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Transport and Loadings of Nutrients and Dissolved Major and Trace Elements in the Yeongsan River, Korea

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Temporal variation of nutrients and dissolved major and trace elements have been studied in the Yeongsan River, Korea. There were significant temporal fluctuations in the concentrations of these elements depending upon the flow condition. NH_4, PO_4, Na, Mg, Ca, K, Mn, Cu, Ni, Zn, Co, As and U concentrations were inversely related to the flow; that is, they are the highest at low flow and the lowest at high flow. It indicates that these elements are derived from point sources such as rock weathering and/or human activities and then diluted by increasing flow. Meanwhile, Fe and Si concentrations varied proportionally to the flow indicating that they are derived from diffuse sources including reactions within soil. The concentration-flow relationships showed that hydrology of the river is the most important factor controlling the chemical composition of the Yeongsan riverwater, which was compatible with the results of R-mode factor analysis.

Key words: nutrients, trace metals, major elements, riverwater, Yeongsan River

INTRODUCTION

Rivers transport a variety of major and trace elements to the ocean in dissolved phase. They are mainly derived from weathering in the continent and/or reactions in soil (Na, Mg, Ca, K, Si) or human activities (inorganic N and P). Trace elements are supplied to the river by continental weathering or artificial pollution. Riverwater quality is usually governed by the transport of these materials and the hydrological parameters of the river (Meybeck, 1993; Jarvie *et al.*, 1997; Neal *et al.*, 1997). There have been many studies for the transport and geochemical budget of dissolved chemical species by rivers (Gibbs 1972; Norton, 1974; Nkounkou and Probst, 1987), long-term monitoring of riverwater quality in world rivers (WHO/UNEP, 1989), and hydrological and chemical control of trace elements in riverwater (Neal *et al.*, 1997). In addition, chemical composition of riverwater together with water discharge has been used to determine the transport pathway of any chemical species and their origin (point or nonpoint source) (Probst, 1985).

The Yeongsan River is located in the southwestern part of the Korean Peninsula and flows from a summit of the Noryung Mountain to the Yellow Sea via southern Mokpo city. The river is 1,472 km long with drainage area of 3,371 km^2. The main stream of the river is 136 km long and discharges freshwater of $2,588\times10^6$ km^3 annually. However, the main stream of the Yeongsan River is highly polluted with 15.7–28.9 mg/l COD at the junction where the Gwangju tributary enters the Yeongsan River (Korea Water Resources Corporation, 1992). The Ministry of Environment has carried out riverwater quality monitoring monthly for general water quality parameters (temperature, pH, DO, BOD, COD, SS and *E-coli*) and specified hazardous material (Cd, CN, Pb, Cr^{6+}, As, Hg and ABS). The monitoring has been done at five sites of the Yeongsan River system (Ministry of Environment, 1998). However, the governmental water quality agency does not monitor for nutrients and major and trace elements even though these are very important parameters in riverwater quality assessment. Furthermore, there is little data or information about nutrients and/or major and trace elements in Korean rivers except Geum River (Shin, 1996; Choi, 1998) and Han River (Lee *et al.*, 1979; Hong *et al.*,

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1989; Choi, 1998). Thus, it is urgent to quantify the concentrations of chemical species, including pollutant materials, and to calculate their transport to the ocean in order to plan for water quality control of the river.

This study was planned and performed in order to (1) monitor the temporal variation of dissolved chemical species (NH_4, PO_4, SiO_2, Na, Mg, Ca, K, Fe, Mn, Zn, Cu, Ni, Co, As and U) in the Yeongsan River; (2) calculate the transport of the dissolved chemical species by the Yeongsan River; and (3) determine the controlling factors of the nutrients and dissolved metal concentrations for the Yeongsan River system.

MATERIAL AND METHODS

Water samples were taken at a site located approximately 0.5 km upstream from the junction where the Hampyeong tributary enters the Yeongsan River (Fig. 1). To monitor temporal variations in the concentrations and transport of dissolved chemical species, we have collected riverwater samples biweekly from July, 1998 to September, 2000. In order to prevent samples from contamination, riverwater samples were directly taken using two separate 1 *l* HDPE bottles. One bottle sample was used for the determination of SPM and nutrient concentration and another for the determination of dissolved major and trace elements.

