Speciation and Dynamics of Dissolved Inorganic Nitrogen Export in the Danshui River, Taiwan

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Abstract

Human-induced excess nitrogen outflowing from land through rivers to oceans has resulted in serious impacts on coastal ecosystem. Oceania, occupied <2.5% land surface, delivers 12% of freshwater and dissolved materials to the ocean in global scale. However, there are limited dissolved inorganic nitrogen (DIN=nitrate+ nitrite+ ammonium) data from Oceania. In this study, we presented DIN concentrations and fluxes from a mountainous river, Danshui River, in a high-standing island, Taiwan. A river monitoring network covering various degrees of landuse and population density was implemented to explore the controlling factors of DIN export. Results showed that DIN concentration increases as the population density increases downstream-ward, accordingly, DIN is low in the headwater (~16μM) and up to ~430 μM at downstream. Similarly, DIN yield increases downstream-ward, ranging from ~160 kg-N/km^2/yr at upstream relatively pristine catchments to 7500 kg-N/km^2/yr at downstream. The ~2x higher DIN yield compared to other world rivers in similar size is caused by dense population coupled with abundant rainfall. As for per capita N yield, a low boundary (~2.5 kg-N/capita/yr) in the Danshui watershed is consistent to that obtained from developed countries. Results also reveal agricultural landuse should be considered while constructing regional DIN model. Unlike most large rivers, the dominating DIN species changed gradually from NO_3^- in the headwater (~97%) to NH_4^+ in the downstream estuary (~60%) due to sewage inputs. Given the analogous watershed characteristics of Danshui River, our case study provides a good example to infer the DIN export from the Oceania rivers.

Keywords: Oceania rivers, Nutrient fluxes, Runoff depth, Population density

1. **Introduction**

Nitrogen, a vital element in living organisms, plays a critical role in controlling primary production in the biosphere. Along with fossil fuel combustion, to meet the food demand of mankind, human has doubled the turnover rate of natural nitrogen cycle in past decades (Galloway and Cowling, 2002; Galloway et al., 2004; Seitzinger et al., 2010). The anthropogenic addition of reactive nitrogen into drainage basins includes atmospheric deposition, direct application of nitrogenous fertilizer, land use change and sewage from city. Excess nitrogen discharged from land to oceans has resulted in seasonal coastal hypoxia, harmful algal blooms, and losses in fishery production in ecosystems (Howarth et al., 1996; Rabalais, 1996; Jickells, 1998; Boesch, 2002; Turner et al., 2003; Galloway et al., 2004; Duan et al., 2007; Conley et al., 2009 Billen and Garnier, 2007; Diaz and Rosenberg, 2008). However, most of current knowledge about dissolved inorganic nitrogen (DIN) export was obtained mainly from larger river systems and developed countries in Europe and North America with much less efforts paid for developing countries in Oceania in tropical western Pacific Ocean, where is occupied by stratified oligotrophic water with limited bio-available nutrients, particularly nitrogenous nutrients (Jiao et al., 2007; Martha and Kristen, 2012).

Oceania, composed of numerous high-standing islands with mountainous watersheds, are featured with active tectonics and extremely high soil erosion (Milliman and Syvitski, 1992). Annually, ~27 tropical cyclones (typhoon) pass through this region bringing torrential rainfall to trigger flushing floods (Webster et al., 2005; Tu and Chou, 2013). Collectively, Oceania discharges 6.8 Bt of sediment annually to the ocean (~40% of the global total) even though these islands account for less than 2.5% of the global land area (Milliman and Farnsworth, 2013). Besides, Oceania rivers deliver ~12% of global fresh water and dissolved solids to the ocean (Seitzinger et al., 2005; Milliman and Farnsworth, 2013) underscoring the potential importance of DIN discharge. The DIN export from Oceania was predicted to increase to over 10% by 2030 as the consequence of urbanization, sanitation, development of sewerage systems, and lagging wastewater treatment (Bouwman et al., 2005). To our knowledge, there is no intensive network of DIN monitoring ever implemented or documented for Oceania rivers, while previous study has shown that the global models are very likely to underestimate nitrogen yields for Oceania rivers via monitoring of DIN in headwater catchments of Taiwan (Lee et al., 2013). In most global models, e.g. NEWS, did not take any Oceania river basin into consideration (Dumont et al., 2005), to better project future DIN discharge from global land surface data from subtropical small watersheds are required.

Countries in Oceania, including Philippines, Indonesia and Papua New Guinea, are all under fast developing stage. Taiwan has geographic and climatic features similar to Oceania islands, i.e., high precipitation, steep slopes, small basin areas, and frequent flood events (Milliman and Farnsworth, 2013). Moreover, the rugged terrain of these islands offer limited space to accommodate cities and agricultural lands, thus, cities all locates at downstream flood plains and inevitably tillage often on steep slope (Lee et al., 2013). With these hydrological and geomorphological similarities, Taiwan rivers have been long taken analogously as Oceania rivers (Kao and Liu, 2000; 2002; Kao et al., 2005). Because of the short water residence time in watershed, rapid flow velocity and high soil erosion, we also expect the controlling factors for DIN export, speciation and dynamics over the river continuum to differ from that in large rivers.

In global models, the most effective parameters for DIN export prediction are population and runoff (Smith et al., 2003; 2005), however, along with continuing growth in global population, per capita food consumption is projected to increase in the next few decades and we also speculate per capita food consumption in Oceania countries may deviates from other continents. Taiwan, one among the most dense population countries in the world, holds 23 million people living on a land surface area of ~36,000 km^2 (i.e., ~638 pl/km^2 (people/km^2)). The population density in the urban areas is much denser; whereas in the suburbs or in upstream catchments the density is <20 pl/km^2. The changing land use at upstream and wastewater disposal from Taipei City at downstream had resulted in significant biogeochemical influence in the receiving water bodies of entire river continuum (Wen et al., 2008). In this paper we investigate the DIN speciation and fluxes in a watershed network from upstream to downstream in the Danshui River in Taiwan with increasing degree of human alteration though different types; we correlate measured terms to runoff depth, land use and population and make a comparison with global dataset. The objectives of this study are (1) to explore the effective factors governing the DIN export and speciation; (2) to construct a more practical equation of DIN discharge for mountainous watershed. Results may serve as a scientific background for stream restoration and nutrient mitigation in Oceania rivers.

2. Materials and Methods

2.1 Danshui Watershed

The Danshuei River is the third largest river in Taiwan (Fig. 1). The Danshui River originates from Mt. Pin-Tian (3,529 m asl) with an drainage area of 2726 km^2. It drains through the capital city, Taipei, at the downstream flood plain. Taipei has 5.7 million people living on an area of 376 km^2, which is equivalent to a population density of 15,200 pl/km^2. The annual precipitation is around 2500-4000 mm/yr and annual mean temperature is about 22℃ for elevation lower than 200 m. Three major tributaries, i.e. Dahan (D), Singdian (S) and Keelung (K) River, merge to the east of Taipei City (Huang et al., 2012a). Among the three major tributaries, Dahan River draining from south to north is the longest one with the stream length of 135 km. The Shihmen reservoir in the middle of Dahan River is one of the most important hydrologic constructions for irrigation, hydroelectric power, water supply, and flood prevention in Taiwan. It serves 365 km^2 irrigation area and 1.8 million people. Another reservoir, Feitsui, located in the middle reach of Singdian River was designed for the drinking water supply for Taipei city, thus, upstream of this reservoir is well preserved. For the entire Danshui watershed, forest is the dominant landuse type (Table 1) but its proportion gradually decreases from ~97% at upstream toward ~75% at downstream (with the exception of D03, D02, and S07 representing the sub-catchments) due to the expansion of human-associated landuses. Consequently, population increases from ~10 pl/km^2 at the headwater to ~2000 pl/km^2 the downstream and reaches the maximum in the district of Taipei City.

2.2 Discharge, landuse, and population data

In Taiwan, Water Resource Agency (WRA) is responsible for monitoring of river discharge. The river discharge was estimated by substituting the consecutive water levels to the individual rating curve which is calibrated by field measurements every year. There are 10 flow gauges in the Danshui watersheds. For the sampling sites without flow gauges, the daily discharges could be derived from an area proportion of the adjacent gauges (Kao et al., 2004; Lee et al., 2013). The landuse data are retrieved from aerial photos taken during 1996–1998 by the National Land Surveying and Mapping Center. Taiwan government carried out a census in around every 10 years. The website of Department of Household Registration, Ministry of the Interior provides the township-based population data. We applied the data of the year 2000 into watershed-based density for further analyses.

