SPATIO-TEMPORAL VARIABILITY OF DISSOLVED NITROGEN IN STREAMS OF DANSHUEI DRAINAGE SYSTEM

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Spatio-temporal investigation of dissolved inorganic nitrogen (DIN; NH$_4$, NO$_2$, NO$_3$) and dissolved organic nitrogen (DON) in the river water was conducted in the Danshuei River drainage system, which drains through uncultivated upstream to downstream having high population density. On average, NO$_3$ is the dominant form of DIN in river water at upstream, while NH$_4$ dominates the middle-down stream river water. Concentrations of DIN showed an increasing trend from up to down stream reach. Inputs from agriculture and urban sewage source significantly affect the spatial pattern of nitrogen speciation and concentration over entire drainage system.

Water runoff and human population are two major factors determining nitrogen export. After logarithmic transformation, the yields of total dissolved nitrogen (TDN) can be parameterized as functions of population density and runoff depth (runoff/area) within the watershed of Danshuei River. This empirical function might be applicable to estimate total nitrogen load for other mountainous small watersheds.

INTRODUCTION

From a global perspective, human activities have more than doubled the amount of nitrogen cycling in terrestrial ecosystems since the industrial revolution (Galloway et al., 1995; Vitousek et al., 1997). These increasing N inputs might result in substantial risks to various aspects for many terrestrial, fresh water and coastal ecosystems (Schindler and Bayley, 1993; Kopacek et al., 1995; Howarth et al., 1996; Vitousek et al., 1997). Galloway et al. (1994) indicated that 2/3 of energy-related N emissions are expected to occur in lower latitude regions by the year 2020. Thus the impacts may become more severe in low-latitude ecosystems relative to those occurring in temperate zones (Downing et al., 1999); however, patterns in nutrient fluxes in low-latitude ecosystems are often less well documented than those for ecosystems in higher latitudes.

Oceania islands in the tropics and subtropics are characterized by mountainous watersheds, high precipitation and high water runoff, which collectively accounts for 12% of the global water discharge (Meybeck et al., 1989; Milliman, 1991). The surface water runoff may deliver in-negligible nutrients to the costal oceans. Estimating
contemporary N fluxes, input-output budget and understanding their sources and controlling factors is thus the urgent task to undertake in order to expand our knowledge of how tropical and sub-tropical watersheds respond to human alterations.

Taiwan is a subtropical mountainous island, 160 km off the southeast coast of mainland China. China is now a major source of atmospheric pollutants for adjacent countries (Bashkin and Park, 1998). Previous reports have indicated that atmospheric DIN deposition in Taiwan ranges from 1400 to 2300 Kg N km\(^{-2}\) y\(^{-1}\) (King et al., 1994; Chen et al., 1998; Lin et al., 2000), which are higher than inputs to most regions in unpolluted areas of Europe (Parker, 1983), North America and Japan (generally < 1500 Kg N km\(^{-2}\) y\(^{-1}\); Ohrui and Mitchell, 1997) and areas of similar latitudes (Prospero et al., 1996). In addition, urbanization and local agricultural activities likely supply additional amounts of nitrogen that can be transported to surface waters and coastal areas. Multi-scale (i.e., local and regional scales) anthropogenic factors in Taiwanese watersheds have likely altered natural patterns in N cycling and thus offer us an opportunity to explore how subtropical watersheds might respond to future changes.

MATERIALS AND METHODS

Study area
The Danshuei drainage basin (Fig. 1) locates at northwestern Taiwan being composed of three tributaries, Keelung (K), Shingdian (S), Dahan streams (D). The basement rocks are mainly Tertiary argillite-slate and metasandstone (Ho, 1975). The basin has the highest elevation of 3524 m with a length of 160 km (Fig. 1) and a mean gradient of 1/30. The annual rainfall ranges from 2000 to 4000 mm y\(^{-1}\) over the entire watershed with a mean of 3000 mm y\(^{-1}\) (Taiwan Hydrological Yearbooks). The dry season is usually from April to June. During summer (late June to September), tropical storms (typhoons) cause torrential rain, which accounts for 50 % of the annual rainfall on average. From late September to the end of March of the next year, the northeast monsoon brings rainfall, which accounts for 35 % of the total annual rainfall. The sudden increase in discharge induced by typhoon is over two orders of magnitude higher than the baseflow during the dry season.

The population density is unevenly distributed in the Danshuei basin ranging from < 10 to over 3000 persons km\(^{-2}\) (Fig. 2). The three tributaries drain through the Taipei city, where has the highest population density in Taiwan, and into the Danshuei estuary. The monitored watershed was ~2200 km\(^{2}\) in size, which excludes the lower reach with tidal effects (Fig. 2) and most of the upper watersheds have population density of < 100 persons km\(^{-2}\).