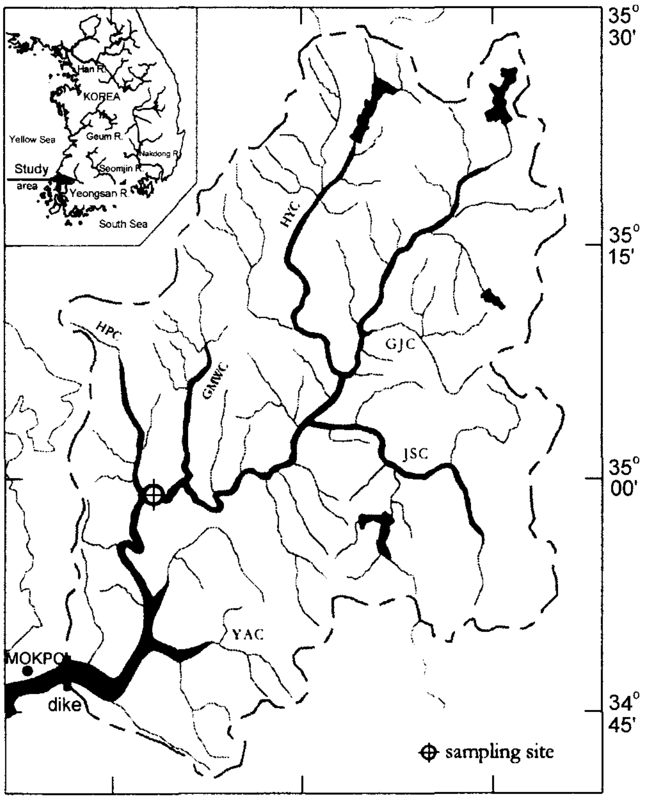

Fig. 1. Drainage basin of the Yeongsan River and the sampling site. GJC: Gwangju channel, HYC: Hwangyong channel, JSC: Jiseok channel, GMWC: Gomakweon channel, HPC: Hampyeong channel, YAC: Yeongam channel.

Water temperature and pH were measured by portable pH meter for the riverwater samples immediately after collection. One bottle of riverwater was filtered through a 0.45 μm GF/C filter paper *in situ*. The filtrate was used for the determination of nutrients (phosphate and silicate) except ammonia. Unfiltered raw riverwater was used for the measurement of ammonia to prevent potential contamination by filtering processes. The filter paper was used for the quantification of SPM concentration. Another bottle was filtered in the laboratory through a 0.45 μm membrane filter paper for the determination of dissolved major and trace elements.

The concentration of nutrients (phosphate, silicate and ammonia) was determined using a spectrophotometer after color development (Ivancîcî and Degobbis, 1984; Fanning and Pilson, 1971; Murphy and Riley, 1962). Dissolved trace metals (Fe, Mn, Co, Ni, Cu, Zn, As and U) were preconcentrated by a factor of 5 before instrumental analysis. Filtered riverwater samples were dried slowly on a hot plate to preconcentrate the dissolved trace metals. The preconcentration was carried out in an air-controlled drying box within a clean booth. Dissolved major elements (Na, Mg, Ca and K) were directly measured without any preconcentration procedure. Concentrations of Na, Mg, Ca and Fe were measured by ICP/AES (ICPS-IV model, SHIMADZ), K by AAS, and other trace metals by ICP/MS (PQ3 model, Thermo Elemental), respectively, of the Korea Basic Science Institute.

RESULTS AND DISCUSSION

Temporal variation of hydrological and physicochemical parameters

The Yeongsan River drains the southwestern part of Korea under the influence of monsoons. Water discharge of the river therefore showed great seasonal variation consisting of high discharge in summer and low discharge from fall to spring. The highest discharge was usually found in September when typhoons approach the Korean Peninsula. Daily discharge at the highest flow was 188 times that at the lowest