2.3 Water sampling and chemistry

Stream water samples were collected at 14 sites in middle and upper reaches in 2002-2004 from the three major tributaries (Figure 1). Table 1 shows the fundamental watershed characteristics (i.e., including flow distance, watershed area, and population density), landuse compositions, and runoff depth for each sampling site. Water quality data reports by EPA (Environment Protection Administration) at downstream in 2002-2005 were taken to complete the full basin scale DIN variability (see Table 1). Information in Table 1 was arranged in sequence according to their distances to the estuary. Note that all stations were set at locations with bridges for water collection in centric channel and 8 among 20 stations (there are 2 more flow gauges where we didn't take samples) are equipped with flow gauges for flux calculation. According to changes in population density and landuse composition, we can see a wide range of human-alteration from upstream to downstream, providing great opportunity to distinguish the urbanization impacts on flux and speciation of DIN. Water samples were collected at different frequency yet basically covered both dry (Nov.-Mar.) and wet season (Apr.-Oct.). The numbers of samples at each site are shown in Table 2.

Water samples were immediately filtered through GF/F filters (0.7 μm) after collection. The filtrates were quick-frozen in liquid nitrogen for water chemistry analyses. Nitrate, nitrite and ammonium content were determined by ion chromatography (IC) using a Dionex ICS-1500 instrument with a detection limit of 0.2, 0.2, and 0.4 μM, respectively. DIN denotes here the summation of nitrate, nitrite, and ammonium concentration. The dissolved oxygen (DO) was measured in situ using the HI9828 probe produced by Hanna Instruments with the accuracy of 3μM.

2.4 Flux calculation

In this study, four commonly used methods (i.e., linear interpolation (LI), global mean (GM), flow weighted (FW), and the rating curve (RC) method) were applied to estimate the individual DIN flux of the 20 sites. Please refer to the Supplementary Information for the details. To prevent subjective or arbitrary choice, the four method-derived fluxes at each site were then averaged and normalized by drainage area to represent flux and yield, respectively.

3. Results

3.1 Spatial distribution of dissolved oxygen and DIN

Results of DIN speciation and concentrations of the 20 sampling sites are listed in Table 2. In Dahan tributary, the annual mean concentration ranged from 21 μM at upstream D13 to 378 μM at downstream EPA1907showing a downstream increasing trend. In general, mean DIN concentration in wet season was lower than that observed in dry season with only two exceptions (D13 at upstream and D03 at downstream). The compositions of DIN species changed along the river. Nitrate dominated in the upstream and ammonium emerged in the downstream. Nitrite played a secondary role in DIN composition which only accounted for <3% of DIN. DO concentration held relatively steady until EPA1907 where it dropped to 34 μM.

In Keelung tributary, annual mean DIN concentration was ~24 μM at the upstream sites and elevated to above 96 μM from K02 toward the downstream. DIN concentration reached the maximum of 284 μM in EPA1905 and was slightly moderated to 272 μM at EPA1906. In the tributary, most of the DIN concentrations in wet season were higher compared to those in the dry season (except at K05). Nitrate could contribute ~94% of DIN in the upstream reach. When river flowed by the middle reach of Keelung River (K02 and K01), ammonium rose an order of magnitude in DIN composition. While in the lowest reach (EPA1905 and 1906), ammonium dominantly accounted for ~68% of DIN concentration. Nitrate only contributed ~29% of DIN. Nitrite was merely ~3% of the DIN. DO concentration began to decrease when river flowed by K03. DO concentrations were ~270 μM in the upstream and were decreasing at a rate of ~3.1 μM /km to 30 μM at EPA1906.

In Sindian tritutary, water sampling sites were actually distributed in three main branches of Sindian River. At S12, annual mean DIN concentration was 19.7 μM comparable to the background sites in Danhan and Keelung River. At S07 and S05 that were located in another branch. S05 was at a small tributary entering the main branch downstream of S07. S05 had DIN concentration of 35μM which was lower than that at S07 (54μM). EPA1910, EPA1908, S03, and EPA1909 in the main stream were located in the urban district. At the downstream reach (between EPA1910-EPA1909), the annual mean DIN concentration ranged from 169 μM to 342 μM.

3.2 DIN concentrations and watershed characteristics

The overall longitudinal patterns of DIN concentration and population density is shown in Figure 2a and 2b, respectively. It is apparent that the annual DIN concentrations well followed the population density. We show the Pearson Correlation Coefficients (ρ) between the observed mean DIN concentrations and the potential controlling factors, including population density, discharge, and landuse compositions in Table 3. For the whole dataset, the DIN concentrations are correlated to population density (ρ= 0.89) and building proportion (ρ= 0.85) but negatively correlated to natural forest proportion (ρ= -0.75) (owing to the competitive relation among natural and building landuse, ρ= -0.80). If we take a closer examination into the upstream and downstream dataset, their controlling factors are different. For the subset of the upstream data, the DIN concentrations (dominated by nitrate) are significantly and positively correlated to discharge (ρ= 0.86) and agricultural landuse proportion (ρ= 0.87). For the downstream dataset, as expected, DIN concentrations are significantly and positively correlated to two population-associated factors, i.e. population density (ρ= 0.78) and building landuse proportion (ρ= 0.71).

3.3 Spatial distribution of DIN species

In general, the DIN concentration increased downstream-ward. However, the DIN compositions evidently changed from upstream (nitrate occupied ~88% DIN) to downstream (nitrate and ammonium both occupied ~50% DIN but ammonium dominated in the most downstream reach). DO concentrations were >200μM in the upstream and <120 μM in the downstream. The proportional compositions of DIN species changed toward the estuary (Figure 3b-3d) while DO tended to decrease (Figure 3a) and each DIN species concentration increased (Figure 3e-3h). Ammonium gradually replaced nitrate as the dominant species toward the estuary. Nitrite proportion reached its maximum in the middle reach where DO concentration remained in a medium level. Nitrite seemed to appear in the most upstream site where DO concentration tended to decrease. The correlation coefficients between DO and nitrate/ammonium proportion are 0.89 and -0.90, respectively (not shown). DIN appears in the form of nitrate at higher dissolved oxygen. On the contrary, ammonium appears at lower dissolved oxygen. Nitrite shows little correlation with dissolved oxygen (ρ=-0.27) and is hardly detected due to its low stability in the water.

3.4 DIN concentrations/yields and runoff

Figure 4 shows the scatter plots of DIN concentration and yields against runoff for the selected upstream and downstream sites at three tributaries. Generally, in the upstream sites (Figure 4a-4c, blue crosses) the higher concentrations were found in the wet season and the DIN concentration corresponded to the discharge patterns resulting in a positive concentration–runoff (C–Q) relation among the sampling periods of 2002-2005. However, for the downstream sites (red circles) the C-Q patterns revealed a relatively scattered but negative relation except Keelung tributary (see Figure 4b) implying different DIN transport mechanisms from the upstream sites. Figure 4d-4f show the log-log relations of observed DIN yields against runoff. The strong, positive correlations illustrate that hydrology exerts strong control on DIN export, particularly for the upstream sites. The relations could be well depicted by a power function with the high coefficients of determination, i.e., R^2 (>0.85), in the upstream sites. For the downstream sites, the relations were relatively scattered. However, $R^2>0.5$ still indicates the dominance of runoff on DIN export.

The cumulative DIN yields for the selected sites are presented in Figure 4g-4l. The daily yields were calculated based on the log-log relation, i.e. power law function, shown in Figure 4d-4f by substituting the 2002-2005 daily runoff into the formula. Note that the cumulative DIN yield of the upstream sites represented a stepwise increasing pattern (Figure 4g-4i) due to typhoon- triggered flood. Such high runoff events contributed a lot in DIN export annually. The cumulative DIN yield of the downstream sites (Figure 4j-4l) revealed a relatively stable increasing trend with a constant increasing rate though the yield rate was ~2x larger after mid-2004. The years of 2002 and 2003, in fact, are dry years with less rainfall. The effect of high runoff event could be also found sometimes at the downstream sites (Figure 4j-4k); however, it is site-dependent due to the spatial heterogeneity of rainfall.

3.5 Spatial distribution of DIN yields

The results of DIN yields of 2003 for the 20 sites are shown in Table 4. Since 2003 is a dry year, these yield numbers may serve as lower boundaries. Note that, the differences among DIN yields derived from four methods- were small with the coefficients of variation (CV) less than 30%, except K04 and EPA1907. The four applied methods, which have been widely discussed in the previous studies (Ferguson, 1987; Preston et al., 1988; Moatar and Meybeck, 2005), have specific advantages but none of them is specifically suitable in our study. To avoid the method-associated bias and the doubt if subjective or arbitrary choice would influence the estimated flux, in Table 4, we took mean values of the four method-derived DIN yield.

In Danhan tributary, DIN yields ranged from 175 at D13 to 2,244 kg-N/km^2/yr at EPA1907. In Keelung tributary, DIN yield was ~605 kg-N/km^2/yr for the upstream sites and abruptly elevated to larger than 1,989 kg-N/km^2/yr from K02 toward the downstream. Although the CV of the calculated yields at K04 was 66%, it did not influence the overall trend of increasing DIN yield toward the estuary. DIN yield at EPA1906 was ~7,500 kg-N/km^2/yr representing the highest DIN yield among all sub-catchments. In Sindian River, S12 represented a background DIN yield at 532 kg-N/km^2/yr. At S07, although it was located in the upstream reach, observation revealed a high DIN yield at 3,400 kg-N/km^2/yr (see below). For the downstream sites, the DIN yields were >2,500 kg-N/km^2/yr. At EPA1909, DIN yield reached 5,295 kg-N/km^2/yr. Similar to the patterns of DIN concentration and population density DIN yields also showed an evident increasing trend toward the estuary in the entire Danshui watershed.