Sampling and analyses
Water samples were taken from 30 stations (Fig. 1) distributed in the drainage system. Sampling was conducted over 2 years including intervals of hourly, 2-3 days, weekly,
monthly and seasonally (wide range of water runoff). The sampling scheme cover wide spatial and temporal scales allowing us to estimate the fluxes and to examine factors governing the transport and distribution of various forms of nitrogen.

Water samples were filtered through GF/F filters immediately after collection. The filtrate were quick-frozen in liquid nitrogen and then kept in an ice chest during transport. The frozen samples were thawed and concentrations of nitrite (NO$_2$) and nitrate (NO$_3$) were measured using colorimetric methods. Nitrate was reduced to nitrite with a cadmium wire, which was activated with a copper sulfate solution, and the nitrite was converted to pink azo dye for colorimetric determination with a detection limit of 0.2 µM (Pai et al., 1990). Ammonium (NH$_4$) was determined by the indophenol blue method (Strickland and Parsons, 1972) with a detection limit of 0.1 µM. DON was calculated by subtracting total DIN from TDN, which is measured as the same method of NO$_3$ after naturalization following total digestion by using potassium persulfate.

**Estimate TDN yields and fluxes**

To estimate the DIN yield, we used the Rating-Curve method. The rating curve depicts the empirical relationship between daily TDN yield ($Y$, Kg N km$^{-2}$ d$^{-1}$) and daily runoff ($Q$, mm d$^{-1}$). The daily runoff was derived by averaging the volume of water discharge by the respective drainage area above Sts. Daily TDN yield is the product of measured TDN concentration and daily runoff. The function $Y (Q) = 10^k * Q^b$, where $k$ and $b$ are the rating coefficient and exponent, can be determined using log-log linear regression and back transformation. After we established the rating curves, we obtained $Y_i$ from any given $Q_i$ for each station. Summarized the estimated daily yield we obtained the mean TDN yield on annual basis ($Y_{annual}$). Annual TDN flux through individual station was then calculated as $Y_{annual}$ times the drainage area above the respective sub-watershed.

**RESULTS AND DISCUSSION**

**Spatial distribution of different forms of nitrogen**

The spatial distributions of DIN concentration and species within the watershed (Fig. 1) are strongly influenced by human activities. Concentrations of total dissolved nitrogen (TDN) observed at upstream stations are much lower than those observed at downstream stations, where has much higher population density. NO$_3$ is the predominant species at the upstream stations, where NO$_3$ comprised ~70% of total DIN, and DON, NH$_4$ and NO$_2$ comprised ~20%, 5% and 1% of total DIN, respectively. By contrast, NH$_4$ and DON dominated the downstream river water. The highest NH$_4$ concentration is over 300 µM.

Hydrological condition plays an important role in nitrogen output from those upstream sub-watersheds that NO$_3$ concentrations varied concomitantly with rates of water discharge (Fig. 2) showing peak values during summer typhoon flood events. The positive correlation between water discharge and concentration (thus flux) illustrates the flushing nature of DIN export. This also indicates the major DIN source is likely the
diffuse type. Such good correlation resulting in positive relationships between DIN yields and water runoff for most stations that we can establish rating curves to estimate the TDN export under various water discharge conditions.

Significant increases of TDN flux from up to down stream water were observed (Figure 3). The increase was attributed to sewage inputs from urbanized lower reach areas. Strong correlations were found among water discharge and population density. Our results showed that hydrologic conditions and human population are two major factors determining the spatial distribution of nitrogen species in river water within the watershed and output from each sub-watershed. After logarithmic transformation, the yields of total dissolved nitrogen (TDN) can be parameterized as functions of population density and runoff depth (runoff/area) within the watershed of Danshuei River. This empirical function might be applicable to estimate total nitrogen load for other mountainous small watersheds in Taiwan.

The observed DIN outputs from upstream stations (less disturbed) are relatively higher than many other watersheds in Europe (Parker, 1983), North America and Japan (generally < 1500 Kg N km$^2$ y$^{-1}$; Ohrui and Mitchell, 1997). Elevated atmospheric DIN input is likely responsible for the high background DIN yield (~600 Kg N km$^2$ y$^{-1}$). However, much higher atmospheric DIN input suggests that ~70% of input is retained or
processed within the Danshuei watershed. Long-term monitoring is needed to evaluate the potential impacts from increasing atmospheric DIN deposition.

Figure 2. Examples of positive correlation between TDN flux and water discharge rate.

Figure 3. The distribution of population density and the TDN flux through stations.
REFERENCES