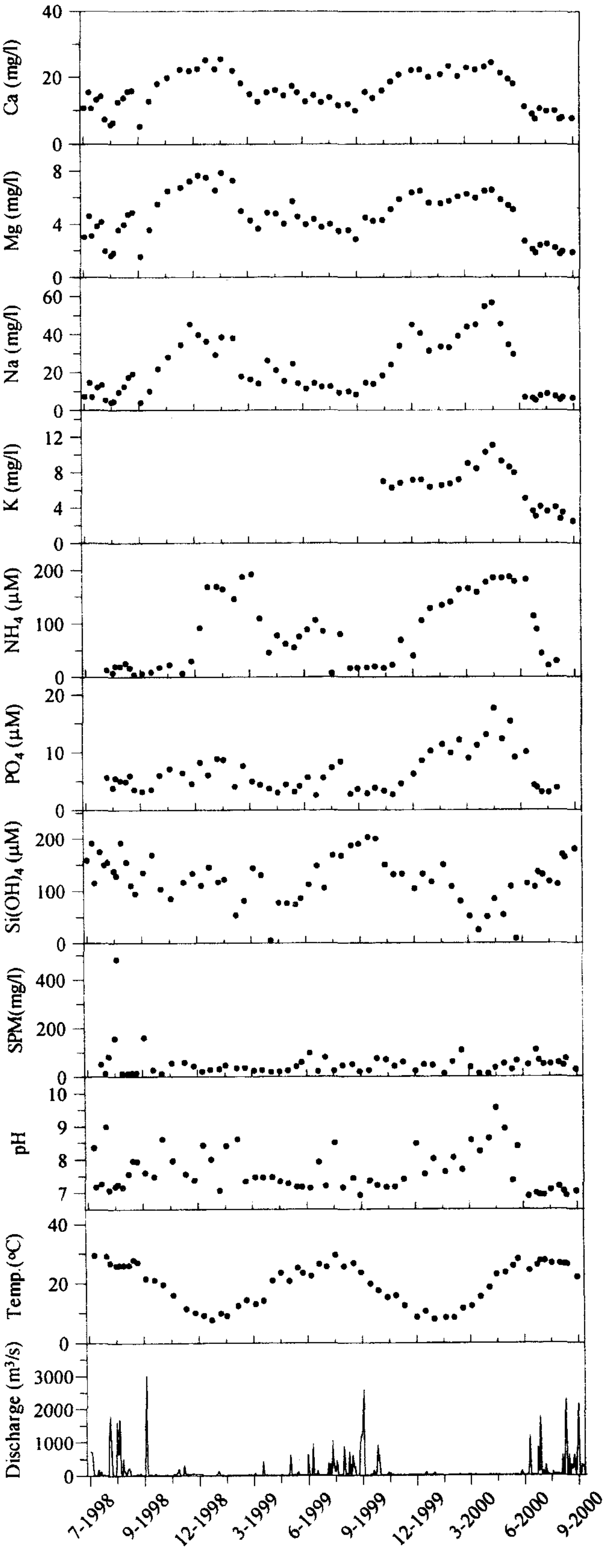

Fig. 2. Temporal variation of water temperature, pH, SPM, nutrients and major elements.

flow (Fig. 2). It is noticeable that daily discharge in the 2000 Spring was significantly lower than in 1999. This was due to the minimal rainfall in the 2000 Spring.

Riverwater temperature was high in summer and low in winter, similar to the flow variation. Temporal changes in pH were highly responsive to the flow variation. It varied 6.9–9.56 from wet to dry season. pHs of the samples taken in the dry period of 2000 were much higher than those in 1999. However, as noted above, it rarely rained in Spring, 2000. The lowered water discharge may have elevated the concentrations of riverwater cations and hence riverwater pH. The SPM concentrations in the Yeongsan River increased during high flow and decreased during low flow. The fluctuation of SPM, however, was not as great as the flow (Fig. 2). The SPM concentration increased rapidly at the early stages of flooding.

Temporal variation of dissolved chemical constituents

The concentrations of ammonia, phosphate and silicate measured during the study period varied 4.4–190 μmol/*l* (av. 37 μmol/*l*), 2.6-18 μmol/*l* (av. 3.9 μmol/*l*) and 5.1-200 μmol/*l* (av. 72 μmol/*l*), respectively. Temporal changes of nutrient concentrations were inversely related to the flow except silicate (Fig. 2). The concentrations of ammonia and phosphate increased during low flow and decreased during high flow. It indicates that ammonia and phosphate are diluted by the flow. Meanwhile, the concentrations of silicate varied proportionally with the water discharge; the highest at high flow and the lowest at low flow. It suggests that the processes governing silicate are different from the processes related to ammonia and phosphate in the Yeongsan River.

The concentrations of major elements were 4.2–57 mg/*l* (av. 8.2 mg/*l*) for Na, 1.5–7.8 mg/*l* (av. 2.5 mg/*l*) for Mg, 5.2–26 mg/*l* (av. 9.1 mg/*l*) for Ca and 2.5–11 mg/*l* (av. 1.2 mg/*l*) for K, respectively. Temporal changes of dissolved major element concentrations were inversely related to the flow variation (Fig. 2); their concentrations showed increases during low flow and decreases during high flow. It indicates that major elements are diluted by flow.

Major elements in riverwater are usually in negative correlation with water discharge because these elements are generally derived from chemical weathering of rock and minerals (Markewitz *et al.*, 2001). Ca, Mg and K showed maximum concentrations during low flow. When water discharge increased, the

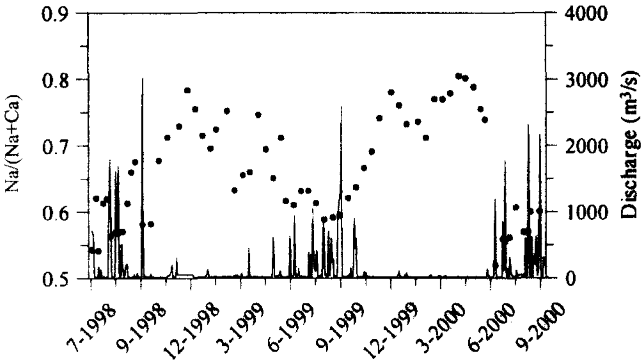

Fig. 3. The variation of Na/(Na+Ca) ratio calculated on a molar basis.

concentrations of Ca, Mg and K decreased as a result of dilution by surface waters entering during rain events. The concentration of Na also increased during low flow and decreased during high flow. However, depending upon the flow condition, the differences between the highest and lowest concentrations are greater for Na than Ca, Mg and K.