3.6 DIN yields and watershed characteristics

The correlation between the calculated DIN yields and watershed characteristics are shown in Table 5. The DIN yield data were also grouped into two subsets. As for the whole data set, DIN yields are positively correlated to population-associated factors, i.e. population density (ρ= 0.85) and building proportion (ρ= 0.88) as the DIN concentration tendency indicates (Table 3). The correlations are more robust while only looking into the downstream subsets (ρ= 0.86 and 0.94 for population density and building proportion, respectively). However, the controlling factors for DIN yields actually change from upstream to downstream. In the upstream, discharge (ρ= 0.89) and agricultural proportion (ρ= 0.86) dominates the DIN export. DIN yields are well correlated to annual DIN concentrations regardless of which subsets.

4. Discussion

4.1 Changes of controlling factors on DIN export

Following previous studies (Smith et al., 2003; 2005), we used logarithmic linear regression model to estimate DIN export. Inclusion of annual runoff depth and population density in the logarithmic linear regression model, as in the global model, produces the best estimation. Table 6 shows the equations derived from this study and those from the references. The intercepts and coefficients of the equation shown in Table 6 are all statistically significant, i.e. $p\text{-value} \ll 0.01$. For our whole data set, the runoff coefficient, 0.79±0.41, is comparable to those of global rivers. However, the population density coefficient, 0.54±0.13, presents a ~50% larger value than those derived from rivers worldwide. The equation for the downstream dataset is similar to the one for whole dataset but with lower runoff coefficient (0.67) and larger population density coefficient (0.58), emphasizing again the significance of population-associated impacts on DIN exports. For the upstream dataset, the population density factor is removed from the equation due to its statistical insignificance. Agricultural landuse proportion is not included in the equation for the same reason, although agricultural proportion is highly correlated to DIN yield in the upstream (Table 5). It turns out that only runoff explains the DIN yield changes, leading to ~1.42 in runoff depth coefficient. Ours results show that the controlling factors for both DIN concentrations and yields change from agricultural proportion and runoff in the upstream to population density and building proportion in the downstream. Apparently, the agriculture-associated inputs (e.g. fertilization) control the DIN export in the upstream whereas the population density-associated inputs (e.g. domestic and industrial sewage) controlled the downstream.

As mentioned earlier, nitrate concentrations at the upstream sites basically increase with the increasing runoff (Table 2 and Figure 4), which illustrates a typical diffuse source where nitrate is carried along the flow pathways (Salmon et al., 2001; Kao et al., 2004). Agricultural landuse along with fertilization superimposes the background nitrate which represents the leaching status of the forest (Lee et al., 2013). Agriculture-associated inputs, e.g. fertilizer, are non-point sources which are diffused by various flow pathways (e.g. surface, subsurface, and groundwater). More runoff can purge out more non-point source from the soil (Lee et al., 2013). Previous studies have investigated less populated large river basins, e.g. Mediterranean and Black Sea river basins where pollution densities are <200 pl/km^2 with basin areas ranging 68-5526x10^{3}km^2. They found that DIN yields are generally best correlated with N fertilizer application and runoff ratio as a quantitative measure of water production in the river basins (Ludwig et al., 2010).

Typhoons, as an important contributor in annual runoff, play significant role in annual DIN export. In the neighborhood watersheds of this study, 4 typhoons bringing ~30-50% annual runoff could trigger ~20-70% annual DIN export dependent on the cultivation level within the watersheds (Lee et al., 2013). The stepwise increasing in cumulative DIN yields for the upstream sites reveal the influence of typhoons on DIN export, of which the yield is couple orders of magnitude larger compared to non-typhoon period. For example, D13 shows an abrupt jump in cumulative DIN yield in the mid-2002, at a rate of ~28kg-N/km^2/day, (Fig. 4g), which is much higher than the following period, at a rate of ~0.38kg-N/km^2/day. Afterwards, the rate remains in a relatively high level during the monitoring period, ~4.2 kg-N/km^2/day. This may imply that either the nitrogen storage in the watershed is sufficient to afford frequent purging or that the nitrogen supply to the watershed system is fast. Widespread anthropogenic N deposition (ANN) might be one of the major N sources in Oceania (Kao et al., 2004). Atmospheric deposition (long-range transport mainly from China, ~2100 to ~3400 kg-N/km^2/year or ~5.8 to ~9.3 kg-N/km^2/day) supplements the N input. The amount of atmospheric deposition is larger than the DIN yields in most of the upstream watersheds (Table 4), implying a large proportion of atmospheric deposition had been retained in the watershed. However, in Taiwan the summer wet season is also the growing season. The rapid soil erosion and fertilizer removal caused by typhoon rain in summer forces farmers to over-use fertilizer in order to maintain the crop production.

Huang et al. (2012) demonstrated that a 1% increment of active farm land use produces an increase in DIN yield from background (~2.2 kg-N/km^2/day) to ~10.4 kg-N/km^2/day. The excellent correlations between DIN concentration/yield and agricultural proportion support the influence of fertilization on DIN export in the river (Table 3 and 5). Besides, the mean runoff in 2004-2005 was ~2x larger than in 2002-2003, which is responsible for the higher DIN yield in 2004-2005, also illustrates the sufficient nitrogen storage in the soil. The estimation of the total N pool in soil at S12 (Owen et al., 2010) is 690900 kg-N/km^2, approximately 1300x the export from the watershed (Table 4), which supports our speculation of sufficient nitrogen storage.

However, K05 shows a contrary case to the other upstream sites and shows a similar case with downstream sites (except those in the Keelung tributary, Table 2). The sewages are usually characterized as point sources owing to the built-in sewer system. Given that DIN concentration/flux is relatively constant from a point source; higher runoff certainly dilutes the riverine DIN concentration. We speculate that at K05 domestic and industrial sewages may dominate riverine DIN. Point sources of DIN might mainly come from two sources, i.e. waste water treatment plant (WWTP) and rain water pumping station (RWPS). With the restriction on the treatment capacity, we presume that WWTP effluent has relatively stable DIN concentration and flux. The DIN of the effluents from the major WWTP in Taipei was measured in previous study in 2001 and was ~1718 μM (~100% ammonium) with treatment capacity of 5x10^5 m^3/day (Wen et al., 2008). Rain water pumping station is designed to pump out the rain water collected by the sewer system within the protecting embankment which prevents the city from being flooded. Therefore, the outflow from RWPS will depend on the magnitude of rainfall event but limited to the maximum capacity of the total pumps. However, the DIN concentration from RWPS may vary, relevant to the surface runoff pathways, e.g. street, playground, park, and etc. Gobel et al. (2007) measured the nutrient concentration of the urban runoff from the roofs with different material and streets with different traffic intensity, showing that ammonium and nitrate concentration ranges from ~5-344μM and ~2-258μM, respectively. Thus we suggest that urban runoff is also an important DIN source in the Danshui River because the WWTP could only deal with <5% daily runoff (average discharge of Danshui River is ~120 m^3/sec). And the

DIN in the effluents contribute <1% of the riverine export. In fact, RWPS releases interior water (inside the embankment) every day mainly by gravity and it starts to pump during high flow period when stream water level exceeds the hydraulic head of RWPS. However, to evaluate the contribution from the RWPS is impossible currently due to lacking of data. Nevertheless, the concentration-runoff relation for K05 revealed a similarity to the downstream cases as shown in Figure 4a and 4c. In fact, the relatively constant export at downstream sites (Figure 4j-4l) during high flow implies that the sewer system somehow integrates different DIN sources from its service area. For example, the water coming from upstream during high flow carries relatively lower DIN concentration may exert dilution effect on the DIN concentration in the downstream. Besides the flood events, the export rates increased synchronously since the mid-2004 (Figure 4j-4l). As mentioned above, the years of 2002 and 2003 are dry years. Thus, typhoon event and monsoon rains control the runoff, consequently, the rate and annual total of DIN yields for entire watershed. Of course, DIN supply needs to be sufficient to support such a ~2x export. Since the increases in DIN yield in 2004 were observed throughout the watershed, we suggest our studied watershed is transport dominated rather than supply-limited. Further investigations, e.g. the measurement of nitrogen isotope ($\delta^{15}N$), could be implemented to identify the sources of DIN (Ohte et al., 2010).

