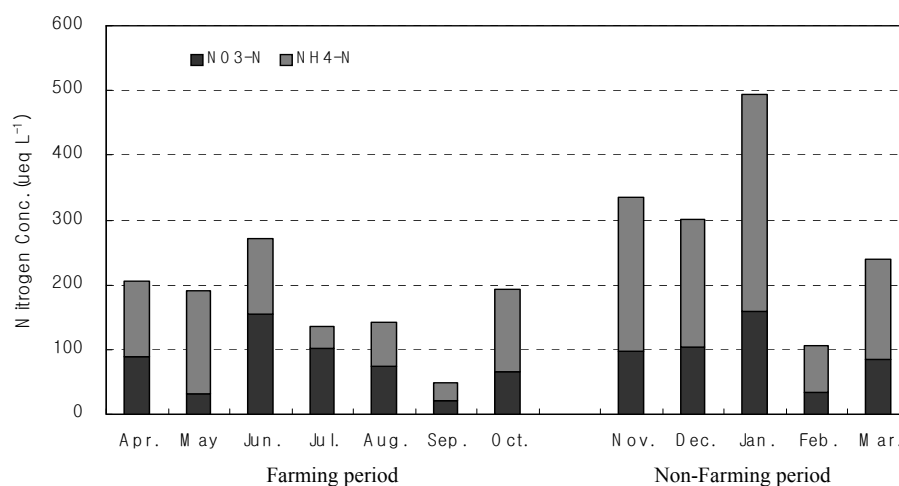

Figure 4. Correlation between pHobs (observed pH) and pHthe (theoretical pH) of rainwater during farming (left; April to October in 2010 and 2011) and non-farming (right; November to March in 2009 and 2010) periods.

study site (pH_{obs}) with the theoretical ones (pH_{the}) from the reference [25]. The pH_{the} value was calculated using: $pH_{the} = -\log([H^+] + [NH_4^+] + [Ca^{2+}])$. The pH measurements biased on the right side of 1:1 line as shown in **Figure 4** indicates that the neutralization of rainwater was considerably progressed during farming and non-farming periods.

Figure 5 shows the monthly variation of NH_4-N and NO_3-N. The annual volume-weighted average concentration of inorganic N in rainwater was high during the non-farming period (295.3 ueq·L^{-1}) and the ones during farming period were higher from April to June and lowest in September. This indicates that cations well represented a seasonal variability. It was known that NH_4 was associated with the most intense traditional agricultural activities, particularly during farming season. However, this study found that the content of NH_4 was also high during non-farming season.

The average monthly ion contents during farming and non-farming periods are listed in **Table 2**. Overall inorganic N contents were much higher during farming period than non-farming period due to high volume of rainfall during farming period. Precipitation was mostly concentrated over Suwon region in August (310.5 mm) and the N loading into soil through rainfall was 5.03 kg·ha^{-1}. In spite of excessive amount of N in rainwater, its availability for crop growth was not high because it was directly discharged into neighboring lakes and streams. In case of sulfate ion (SO_4^{2-}), the highest amount was monitored in soil during August (15.9 kg·ha^{-1}). From April to October, the major observed ion contents for crop growth, SO_4^{2-}, Ca^{2+}, K^+ and Mg^{2+}, were 49.4, 5.5, 18.1 and 1.4 kg·ha^{-1}, respectively. Based on previous reference, it was presumed that sulfuric acid from sulfur dioxide (SO_2), Na^+/Mg^{2+} and Ca^{2+} were from the combustion of fossil fuel and coal, sea salt, and soil/building

Figure 5. Monthly change of inorganic nitrogen of rainwater collection in Suwon region during farming (left; April to October in 2010 and 2011) and non-farming (right; November to March in 2009 and 2010) periods.

Table 2. Monthly change of inorganic ion contents in Suwon during farming and non-farming periods.

Periods		T-N	SO_4^{2-}	Cl^-	Ca^{2+}	K^+	Mg^{2+}	Na^+
		(kg·ha^{-1})						
Farming	Apr.	2.44	5.98	0.33	1.15	0.42	0.42	0.57
	May	1.31	2.98	0.27	0.68	0.34	0.34	0.66
	Jun.	2.98	8.19	0.29	0.68	0.17	0.15	2.14
	Jul.	2.77	9.21	0.49	0.70	1.39	0.17	2.40
	Aug.	5.03	15.88	8.42	0.69	13.53	0.18	3.14
	Sep.	0.69	4.19	0.67	0.93	0.35	0.04	2.08
	Oct.	1.74	3.02	1.73	0.64	1.92	0.09	1.10
Non-farming	Nov.	1.04	3.16	1.36	0.39	0.01	0.06	0.47
	Dec.	0.14	0.44	0.36	0.09	0.03	0.04	0.39
	Jan.	1.18	2.43	0.95	0.47	0.10	0.09	0.77
	Feb.	1.69	6.32	2.55	0.59	0.73	0.17	3.04
	Mar.	0.93	3.06	1.21	0.46	0.09	0.04	1.74

Table 3. Source identification of ionic species in rainwater by factor analysis.