The ratio of Na/(Na+Ca) is used to infer whether the riverwater cations are derived from precipitation inputs or mineral weathering. A ratio approaching one indicates little contribution from mineral weathering, while a smaller ratio indicates greater weathering inputs (Drever, 1997; Markewitz *et al.*, 2001). In the Yeongsan River, the ratios of Na/(Na+Ca) are 0.52–0.80. It becomes highest at low flow and lowest at high flow, varying inversely with the flow (Fig. 3). It is in contrast with the thought that weathering inputs are the greatest during low flow. Except in coastal areas, elevated concentrations of Na are characteristic of domestic effluent in rivers draining urban industrialized areas (Jarvie *et al.*, 1997). Storm flows during the period of high discharge may dilute the concentrations of Na more rapidly than the weathered products of Ca, Mg and K. It may result in high Na/(Na+Ca) ratio in the dry period and low ratio in the wet period.

Temporal variations of dissolved trace elements were closely related to the flow variation (Fig. 4). In general, the concentrations of dissolved trace elements increased during low flow and decreased during high flow except Fe. Dissolved Mn, Zn, Cu, Co, Ni, U and As clearly show the opposite trend to the flow variation; their concentrations were highest at low flow and lowest at high flow. However, the concentrations of dissolved Fe covaried with flow. It suggests that there may be at least two different sources of trace metals in this river.

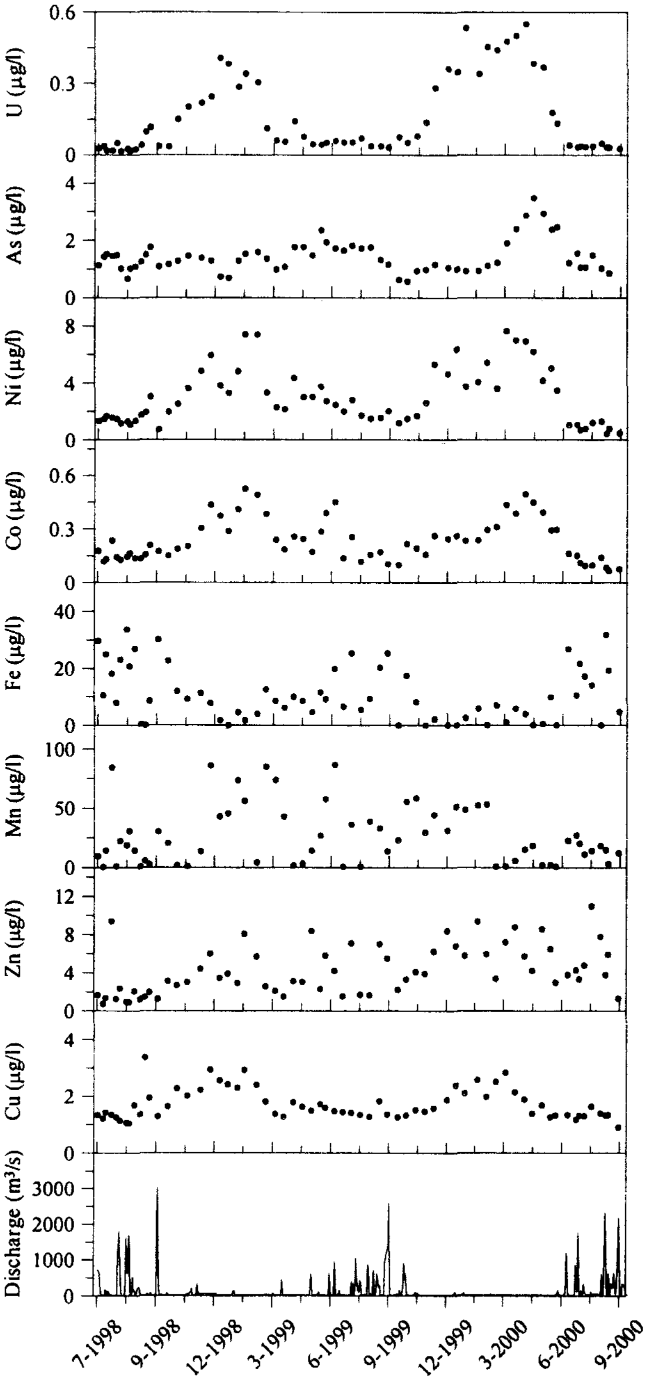

Fig. 4. Temporal variation of dissolved trace elements.