4.2 Implications of DIN yields in Danshui River

Figure 5 shows the relations between DIN yields of Danshui River and other global rivers against runoff (Figure 5a), population density (Figure 5b), and agricultural proportion (Figure 5c) for comparison. In the global spectrum, the Danshui River exports ~$2x10^5$ mol/km^2/yr of DIN, which is almost the world's highest DIN yield. High runoff depth and dense population density is the major causes. In terms of DIN flux, the Danshui River could export ~14000 ton-N/yr, that is ~20x higher than the estimation by the equation in Smith et al. (2003)(Table 6). In fact, consider the regional differences and watershed scale, Smith et al. (2005) updated their database and constructed watershed area-dependent equations to re-calculate global DIN export by compiling 496 rivers with different drainage areas around the world. Similarly, they suggested runoff coefficient and population density are dominant factors for DIN export estimation. However, our observation is still ~50% higher than the updated DIN yield (Table 6). Since both factors, high runoff and dense population are common features in Oceania region. Here, we summarize some basic basin characteristics, including watershed area, river length, maximum relief, and population density, for the selected Oceania rivers in Philippines, Indonesia, and Papua New Guinea in Figure 6 (Milliman and Farnsworth, 2013) to show the representativeness of Danshui River for rivers in high-standing Oceania islands.

Total 92 selected rivers draining ~1.4x10^{6} km^{2} surface land area, about ~45% of the Oceania. The Danshui River has 2697km^{2} in watershed area, 125km in flow length, 3529m in maximum relief, and ~2m in runoff, which are representative of the features of the Oceania rivers. In terms of population density, basin-based data are not available; therefore, the country-based data and the population densities in the biggest cities of each country are presented instead. Taiwan is the densest country among the Oceania islands, and Danshui River basin could stand for the densest basin because it drains through the Taipei City. Danshui River can be a case of future cities in Oceania in terms of population density. Meanwhile, we obtained a number of ~2.5 kg-N/capita/yr, which is slightly lower than the global mean value of 2.99 kg-N/capita/yr (compiled 79 of 88 rivers around world, mainly from dataset used in Liu et al., 2010 and He et al., 2011; 9 outliers were excluded). Given DIN to be runoff-controlled, our value for 2003 should be a lower boundary for DIN yield per capita. Using the 2004 runoff data, we would get ~4.3 kg-N/capita/yr since runoff in 2004 is ~2x larger than in 2003. Potentially, the number of 2.5-4.3 can be applied onto regional model for DIN export.

Our study reveals that the watershed area of Danshui River occupies 1.8x10^{-3}% of the land surface area of the Earth but discharges ~60 x10^{-3}% (~14000 ton-N/yr) of the annual global DIN export to the ocean (24.8 Tg-N, Seitzinger et al., 2005), implying a disproportionate DIN yield from small mountainous rivers underscoring their importance in ecological footprint (Billen et al., 2010) and global nitrogen cycles. Smith et al. (2005) does not include agricultural landuse in their model, yet, in our case agricultural landuse has a primary effect on DIN yield in non-populated area (Table 3 and 5). It has been found that more DIN can be flushed out with increasing extent of agricultural activities in a watershed (Huang et al., 2012b; Lee et al., 2013). Hence, more investigations on areas where diffuse source dominates with low population density are required in such high runoff mountainous watersheds. This might be also important in the global DIN export estimations for regions having such condition, e.g. Australia, South Africa and South America where fertilization is considered the most significant source of DIN export to the ocean (Dumont et al., 2005; Seitzinger et al., 2005).

Besides statistical models, Seitzinger et al. (2005) developed a hybrid statistical-process based model, NEWS (Nutrient Export from Watersheds), which is popular and well-accepted in estimating global nutrient export from 5761 watersheds. Via a function of land use, nutrient inputs, hydrology, and other factors, their DIN yield estimation for the Oceania is ~720 kg-N/km^2/yr, which resembles that obtained from relatively pristine upstream catchments (Kao et al., 2004; Lee et al., 2013 and this study) being far lower than that from the Danshui River (7500 kg-N/km^2/yr).

4.3 Transformation among DIN species

The compositions of DIN species change from the headwater to the estuary (Figure 3). The riverine nitrate is mainly influenced by soil leaching in the upstream. High temperature in summer may enhance the rates of decomposition of organic matter and nitrification within a watershed during growing season. Moreover, excess rainfall forces farmers to apply much more ammonium sulfate and urea in hope to help crop growth. Ammonium in the leachate is quickly oxidized to nitrite and nitrate. Fertilization raises the background nitrate concentration in the leachate (Lee et al., 2013). In addition, basing on the isotopic compositions of δ^{15}N and δ^{18}O in nitrate, previous study indicated denitrification process was insignificant in the upstream mountainous watersheds even in the cultivated watersheds due to rapid infiltration (Peng et al., 2012). Previous study also shows that ammonium and nitrite concentrations in the headwater catchments of Taiwan are almost not detectable (Wen et al., 2008; Lee et al., 2013).

While in the downstream, concentrated population and sewage system facilitate the input of pollutant into the river. Current research found that particulate organic matter in the downstream estuary mainly consists of phytoplankton feeding ammonium as the major nutrient source (Cheng, 2010; Liu et al., 2013). Eutrophication has resulted in hypoxia, the depletion of oxygen in the estuarine water column. The Ecopath with Ecosim software system was used to construct a mass-balanced trophic model for the Danshui estuary, also suggesting the estuary is a heterotrophic ecosystem. More organic matter is consumed than produced in the estuary (Lin et al., 2007), leading to the depletion of dissolved oxygen and the release of ammonium (from decomposition of organic matter) in the water. Low dissolved oxygen further impedes the oxidation of ammonium, resulting in the dominance of ammonium in DIN species (Figure 3).

The mountainous small rivers in Taiwan or Oceania are characterized by shallow depth, short length and high speed flow. The water parcel only takes 5 hours in high flow condition and ~24 hours in low flow to travel from upstream at 2000 m elevation to downstream outlet (Huang et al., 2012c). Apparently, the short residence time, intensive physical process coupled with inputs from variable water sources make the on-site nutrient uptake and/or diel variation of DO difficult to be detected by concentration changes. However, the biological effect accumulates longitudinally downstream. It is a complex process regarding the in-stream DO changes associated with organic matter decomposition, aeration in the air-water interface, nitrification rate, denitrification rate, and some physical parameters such as stream temperature, turbulence, and etc (Hsiao et al., 2013; Bailey and Ahmadi, 2014). Current dataset does not allow in-depth discussion about the in-stream processes. However, we found that nitrification alone could explain largely the downstream DO reduction. In the nitrification process, the productions of 1 mole nitrite and nitrate from ammonium consume 1.5 and 2 mole DO, respectively. In the calculation, we assumed the DO consumption merely resulted from the nitrification and DO began to decrease at 267 μM, the highest mean DO among the sites (use 2003 data only). Figure 7a shows the estimated DO (red open circles) could follow the spatial pattern of measured DO (blue solid circles) and fall within the measured variability of DO, implying the nitrification might play an important role in our river system. In this estimation, all nitrate was assumed as end-product from ammonium in the stream, yet, whether the ammonium was allochthonous or derived from organic nitrogen is not known. A lot more in-stream processes, such as ammonium/nitrate assimilation and nitrate removal (denitrification/anammox) should have involved in the speciation transformation during transport downstream; further investigations regarding the in-stream processes is required though our simple estimate gave overall fairly-good estimation.

It is interesting to note that the Danshui River exports the most of DIN in the form of ammonium, unlike most large rivers that export DIN in the form of nitrate (Figure 7b). For example, the Scheldt River originating in France exports more ammonium than nitrate. In Scheldt River, denitrification is observed even during the winter when the bacterial activity is lowest. Most of the nitrate is consumed in the upper part of the estuary, where partially anaerobic conditions prevail. Approximately 30% of the total dissolved nitrogen input to the estuary from the Scheldt River is lost to the atmosphere by denitrification in the estuarine zone (Wollast, 1983). From the selected rivers in Table 7, it is found that the larger the watershed and the longer the river length are, the smaller the ratio of ammonium to nitrite+nitrate is, implying nitrification might dominate in the estuaries of large rivers. However, the water residence time in estuary of mountainous river is shorter not allowing much total nitrogen removal to occur. The similarity between our and global mean DIN yield per capita may serve as a side evidence further supports our notion.

5. Conclusion

It is well known that human activities will enhance the nitrogen export from land to ocean thus alter the biogeochemical cycles in coastal zones. The Oceania has been identified as a hotspot of global DIN export, but much less effort was paid for Oceania rivers where are now developing rapidly. The Danshui River holds the highest DIN yields among world rivers due to high runoff, which could a role model for the Oceania rivers. The positive correlation between runoff and DIN yield/flux reveals that hydrology exerts strong control on DIN export, i.e., DIN in our study area is transport-dominated. The low yield in upstream, though basing on dry year data, indicates the forested watershed retains most of the DIN from atmospheric deposition (>2100 kg-N/km^2/yr) even though typhoon in summer growing season flushes more DIN out of the system. This study presents a low boundary of per capita DIN export, ~2.5 kg-N/km^2/yr, by calculating the value in a dry year. Followed the yield equation built in this study, a runoff of ~2.4m, which is very common for the Oceania region, would give a per capita export of ~2.99 kg-N/km^2/yr, similar to the world average. However, the DIN export from the low population density area should not be ignored since agricultural activities contribute a lot, given the common behavior of over-fertilization. Besides, small watershed, short length and high relief, the common features for the Oceania river, result in short residence time of river water impeding the removal of nitrogen. This is the first paper investigating DIN speciation and distribution in basin scale networks in Oceania region under wide range of human alteration. The investigation of the in-stream processes will be our next goal to fully understand the Oceania rivers. Our observational data enriches the global river database benefiting our understanding on the nutrient export from small watersheds serving as a scientific background for stream restoration and nutrient mitigation in Oceania rivers.