Periods	Principle Component (PC)	Percentage Variance (%)	Component of high loading	Potential sources identified
Farming	PC1	28.7	K^+, Cl^-	Sea and soil
	PC2	23.1	SO_4^{2-}, NH_4^+, Na^+	Agricultural activity sea and soil vehicular emission
	PC3	17.4	Ca^{2+}, Mg^{2+}, NO_3^-	Sea and soil Vehicular emission
Non-farming	PC1	43.7	NH_4^+, SO_4^{2-}, NO_3^-	Human and animal waste vehicular emission + fossil fuels combustion
	PC2	37.4	Na^+, Cl^-, Mg^{2+}, K^+	Sea and soil
	PC3	18.9	Ca^{2+}	Sea and soil

materials [25].

The assessment of emission source for chemical ions in rainwater was determined based on the PCA and the results are shown in **Table 3**. The factor loadings showed that the data synthesized into three factors with Eigin values, cut-off at greater than unity and explained about 80% of the total variance.

The fact that many activities by human and heavy traffic existed in Suwon region was reflected in the selection of factors for statistical analysis. During farming period, three factors were chosen as the following: 1) K^+ and Cl^- from natural sources (sea and soil); 2) SO_4^{2-}, NH_4^+ and Na^+ from natural sources (sea and soil) and anthropogenic sources (agricultural activity, vehicular emission + fossil fuels Combustion), and 3) Ca^{2+}, Mg^{2+} and NO_3^- from natural source (sea and soil) and anthropogenic source (vehicular emission). In case of non-farming period, three factors were chosen as the following: 1) NH_4^+, SO_4^{2-} and NO_3^- from anthropogenic sources (human and animal waste, vehicular emission + fossil fuels combustion), 2) Na^+, Cl^-, Mg^{2+} and K^+, and 3) Ca^{2+} from natural source (sea and soil).

4. ACKNOWLEDGEMENTS

REFERENCES

[1] Chudaeva, V.A., Urchenko, S.G., Chudaev, O.V., Sugimory, K., Matsuo, M. and Kuno, A. (2006) Chemistry of rainwaters in the south Pacific area of Russia. *Journal of Geochemical Exploration*, **88**, 101-105. doi:10.1016/j.gexplo.2005.08.020

[2] Wang, T.J., Jiang, F., Li, S. and Liu, Q. (2007) Trends in air pollution during 1996-2003 and cross-border transport in city clusters over the Yangtze River Delta Region of China. *Journal of Terrestrial*, *Atmospheric and Oceanic Science*, **5**, 995-1009. doi:10.3319/TAO.2007.18.5.995(A)

[3] Scorer, R.S. (1994) Long distance transport, acid rain. Gordon & Breach Science Publishers, New York.

[4] Cheng, M.C., You, C.F., Lin, F.J., Huang, K.F. and Chung, C.H. (2011) Sources of Cu, Zn, Cd and Pb in rainwater at a subtropical islet offshore northern Taiwan. *Atmospheric Environment*, **39**, 6175-6183.

[5] Charron, A., Plaisance, H., Sauvage, S., Coddeville, P., Galloo, J.C. and Guillerm, R. (2000) A study of the source receptor relationships influencing the acidity of precipitation collected at a rural site in France. *Atmospheric Environment*, **34**, 3665-3674. doi:10.1016/S1352-2310(00)00096-0

[6] Rinallo, C. (1992) Effects of acidity of simulated rain on the fruiting of "summerred" apple trees. *Journal of Environmental Quality*, **21**, 61-68. doi:10.2134/jeq1992.00472425002100010009x

[7] Wang, C., Guo, P., Han, G., Feng, X., Zhang, P. and Tian, X. (2010) Effect of simulated acid rain on the litter decomposition of Quercus acutissima and Pinus massniana in forest soil microcosms and the relationship with soil enzyme activities. *Science of the Total Environment*, **408**, 2706-2713. doi:10.1016/j.scitotenv.2010.03.023