Concentrations of trace elements were n.d.–34 µg/*l* (av. 21 µg/*l*) for Fe, 0.6–87 µg/*l* (av. 25 µg/*l*) for Mn, 0.07–0.52 µg/*l* (av. 0.16 µg/*l*) for Co, 0.46–7.6 µg/*l* (av. 1.4 µg/*l*) for Ni, 0.91–3.4 µg/*l* (av. 1.3 µg/*l*) for Cu, 0.76–11 µg/*l* (av. 3.0 µg/*l*) for Zn, 0.58–3.5 µg/*l* (av. 1.1 µg/*l*) for As and 0.01–0.55 µg/*l* (av. 0.04 µg/*l*) for U. The concentrations of dissolved As

Table 1. Concentrations of nutrients and dissolved major and trace elements in the Yeongsan River and other rivers.

Rivers	Na (mg/l)	Na (mg/l)	Ca (mg/l)	K (mg/l)	NH_4 (μM)	PO_4 (μM)	$Si(OH)_4$ (μM)	Fe (μg/l)	Mn (μg/l)	Co (μg/l)	Ni (μg/l)	Cu (μg/l)	Zn (μg/l)	As (μg/l)	U (μg/l)	References
Yeongsan	8.2	2.5	9.1	1.2	37.1	3.9	72.2	21.4	25.4	0.2	1.4	1.3	3.0	1.1	0.04	this study
Geum	16.5	3.2	17.3	4.2	131.6	3.0	110.0	50.7	49.4	0.3	2.0	2.1	2.2		0.21	1,2
Han																
North	2.3	1.0	3.5	0.8			18.3									3
South	2.8	3.1	18.4	1.0			91.7									4
Lower reach								3.7-54.4	0.28-64.9	0.05-0.45	0.3-5.5	0.58-3.74	0.06-19		0.05-0.46	2
Aprok						0.0	168.4									5
Rhine	99.0	10.8	84.0	7.4	92.9	11.3	91.7	35.0	5.2		20.0	34.0	330.0	13.0		6,7,8
Changjiang	4.1	6.4	45.0	4.1	14.6	0.6	95.0		0.5-1.5	0.1	0.12-0.29	1.14-1.33	0.04-0.08			5,9,10,11
Huanghe	49.0	22.0	50.0	2.4		0.4	296.0		0.55-2.20	0.006-0.03	0.29-0.59	0.95-1.53	0.065-0.33			5,9,12
World average	5.3	3.1	13.3	1.5	1.1	0.3	173.3	40.0	8.2	0.2	0.5	1.5	0.6	1.7	0.24	8,13,14

(1) Shin, 1996; (2) Choi, 1998; (3)Hong *et al.*, 1989; (4) Lee *et al.*, 1979; (5) Zhang, 1996; (6) Zobrist and Stumm, 1980; (7) Salomons and Förstner, 1984; (8) Meybeck, 1993; (9) Hu *et al.*, 1982; (10) Edmond *et al.*, 1985; (11) Elbaz-Poulichet *et al.*, 1990; (12) Zhang and Huang, 1993; (13) Martine and Whitfield, 1983; (14) Martine and Windom. *1991*

in the Yeongsan River meet the requirements of the riverwater quality standard designated in 1998 by the Ministry of Environment (the concentration of As can not be higher than 0.05 mg/*l*). Since the riverwater quality standards of the Ministry of Environment do not designate concentration limits for the other elements studied in this paper, we cannot compare the concentrations of other elements. But, the concentrations of trace elements dissolved in the Yeongsan River are relatively low compared to other polluted rivers (Table 1). For the majority of elements in which concentrations vary inversely with flow, flow variation is higher or much higher than concentration variation of the elements. This means there may be other sources of the dissolved chemical species in the surface runoff which enter the riverwater during rain events.

Evolution of dissolved chemical species with discharge

The relationship between the concentration of a dissolved chemical species and water discharge can provide information about sources of the species dissolved in riverwater (Holland, 1984; Probst *et al.*, 1992; Meybeck, 1993; Elbaz-Poulichet *et al.*, 1996). Fig. 5 and 6 show the relationships between the concentrations of dissolved chemical species and the instantaneous water discharge in the Yeongsan River. The concentrations of ammonia and phosphate are inversely related with the flow; they are concentrated at low flow and diluted at high flow. It indicates that the ammonia and the phosphate mainly come from point sources of industrial or domestic effluent. In the drainage area of the Yeongsan River, there are wide agricultural areas and stock-raising farms (Yeo-