6. Acknowledgements

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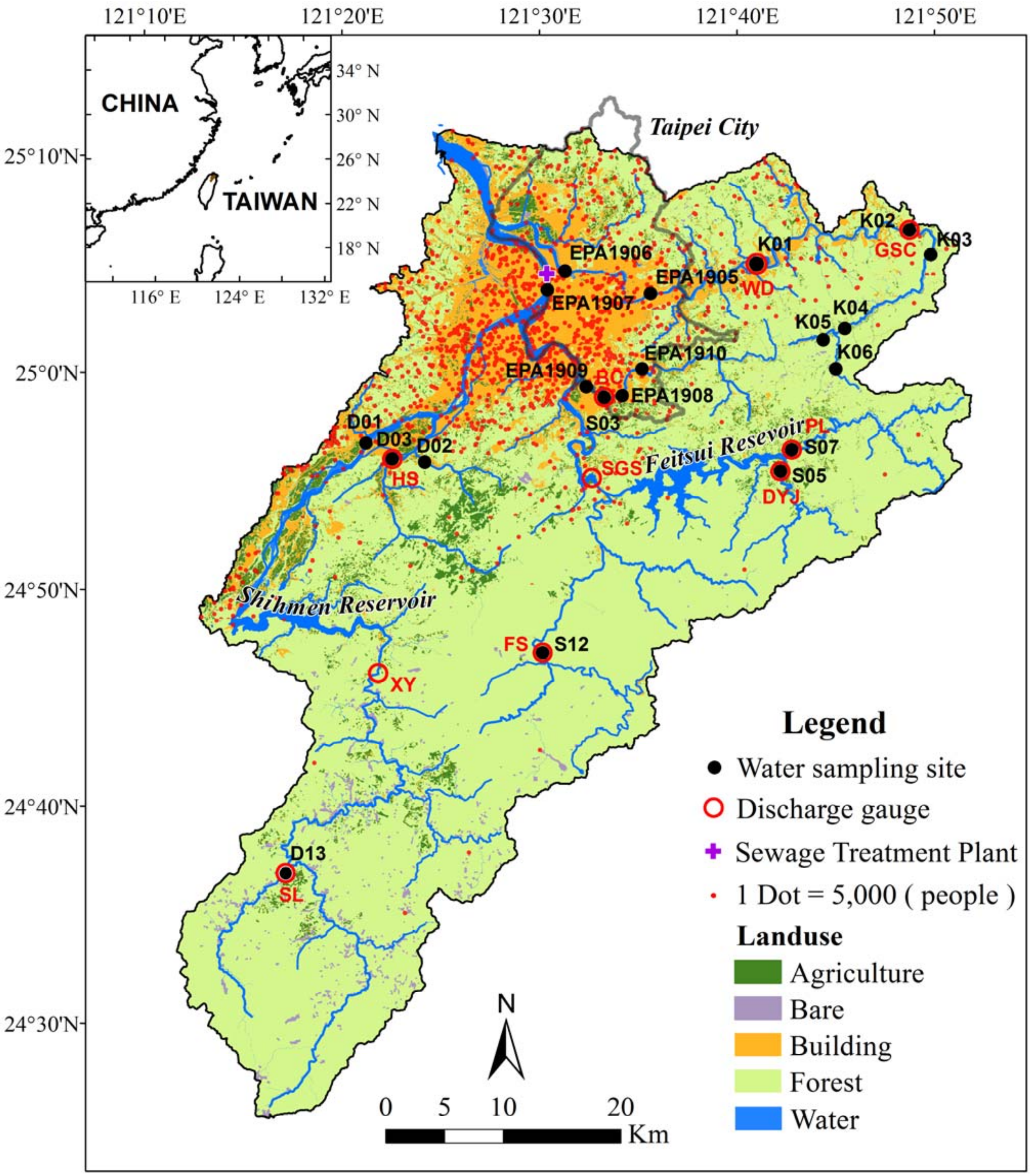

Figure 1. The map of landuse and poupulation density distribution in Danshui River watershed. The landuse and population data is sourced from the Minstry of Interior. Locations of water sampling sites (black dots), runoff gauges (red circle), and sweage treatment plant (cross symbol) are marked. The grey curve represents the boudary of Taipei City.

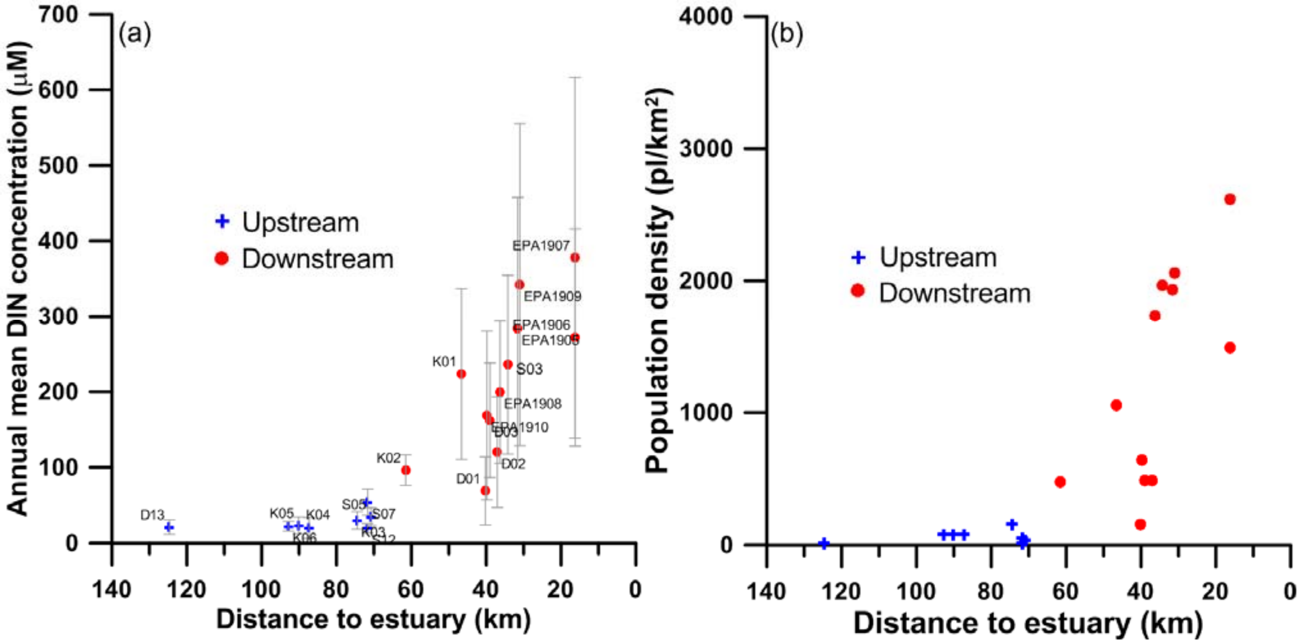

Figure 2. Longitudinal distributions of (a) measured DIN concentrations and (b) population density along Danshui River. Bar in (a) represents the standard deviation of measurements. The blue crosses and red circles indicate the upstream and downstream sites, respectively.

