Discrimination of Atmospheric versus Lithogenic Contribution to the Chemistry of Pristine Stream Water: A Study from the East of Seoul Metropolitan City, Korea

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In Seoul and the adjacent area, intense industrialization and urbanization since last 30 years have extensively disturbed the natural environments including air and streams. The pollution of air in Seoul and adjacent area has been studied by many researchers. However, the relationship between the degradation of surface water quality and the air pollution in a regional scale has not been studied. The careful examination of the chemistry of pristine stream waters around a metropolitan city is very helpful to evaluate the air-water relationship in environmental view, because the water chemistry is largely controlled by the input of air pollutants in addition to water-rock(soil) interaction, with a minimal contribution from surface pollutants.

For this study we have collected a total of 65 surface waters in the pristine streams in the east of Seoul (Fig. 1), in order to evaluate the effects of air pollution on the surface waters. It is noteworthy that air pollutants emitted in Seoul area are mostly transported to the study area, as the regional wind blows are dominated by westerlies (Fig. 2). The collected samples were analyzed for major cations and anions (Table 1).

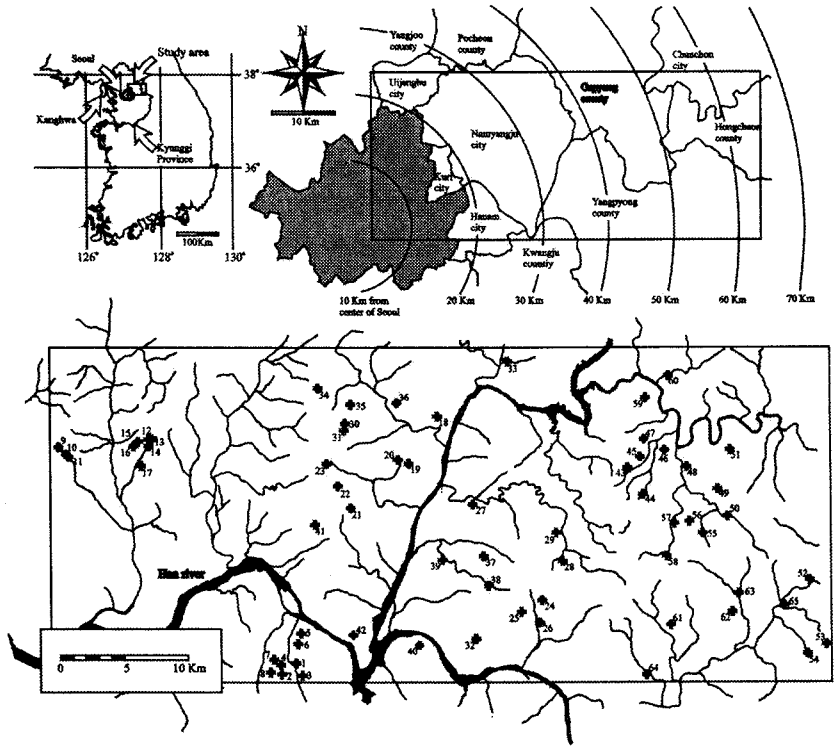

Fig. 1. Location map of the study area, showing the sampling sites. The distance scale is measured from the City Hall.

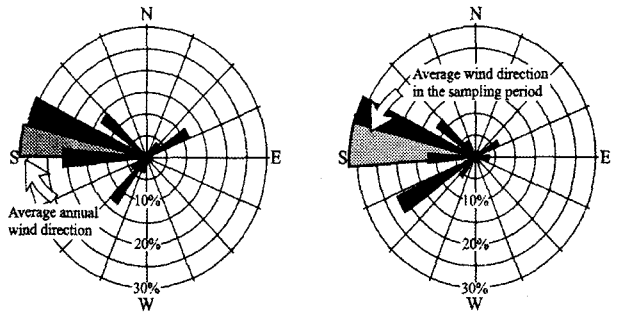

Fig. 2. The rose diagram showing the direction of wind blow in the Seoul area in 1998 and sampling periods. It is noteworthy that the study area is located in the westerlies' region.

Table 1. Mean values of physicochemical data of pristine stream waters in this study

Distance (Km)	number of samples	pH	TDS (mg/l)	Dissolved constituents (mg/l)									
				Na^+	K^+	Mg^{2+}	Ca^{2+}	SiO_2	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	F^-
10-20	9	6.4	54.0	5.9	0.6	1.3	7.6	-	8.3	15.3	5.9	9.0	0.1
20-30	13	6.7	59.4	4.4	0.7	1.7	7.7	-	5.2	9.3	19.6	10.7	0.1
30-40	14	7.2	55.8	3.7	0.7	1.7	7.5	9.3	3.1	4.7	20.8	10.2	0.0
40-50	7	6.9	51.2	2.7	0.5	1.5	5.9	7.7	2.1	3.4	20.6	8.9	0.0
50-60	16	7.0	44.3	2.9	0.6	1.5	6.4	6.2	2.3	4.5	13.3	10.4	0.1
60-70	6	6.5	50.6	3.8	1.0	1.3	6.7	6.8	1.9	4.3	16.9	10.1	0.1

Measured SO_4^{2-} concentration in the pristine streams located near the Seoul (within 20 km) is very high (mean 15.3 mg/l; Table 1). This level is higher than that of worldwide river waters (mean 11.2 mg/l) and surface waters from remote area in the Far East. At the distance between 20 and 30 km, the mean value decrease down to 9.3 mg/l. At the distance between 30 and 70 km, the mean concentrations are lowered below 4.7 mg/l. The examination of the spatial distribution, based on graphical representation and statistical evaluation (Fig. 3), clearly shows that SO_4^{2-} concentration is decreased with increasing distance.