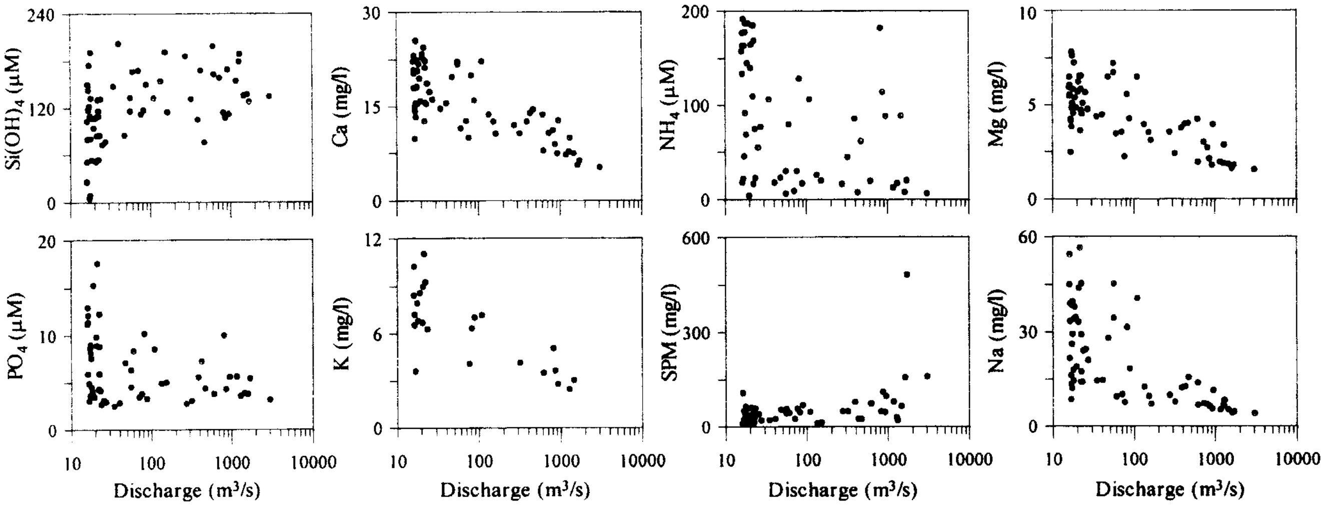

Fig. 5. Concentration-discharge relationships of nutrients and major elements.

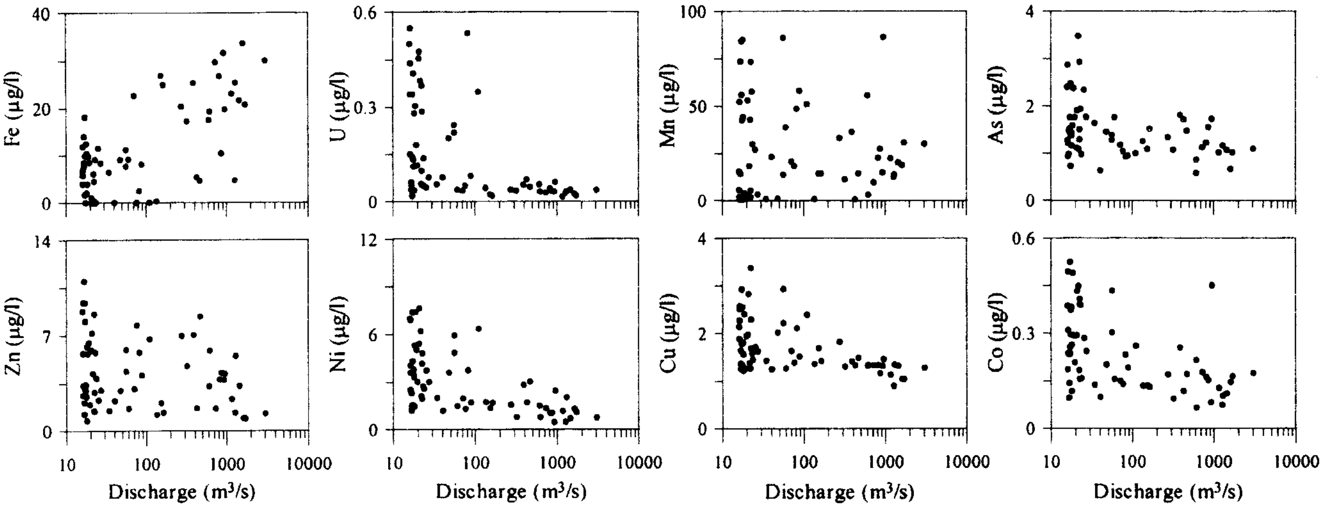

Fig. 6. Concentration-discharge relationships of dissolved trace elements.

ngsan River Environment Management Office, 2002, on web). Moreover, the Yeongsan River flows through many industrial and urban areas. Thus, domestic sewage and wastes from agricultural activities and stock-raising farms may be the point sources of ammonia and phosphate. Meanwhile, the concentrations of silicate are positively correlated with the flow. It indicates that the silicate is derived from the weathering of silicate or aluminosilicate minerals in the drainage basin (Martin and Meybeck, 1979).