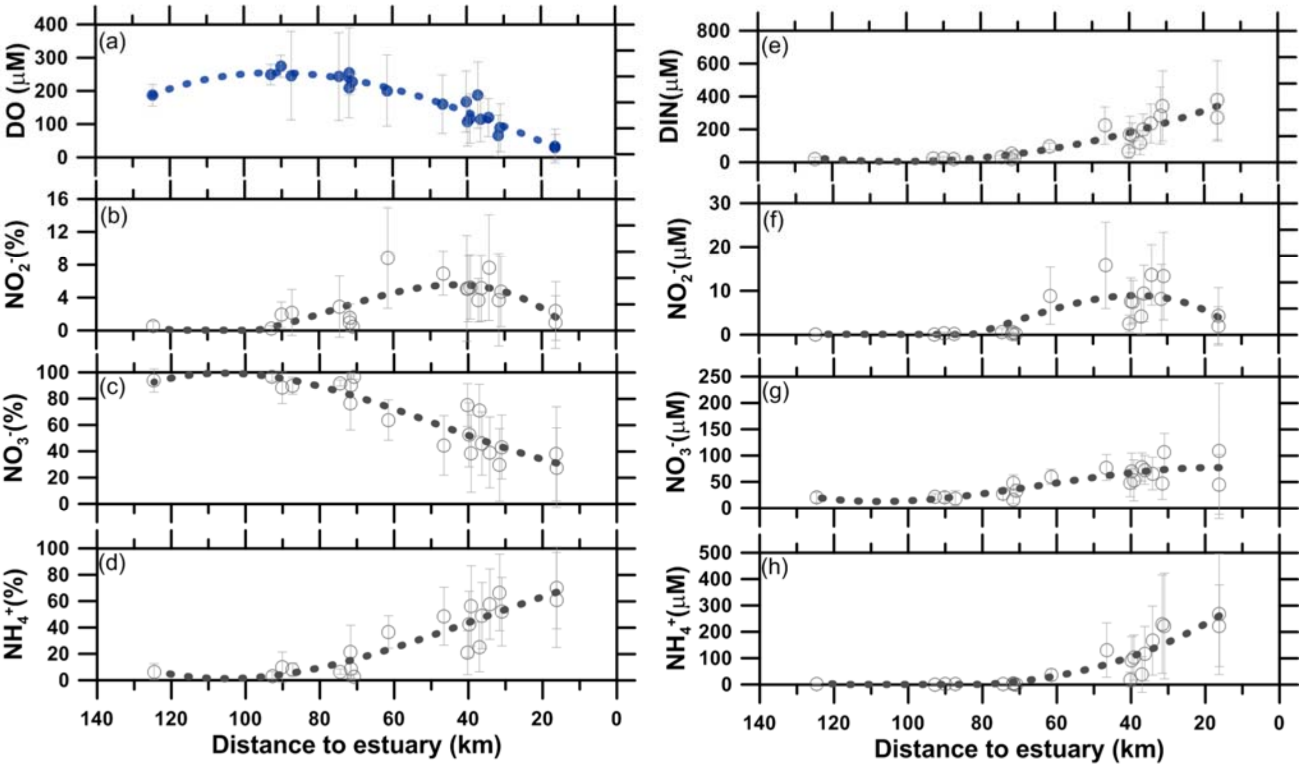

Figure 3. Longitudinal distributions of (a) dissolved oxygen, relative proportions of three DIN species, i.e. (b) nitrite, (c) nitrate, and (d) ammonium, concentrations of (e) DIN, (f) nitrite, (g) nitrate, and (h) ammonium along Danshui River. Data covers year of 2002-2005. Dashed lines are polynomial fitting line as references.

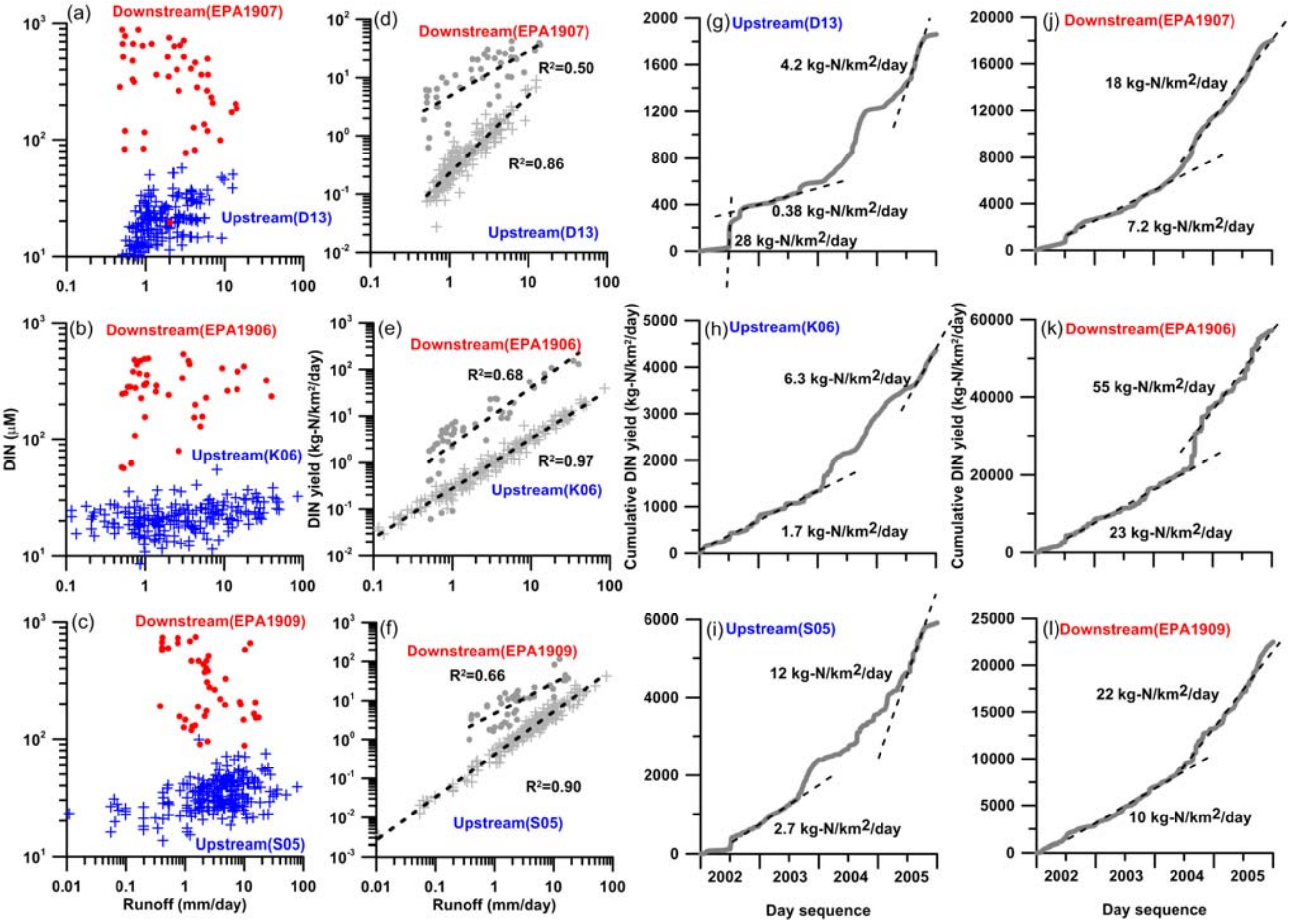

Figure 4. Scatter plots of (a, b, c) DIN concentration against runoff, (d, e, f) daily DIN yield against runoff, and cumulated yields (g through l) of selected upstream and downstream sites. Dashed lines in d, e, f stand for regression relations and in g, h, i, j, k, l indicate the mean yields of the window periods.

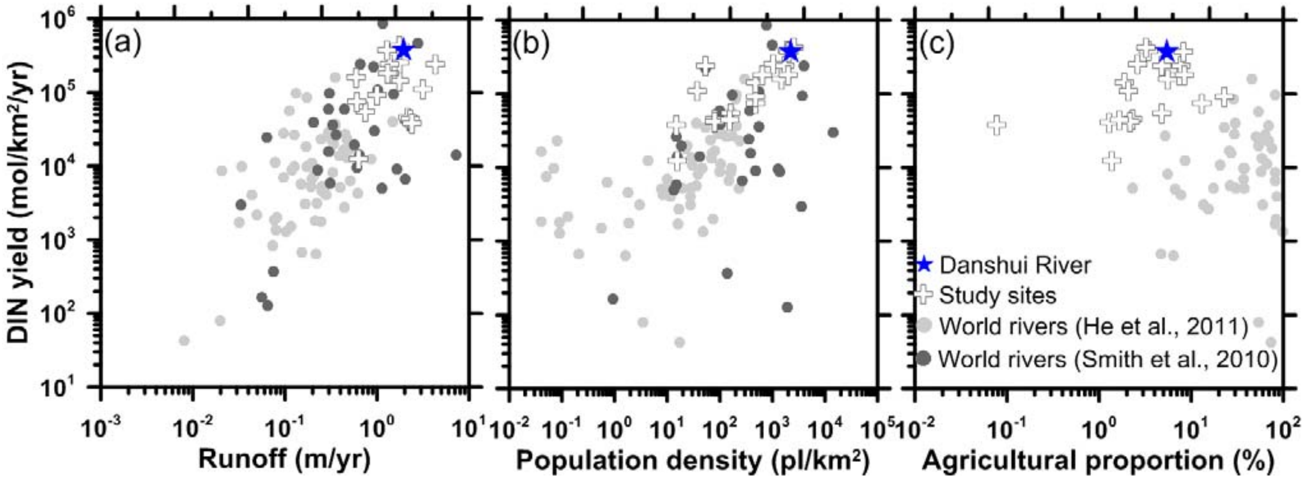

Figure 5. Scatter plots of DIN yields against (a) runoff, (b) population density, and (c) agricultural proportion. The main outlet of Danshui River and upstream observational data are plotted with global river data.