Figure 4 indicates that the observed stream water chemistry is very similar to the general rain water chemistry. Therefore, the water chemistry is mainly formed by atmospheric processes and water-rock(soil) interaction. In order to evaluate the relative contribution of atmospheric versus lithogenic processes to the generation of the observed water chemistry, we performed the mass balance modeling (Table 3).

The result clearly shows that the chemistry of pristine stream waters is characterized as diluted water that is similar to rain water. The concentrations of SO_4^{2-}, Na^+ and Cl^- are largely explained

by the dissolution of dry deposition. Because there is no geological source of SO_4^{2-} in the study area and the SO_4^{2-} concentration changes continuously with the distance from Seoul, we conclude that the study area receives long-range transport (at least 30 km away from the center of Seoul city) of sulfur through atmosphere by westerlies. However, the variation of the $Mg^{2+}/(Mg^{2+} + Ca^{2+})$ ratio is explained by water/rock interaction in short reaction time in the water course. Toward the remote area (e.g., Yangpyung and Hongcheon area) the stream water chemistry is more strongly controlled by the weathering of rock-forming minerals in the water course.

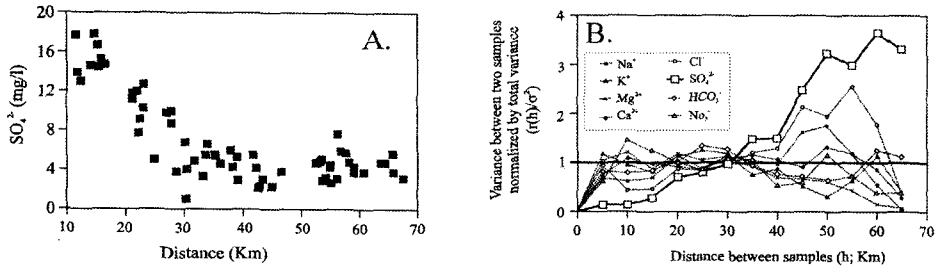

Fig. 3. A) The SO_4^{2-} concentration versus distance (from the City Hall) diagram. B) Semi-variogram showing the variance between two couples. It is noteworthy that all ions except SO_4^{2-} are converging to the total variance.

Table 2. Summary of the reaction sequence proposed for the hydrochemical evolution (from rain water) of pristine stream waters in this study

	Dissolved constituents (μmol/l)								
	H^+	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Rain water	17.3	46.7	10.6	3.4	1.5	11.2	11.2	22.5	0.0
Evapotranspriration	23.7	64.0	14.5	4.7	2.0	15.4	15.3	30.8	0.0
Dissolution of dry deposition	-	-	217.4	-	-	128.8	217.4	128.8	-
NH_4^+ assimilation	-	-64.0	-	-	-	-	-	-	-64.0
Calcite dissolution	-	-	-	-	-	46.0	-	-	92.0
Albite dissolution	-	-	24.6	-	-	-	-	-	24.6
Mica dissolution	-	-	-	11.5	5.8	-	-	-	23.0
Chlorite dissolution	-	-	-	-	47.0	-	-	-	47.0
Acid neutralization	-23.3	-	-	-	-	-	-	-	-23.3
Calculated net effect	0.4	0.0	256.5	16.2	54.8	190.2	232.7	159.6	99.3
Observed net effect	0.4	0.0	256.5	16.2	54.8	190.2	232.7	159.6	96.0
Residuals (unexplained)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-3.3

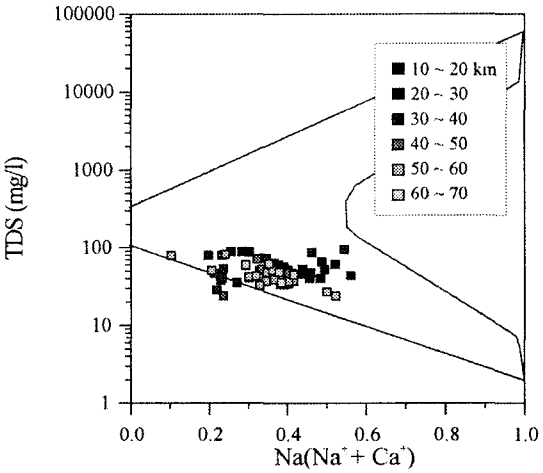

Fig. 4. Boomerang diagram of the pristine stream water compositions, showing the hydrochemical similarity of the water samples with general rain water.

We are now conducting further studies to collect sulfur isotope data for elucidating the source(s) of sulfate sulfur and to estimate the emission rate of atmospheric pollutants in Seoul. This study will be helpful to understand the air-water relationship in environmental view around the metropolitan area.

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