The relationships between the concentrations of the dissolved metals and the flow show two distinct geochemical patterns (Fig. 5 and Fig. 6). The first pattern is observed for Na, Mg, Ca, K, Zn, Cu, Co, Ni, U and As. The concentrations of these elements are highest at low flow and decrease as flow increases. Metal concentrations in riverwater are usually in negative correlation with water discharge. During low base-flow conditions, major elements such as Na, Mg, K and Ca are supplied from the weathering of bedrocks and/or anthropogenic activities and hence at their highest concentrations. As water discharge increases, these cation concentrations decrease because the riverwater is diluted by surface waters (Probst, 1985).

The second pattern is observed for Fe of which concentrations increase with increasing flow. It indicates that the main source of dissolved Fe is min-

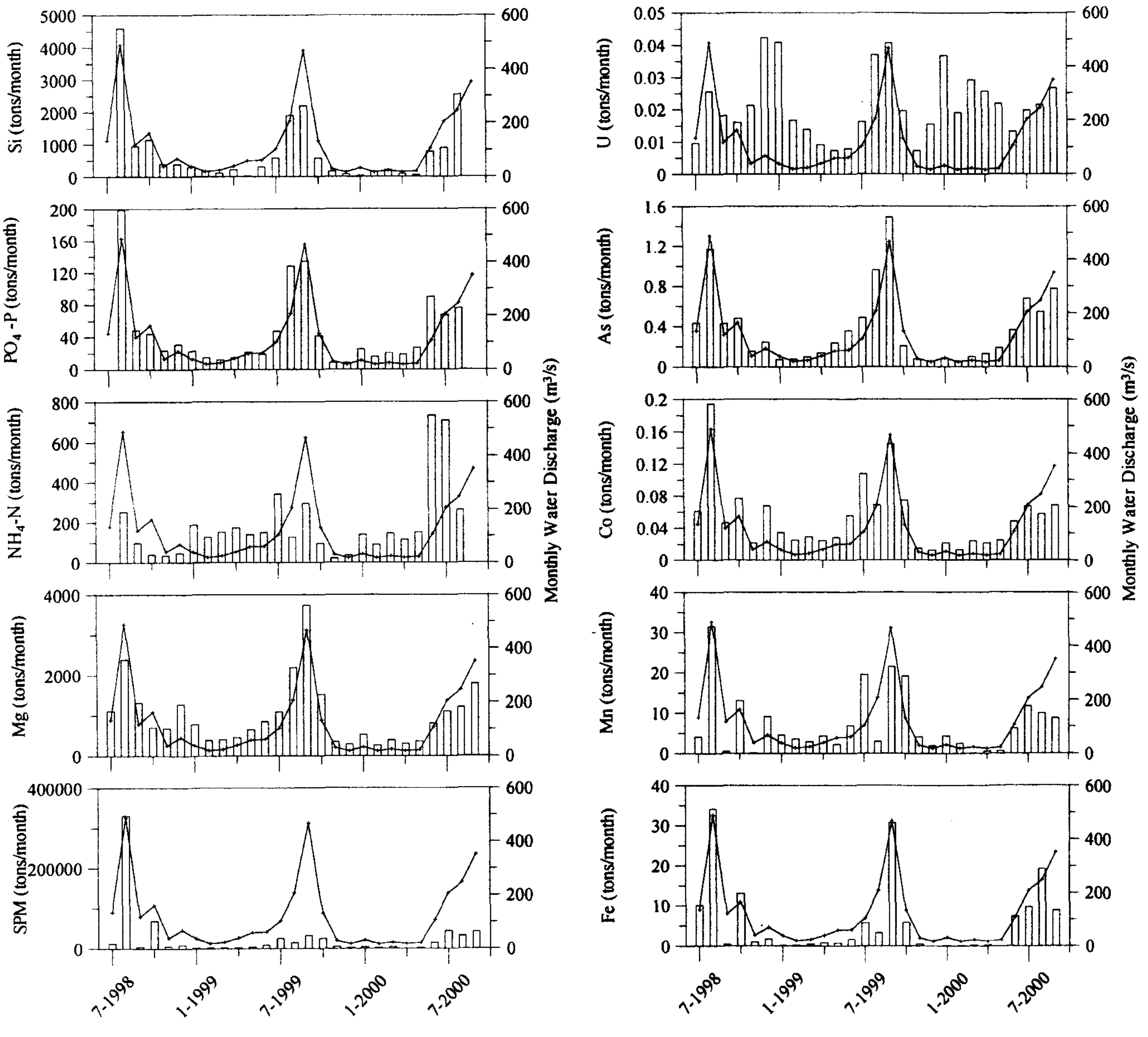

Fig. 7. Monthly transport of SPM, major elements and trace elements by the Yeongsan River.

eralogical/diffuse rather than industrial/point because significant fraction of dissolved Fe is in colloidal form in riverwater (Boyle *et al.*, 1977) and microparticulate materials passing through the filters are entering rivers at high discharge (Neal *et al.*, 1997). In this study, the colloidal Fe is thought to be leached from soil particles.