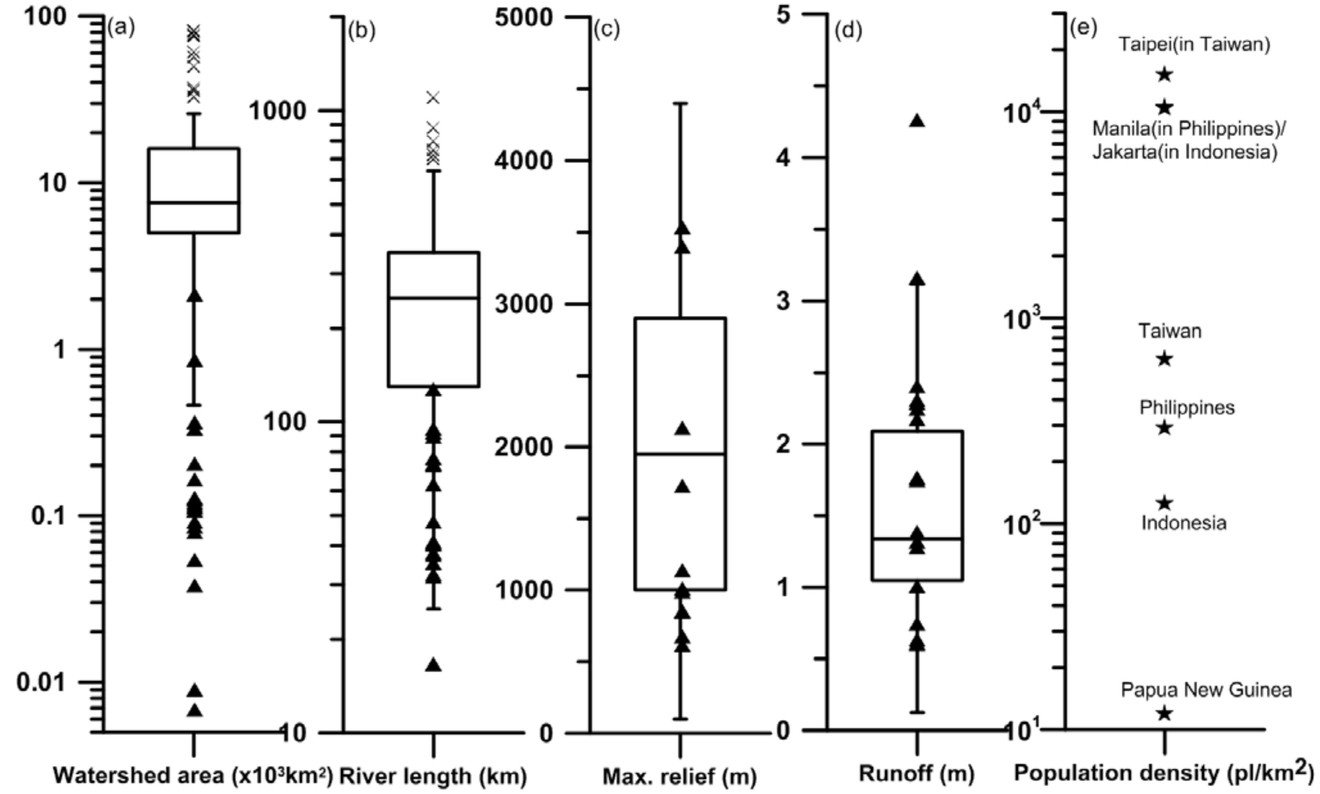

Figure 6. The spectra of characterized parameters, (a) watershed area, (b) river length, (c) maximum relief, (d) runoff, for Oceania rivers, and (d) population density in the Oceania country and its city.

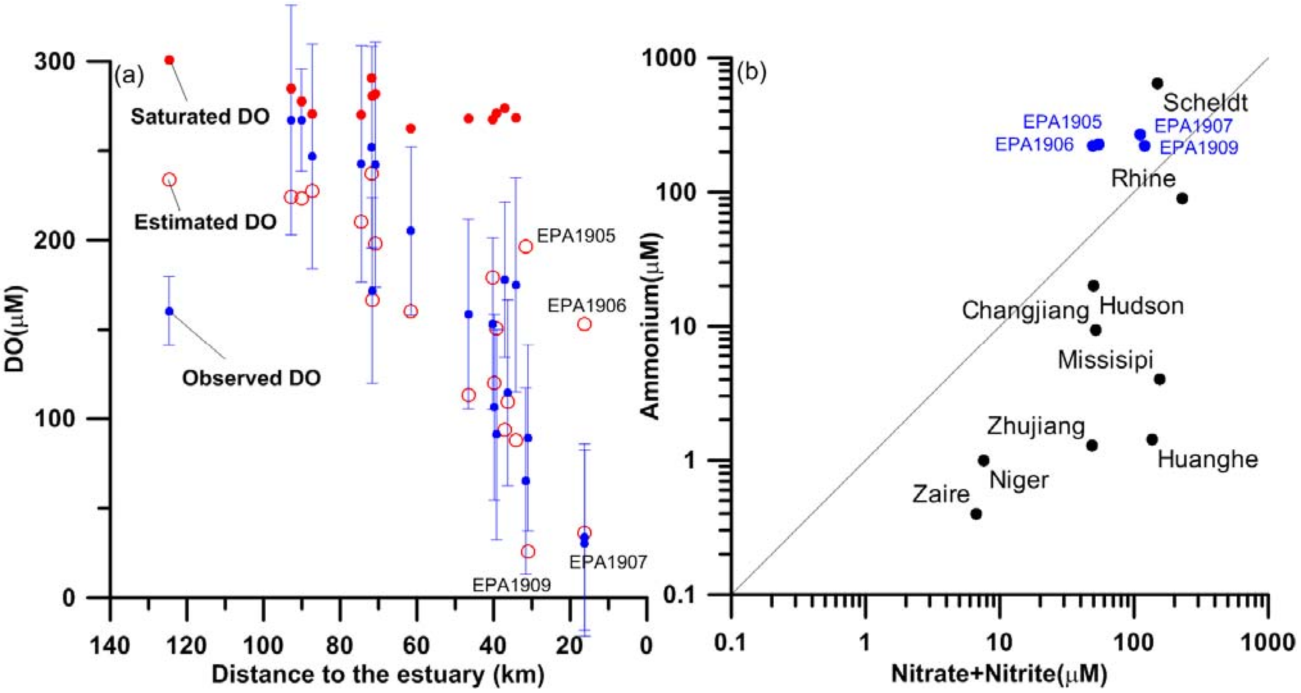

Figure 7. (a) Longitudinal distribution of DO along the Danshui River, and (b) the relations between ammonium against nitrate+nitrite concentration. In (a), the saturated DO (red dots), observed DO (blue dots with standard variations, 2003 data), and the estimated DO by considering nitrification only (red open circle; 2003 data) are shown for comparison. In (b), some large rivers are pulled together for discussion; meanwhile, 1:1 line is shown.

Table 1. Watershed characteristics, landuse compositions, discharge and rainfall for each sampling site and represented watersheds. Upstream sites are colored in grey. The distance is measured from the shoreline. Tidal excursion distance is ~10-20km upriver, depending on tidal range and weather conditions. Bare landuse usually covers landslide and outcrop.

		Watershed characteristics			Landuse Composition					Runoff(2003)			
Site ID	Tributary	Distance	Area	Population	Building	Agricultural	Natural	Water	Bare	Gauge	Annual	Dry	Wet
		(km)	(km^2)	(pl/km^2)	(%)	(%)	(%)	(%)	(%)		(mm)	(mm)	(mm)
D13	D	125	119	16	0.2	1.4	96.7	0.7	1.0	SL	632	223	407
D01	D	40	857	158	3.6	4.8	87.7	2.9	1.0	XY	740	264	474
D03	D	39	126	489	4.0	13.1	81.9	0.9	0.1	HS	606	285	321
D02	D	37	54	488	5.0	23.1	70.8	0.7	0.5	HS	1003	574	431
EPA1907	D	16	2101	1492	8.9	5.6	82.3	2.7	0.5	XY, SGS	595	197	397
K06	K	93	7	81	1.5	1.3	96.4	0.6	0.2	GSC	2243	1088	1155
K05	K	90	9	81	4.6	2.3	91.9	1.0	0.2	GSC	2170	1052	1117
K04	K	87	37	81	3.1	2.2	93.4	1.1	0.2	GSC	2305	1118	1187
K03	K	74	85	157	3.2	1.7	93.6	1.4	0.1	GSC	2279	1105	1173
K02	K	62	124	476	6.9	1.9	89.5	1.7	0.1	GSC	1741	844	897
K01	K	47	203	1054	11.4	2.6	84.0	1.9	0.0	WD	1757	959	799
EPA1905	K	32	328	1930	15.4	3.5	79.2	1.9	0.0	WD	1757	959	799
EPA1906	K	16	361	2618	19.9	3.2	74.6	2.1	0.0	WD	1757	959	799
S12	S	72	163	15	0.3	0.1	98.4	0.5	0.6	FS	2401	1109	1290
S07	S	72	111	54	2.0	4.8	91.8	1.3	0.1	PL	4259	1718	2534
S05	S	71	79	38	0.8	2.1	96.0	0.9	0.1	DYJ	3158	1295	1858
EPA1910	S	40	91	645	8.6	7.5	82.8	1.1	0.0	BC	1378	635	741
EPA1908	S	36	106	1737	13.0	7.7	78.1	1.1	0.0	BC	1375	634	740
S03	S	34	111	1969	13.9	8.5	76.5	1.2	0.0	BC	1311	605	706
EPA1909	S	31	115	2061	16.0	8.2	74.5	1.2	0.0	BC	1273	587	685
Danshui River			2697	2187	14.1	5.4	77.2	2.8	0.4		1938	971	968

Table 2. Observed dissolved oxygen (DO), DIN concentrations, compositions of DIN species and their corresponding sample numbers and sampling period. Upstream sites are colored in grey.