[8] Cronan, C.S. and Schofield, C.L. (1979) Aluminum leaching response to acid precipitation: Effects on high-elevation watersheds in the Northeast. *Science*, **204**, 304-306. doi:10.1126/science.204.4390.304

[9] Contardi, V., Franceschi, E., Bosia, S., Zanicchi, G., Palazzi, D., Cortessogno, L. and Gaggero, L. (2000) On the conservation of architectural artistic handwork of the "Pietra di Finale". *Journal of Cultural Heritage*, **2**, 83-90. doi:10.1016/S1296-2074(00)00159-X

[10] Okochi, H., Kameda, H., Hasegawa, S., Saito, N., Kubota, K. and Igawa, M. (2000) Determination of concrete structures by acid deposition—An assessment of the role of rainwater on deterioration by laboratory and field exposure experiments using mortar specimens. *Atmospheric Environment*, **34**, 2937-2945. doi:10.1016/S1352-2310(99)00523-3

[11] Peart, M.R. (2000) Acid rain, storm period chemistry and their potential impact on stream communities in Hong Kong. *Chemosphere*, **41**, 25-31. doi:10.1016/S0045-6535(99)00386-0

[12] Arsene, C., Olariu, R.I. and Mihalopoulos, N. (2007) Chemical composition of rainwater in the northeastern Romania, Iasi region (2003-2006). *Atmospheric Research*, **41**, 9452-9467.

[13] Sakihama, H., Ishiki, M. and Tokuyama, A. (2008) Chemical characteristics of precipitation in NH_3-affected areas. *Atmospheric Environment*, **22**, 1689-1698.

[14] Ozeki, T., Ihara, T. and Ogawa, N. (2006) Study of pollutants in precipitation (rain and snow) transported long distance to west coasts of Japan Islands using oblique rotational factor analysis with partially non-negative constraint. *Chemometrics and Intelligent Laboratory Systems*, **82**, 15-23. doi:10.1016/j.chemolab.2005.05.012

[15] Tu, J., Wang, H., Zhang, Z., Jin, X. and Li, W. (2005) Trends in chemical composition of precipitation in Nanjing, China, during 1992-2003. *Atmospheric Research*, **73**, 283-293. doi:10.1016/j.atmosres.2004.11.002

[16] Kang, G.G., Collett, J.L., Shin, D.Y., Fujita, S.I. and Kim, H.K. (2004) Comparison of the chemical composition of precipitation on the western and eastern coasts of Korea. *Water*, *Air*, *and Soil Pollution*, **151**, 11-34. doi:10.1023/B:WATE.0000009854.40334.da

[17] Ko, B.G., Kim, M.K., Lee, J.S., Kim, G.Y., Park, S.J. and Kwon, S.I., Jung, G.B. and Lee, D.B. (2010) Chemical properties and nutrient loadings of rainwater during farming season. *Korean Journal of Soil Science and Fertilizer*, **43**, 578-583.

[18] Lee, J.S., Jung Y.K. and Lee, K.S. (1999) Chemical composition of rainwater in Taean area. *Korean Journal of*

Environmental Agriculture, **18**, 204-208.

[19] Lee, J.S., Jung, G.B., Shin, J.D. and Kim, J.H. (2004) Chemical properties of rainwater in Suwon and Taean area during farming season. *Korean Journal of Agricultural and Forest Meteorology*, **6**, 250-255.

[20] Lee, J.S., Kim, M.K., Park, S.J., Choi, C.M. and Jung, T.W. (2009) Neutralization of acidity and ionic composition of rainwater in Taean. *Korean Journal of Soil Science and Fertilizer*, **42**, 336-340.

[21] American Public Health Association (1995) Standard methods for the examination of water and waste, 20th Edition, Washington DC.

[22] Ministry of Environment (2008) Standard methods of water sampling and analysis. Ministry of Environment, Incheon.

[23] Christian, E.J. (1963) Air chemistry and radioactivity. Academic Press, England.

[24] Fujita, S.I., Takahashi, A., Weng, J.H., Huang, L.F., Kim, H.K., Li, C.K., Huang, F.T. and Jeng, F.T. (2000) Precipitation chemistry in East Asia. *Atmospheric Environment*, **34**, 525-537. doi:10.1016/S1352-2310(99)00261-7

[25] Galloway, J.N., Zhao, D., Xiong, J. and Likens, G.E. (1987) Acid rain: China, United States, and a remote area. *Science*, **236**, 1559-1562. doi:10.1126/science.236.4808.1559