Average concentrations of dissolved chemical species in the Yeongsan River were compared with other rivers (polluted and unpolluted) and to the world average (Table 1). Concentrations of silicate, Na, Mg, Ca, K, Fe, Co, Ni, Cu, As and U were similar to the world average. Concentrations of ammonia, phosphate, Mn, Zn and Ni were much higher in the Yeongsan River than the world average. The high concentrations of these elements may be due to many industrial complexes and urban residential areas throughout the drainage basin that discharge great industrial and domestic sewage to the Yeongsan River. Extensive agricultural activity and livestock raising in the drainage areas may be another reason for the elevated nutrient concentrations (ammonia and phosphate). Domestic sewage may also contribute to the elevated nutrient concentrations.

Transport of dissolved chemical species by the Yeongsan River

Monthly discharges of dissolved chemical species are calculated and shown in Fig. 7. The solid line represents monthly averaged water discharge and the open bars indicate monthly flux of dissolved chemical species. In general, monthly variation of dissolved chemical species, except ammonia and U, follows monthly averaged water discharge. It indicates that despite the concentration variations, the transport of dissolved chemical species is mainly controlled by the river flow. Meanwhile, monthly discharges of dissolved U show the peak values both at highest and lowest flow. Monthly discharge of U flux at low flow is high because U concentrations are much higher at low flow than those at high flow. For ammonia, it is notable that monthly averaged fluxes are highest at the early stage of flood in Summer, 2000, which started after a long dry period. Based on the monthly discharges of each dissolved chemical species, the Yeongsan River transported 126,440 tons of SPM annually for 1999. The river also transported 1,847 tons N-NH_4, 470 tons P-PO_4, 6,643 tons Si, 44,700 tons Na, 12,693 tons Mg, 42,971 tons Ca, 50 tons Fe, 93 tons Mn, 0.6 tons Co, 7.4 tons Ni, 4.8 tons Cu, 14.5 tons Zn, 4.3 tons As and 0.2 tons U annually in dissolved phase during 1999.

Controlling factors of the nutrients and dissolved metal concentrations

The concentrations of nutrients and dissolved metals in riverwater are determined by several factors such as flow variation, weathering characteristics of the drainage system, type of soil use, the degree of human impacts etc. In order to understand the factors determining the concentrations of dissolved chemical species in the Yeongsan River system, we carried out a statistical approach. Table 2 shows the results of R-mode factor analysis by PCA method. Three factors were extracted that explain 80% of total variance. The first factor is interpreted as the hydrology effect that explains 54% of total variance. This factor dominates ammonia, phosphate, Na, Mg, K, Ca, Co, Cu, Ni, and U as negative loading. These elements are thought to be derived mainly from point sources of industrial waste, domestic sewage or weathering products and diluted by increasing flow. Fe and silicate have positive loading on the first factor, which

Table 2. R-mode factor loadings by PCA method

	Factor 1	Factor 2	Factor 3	Communality
Discharge	-0.66		0.40	0.69
pH	0.88			0.82
Temp.	-0.49	0.80		0.95
SPM	-0.49		0.51	0.51
NH_4	0.61	0.54	0.36	0.80
PO_4	0.77			0.75
$Si(OH)_4$	-0.60	-0.59		0.72
Na	0.98			0.95
Mg	0.93			0.94
K	0.93			0.90
Ca	0.94			0.96
As	0.61	0.72		0.92
Co	0.94			0.95
Cu	0.57	-0.50		0.59
Fe	-0.67			0.58
Mn		-0.79		0.71
Ni	0.93			0.88
U	0.89			0.87
Zn			-0.76	0.74
Variance	0.54	0.18	0.08	

Factor 1; Hydrologic control (dilution and flushing)
Factor 2; Biogeochemical (precipitation)
Factor 3; Other sources in low water period

indicates Fe and silicate are derived from diffuse sources (reactions within soil layer).

The second factor explains 18% of total variance and dominates the concentrations of Mn and As as negative loading. It is related to temperature as positive loading. In riverwater, the oxidation of Mn(II) to Mn(II) is favoured in the presence of organic matter at high temperature (Ponter *et al.*, 1990; 1992). Thus, the second factor is considered as the biogeochemical reaction factor.

The third factor explains 8% of total variance and dominates SPM and Zn as positive and negative loading, respectively. In riverwaters, particle-related reactions control the concentrations of dissolved Zn together with pH (Shiller and Boyle, 1985). The third factor, however, describes only SPM and Zn, and pH has no loading on this factor, which makes it difficult to identify the third factor. We suspect that the contribution of atmospheric input may play a role in the concentration of dissolved Zn during the dry period.

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