Site ID	Sample number	Sampling period	DIN concentration(μM)						DIN species (%)			DO(μM)
			Annual		Dry season		Wet season		NO_3	NO_2	NH_4	
			mean	std	mean	std	mean	std				
D13	198	2002/2/24-2004/4/15	21.1	9.5	17.6	6.7	24.5	10.6	94	1	6	187
D01	21	2002/2/24-2004/3/31	68.9	44.8	76.0	54.3	63.1	34.1	75	5	21	168
D03	21	2002/2/24-2004/3/31	162.4	75.9	160.0	73.8	164.3	77.6	38	5	56	117
D02	21	2002/2/24-2004/3/31	120.3	73.1	133.5	94.2	108.3	42.9	71	4	25	187
EPA1907	45	2002/1/15-2005/12/13	377.8	239.2	433.8	251.0	324.3	214.2	38	1	61	34
K06	203	2002/3/29-2004/4/30	22.1	6.2	21.1	5.6	23.3	6.6	96	0	3	249
K05	203	2002/3/29-2004/4/30	23.2	11.1	24.0	10.4	22.2	11.8	88	2	10	274
K04	8	2002/2/28-2004/2/10	20.1	13.8	16.0	8.2	26.2	17.8	90	2	8	246
K03	8	2002/2/28-2004/2/10	29.8	11.5	28.7	6.6	31.5	16.1	92	3	7	243
K02	8	2002/2/28-2004/2/10	96.3	20.0	89.1	14.3	103.4	22.3	64	9	37	201
K01	21	2002/2/28-2004/3/31	223.8	113.3	188.3	113.1	256.0	103.4	44	7	49	160
EPA1905	45	2002/1/14-2005/12/12	283.8	173.8	273.7	185.3	293.5	161.6	30	4	67	65
EPA1906	45	2002/1/14-2005/12/12	272.2	143.9	262.5	155.6	281.4	131.1	28	2	70	30
S12	8	2002/2/27-2004/2/12	19.7	6.0	17.2	6.3	23.3	3.0	77	2	22	255
S07	389	2002/2/28-2005/12/29	54.1	17.3	50.2	13.9	57.8	19.3	90	1	9	210
S05	389	2002/2/28-2005/12/29	34.8	11.8	32.9	9.0	36.6	13.7	97	0	3	228
EPA1910	45	2002/1/16-2005/12/13	168.6	111.6	158.7	74.6	178.1	137.3	52	5	42	107
EPA1908	45	2002/1/16-2005/12/13	199.4	94.0	205.2	82.3	193.9	103.7	46	5	49	115
S03	52	2002/1/5-2004/3/31	236.2	118.7	273.6	138.4	200.3	81.0	39	8	58	120
EPA1909	45	2002/1/16-2005/12/13	342.1	213.4	358.8	211.4	326.1	214.1	43	5	52	89

Table 3. The correlation matrix among population density, runoff and landuse composition. The correlation coefficients are shown. The observed DIN concentrations are grouped into two subsets, i.e. upstream and downstream data.

	Pop (pl/km^2)	Q(mm)	Building (%)	Agri. (%)	Natural (%)	Water (%)	Bare (%)
Pop (pl/km^2)	1	-0.30	0.97*	-0.11	-0.70*	0.19	-0.38
Q (mm)		1	-0.29	-0.41	0.49	-0.26	-0.35
Building (%)			1	0.16	-0.80*	0.42	-0.51
Agricultural (%)				1	-0.71*	-0.16	-0.03
Natural (%)					1	-0.28	0.33
Water (%)						1	0.10
Bare Land (%)							1
All data	0.89*	-0.45	0.85*	0.29	-0.79*	0.50	-0.35
Upstream	0.04	0.82*	0.01	0.86*	-0.49	0.54	-0.49
Downstream	0.78*	0.07	0.68*	-0.24	-0.39	0.18	-0.35

*denotes the significant correlation

Table 4. The calculated DIN yields at each sampling sites. Four calculation methods are applied in this study. Only runoff data in 2003, a dried year, was used to represent a lower boundary of DIN export in the study site. Upstream sites are colored in grey.

	DIN yield (kg-N/km^2/yr)						
Site ID	LI	GM	FW	RC	Mean	Std	CV(%)*
D13	183	160	179	178	175	10	5.8
D01	789	831	738	684	760	64	8.4
D03	936	1055	1183	1048	1056	101	9.6
D02	1354	1294	1236	1210	1274	64	5.1
EPA1907	2684	2931	2167	1193	2244	770	34.3
K06	586	528	632	576	581	43	7.3
K05	619	543	666	746	643	85	13.2
K04	222	394	618	1105	585	383	65.5
K03	389	560	720	781	613	176	28.7
K02	2465	2146	1913	1431	1989	435	21.9
K01	3886	3698	3708	3066	3590	360	10.0
EPA1905	6180	6525	5136	3799	5410	1226	22.7
EPA1906	6455	7525	7606	8152	7434	709	9.5
S12	495	485	565	581	532	48	9.1
S07	3444	3424	3465	3265	3400	91	2.7
S05	1554	1569	1598	1518	1560	33	2.1
EPA1910	2652	2787	2296	2358	2523	235	9.3
EPA1908	3473	4211	2799	2905	3347	648	19.3
S03	2929	2614	2446	2206	2549	304	11.9
EPA1909	5649	6790	4242	4501	5295	1169	22.1

*CV denotes coefficient of variation.

Table 5. The correlation coefficients correlating the calculated DIN yields to annual mean DIN concentration, runoff, population density, and landuse composition. The DIN yields are grouped into two subsets, i.e. upstream and downstream data.

	DIN(μM)	Pop (pl/km^2)	Q(mm)	Building (%)	Agri. (%)	Natural (%)	Water (%)	Bare (%)
Whole data	0.79*	0.85*	0.04	0.88*	0.05	-0.65	0.39	-0.53
Upstream	0.97*	-0.10	0.89*	-0.01	0.86*	-0.46	0.42	-0.49
Downstream	0.71*	0.86*	0.66	0.94*	-0.42	-0.43	0.12	-0.53

*denotes the significant correlation

Table 6. Yield equations as a function of annual runoff and population density. Smith et al. (2005) generated different yield equations for different basin size groups.

Data source	Basin size (km^2)	Intercept*	Runoff coeff.	Population coeff.	No. data	R^2	Est. Danshui DIN export (ton-N/yr) / yield (kg-N/km^2/yr))
This study (Upstream)	6-162	4.22±0.27	1.42±0.66	-	8	0.82	NA
This study (Downstream)	53-2101	3.49±0.60	0.67±0.42	0.58±0.20	12	0.91	NA
This study (Whole data)	6-2101	3.56±0.37	0.79±0.41	0.54±0.13	20	0.81	14569 / 5402
Smith et al. (2003)	10^1-10^7	3.99	0.75	0.35	165	0.59	659 / 244
Smith et al. (2005)	$<10^2$	4.32±0.14	0.82±0.23	0.20±0.07	62	0.19	NA
	10^2-10^3	4.09±0.09	0.61±0.10	0.38±0.06	157	0.33	NA
	10^3-10^4	3.97±0.06	0.64±0.08	0.38±0.05	155	0.39	10001 / 3708

*Yield equation: $\log(DIN_y)$= Intercept + Runoff coefficient × $\log(Q/1000)$+ Population coefficient × $\log(Pop)$, DIN_y is DIN yield in (mol/km^2/yr), Q is annual runoff depth in (mm), Pop is population density in (people/km^2), all the coefficients in the table are statistically significant, i.e. p-value<<0.01; - denotes the parameter is not used in the equation.

Table 7. The observed concentrations of ammonium and nitrate+nitrite in some large rivers and in the Danshui River and their watershed characteristics (watershed area and river length).

River*	Area (10^3km2)	Length (km)	NO_3+NO_2 (μM)	NH_4 (μM)	NH_4/ NO_3+NO_2	Reference
Zaire	3800	4700	6.7	0.4	0.06	Van Bennekom et al. (1978)
Mississippi	3300	5900	156	4	0.03	Ho and Barret (1977)
Niger	2200	4000	7.6	1	0.13	Van Bennekom et al. (1978)
Changjiang	1800	6300	52.1	9.4	0.18	Duan et al., (2000)
Huanghe	750	5500	136.0	1.4	0.01	Duan et al., (2000)
Zhujiang	490	2200	48.4	1.3	0.03	Duan et al., (2000)
Rhine	220	1400	230	90	0.39	Zobrist and Stumm (1981)
Hudson	34	490	50	20	0.40	Deck (1981)
Scheldt	22	430	150	650	4.33	Wollast (1976)
Danshui	2.7	160	49-120	222-267	1.8-4.5	This study(EPA1905-1907,1909)

*: Area and length of the selected river basins are derived from Milliman and Farnsworth (2013)