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Carbon dioxide and methane emissions from Tanswei River in Northern Taiwan

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ABSTRACT

To investigate the Green House Gas (GHG) emissions from rivers in Taiwan, environmental conditions, water qualities, and emissions of CO_2 and CH_4 were determined in the Tanswei River of Northern Taiwan, and the correlations between GHG emissions and water quality were also studied. Atmospheric CO_2 concentrations were 347.4–409.7, 342.8–417.3 and 348.5–417.0 ppm in the up–, mid– and down–stream areas, respectively; while atmospheric CH_4 concentrations were 1.59–1.98, 1.74–2.20 and 1.60–2.43 ppm, respectively. Using the headspace method with brown color bottle, CO_2 concentrations were 665–6 917, 1 485–9 369 and 1 443–9 637 ppm, respectively; while CH_4 concentrations fell into the range of 11.8–309.0, 66.0–6 288.2 and 24.1–4 627.5 ppm, respectively. Using the static–chamber method, CO_2 emission rates were –22.3–140.5, –31.7–194.7 and –27.5–226.6 mg m^{-2} h^{-1}, respectively; and CH_4 emission rates were 0.02–5.52, 1.55–144.54 and 0.11–14.10 mg m^{-2} h^{-1}, respectively. CO_2 and CH_4 emission rates had higher values in the mid– and down–stream areas than those in the up–stream area because of the input of industrial, livestock and domestic wastewaters in mid– and down–stream areas. CO_2 emission rates were negative might be because of the measurement times were at noon and some photosynthetic microbes and microalgae in the water were undergoing active photosynthesis. There is a good correlation between the results of headspace and static–chamber methods. CO_2 emissions had very significant positive correlations with Biochemical Oxygen Demand (BOD) and Suspended Organic Matter (SOM); and significant negative correlation with Dissolved Oxygen (DO). CH_4 emission had very significant positive correlations with BOD, SOM and ammonium nitrogen (NH_4–N); significant positive correlation with Suspended Inorganic Matter (SIM); very significant negative correlation with DO; and significant negative correlation with redox potential (Eh). DO, Eh, SOM, SIM and NH_4–N were the major factors that affected CO_2 and CH_4 emissions from water. In the assessment of carbon deposited amount from river to ocean, the annual carbon flows of Tanswei River were estimated with the annual flow amounts and COD, it were 8.9×10^3, 1.8×10^4, 3.9×10^4, 2.7×10^4 and 1.2×10^4 tons in 2003, 2004, 2005, 2006 and 2007, respectively.

Keywords: *Greenhouse gas emissions, river, emission rate, water quality, carbon flow*

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1. Introduction

Carbon dioxide and methane are the important long–lived Green House Gases (GHGs) because of their high potentials for thermal absorption, and they contribute 9–26% and 4–9% to global warming, respectively (Kiehl and Trenberth, 1997; Schmidt et al., 2010). Increasing concentrations of the long–lived GHGs have led to a combined Radiative Forcing (RF) of 2.63±0.26 W m^{-2}, and 9% increase since 1998 (Cicerone and Oremland, 1988; Forster et al., 2007). In nature, carbon is cycled among various atmospheric, oceanic, land biotic, marine biotic and mineral reservoirs. The largest fluxes occur between the atmosphere and terrestrial biota, and between the atmosphere and surface water of ocean (Chen, 2002; Abril et al., 2005; Hirota et al., 2007; Han et al., 2012). Carbon predominantly exists in its oxidized form as CO_2 in the atmosphere. Atmospheric CO_2 is part of this global carbon cycle, and therefore, its fate is a complex function of geochemical and biological processes. CH_4 affects the concentrations of water vapor and ozone in the stratosphere and plays a key role in stratospheric chlorine chemistry (Simpson et al., 2006). Climate changes will follow an increase in atmospheric levels of GHGs, and there is intense interest in the sources and emissions of these gases. River respiration of organic matter is a potentially major source of CO_2, and plays a major role in contributing to the atmospheric concentrations of other GHGs (Battin et al., 2008; Butman and Raymond, 2011).

In aquatic ecosystems, CH_4 is formed under anaerobic conditions in the bottom sediment and transported by diffusion in the water layer via molecular diffusion, bubbles and plants (Yang and Chang, 1998).The major sites of biological CH_4 production are sediments, rice paddies, animal wastes, ruminants, termite digestive systems, landfills and wetlands under highly reduced environments (Yang, 1998; Chang and Yang, 2003; Hegde et al., 2003; Yang et al., 2003; Hirota et al., 2007; Chen et al., 2008; Chang et al., 2009a; Chang et al., 2009b; Kim and Yi, 2009; Yang et al., 2009). Recently, the importance of lakes and wetlands as the major natural sources of atmospheric CH_4 has been shown both regionally and globally (Chang and Yang, 2003; Huttunen et al., 2003; Abril et al., 2005; Guerin et al., 2007; Hirota et al., 2007). In Taiwan, there are five longitudinal mountain ranges which occupy half area of the island, so the rivers are short and steep. The rainfall distribution is highly uneven, both temporally and spatially, and about 78% of rainfall is concentrated in raining seasons from May to October. The annual rainfall in mountain area is more than 8 000 mm, while it is less than 1 200 mm in plain (Water Resources Agency/Taiwan, 2012). There are 129 rivers and about 80 reservoirs and diversion dams in Taiwan that supply 180 hundred million tons of water each year. Total length of the major rivers is 2 933.9 km. 1 912.3 km (65.2%)

was classified as fair, 264.9 km (9.0%) was slightly polluted, 632.2 km (21.5%) was moderately polluted, and 124.5 km (4.2%) was heavily polluted in 2010 (Environmental Protection Administration/Taiwan, 2012). In addition, the deteriorated or polluted condition continuously increased at the rate of 1.1% y^{-1}. Methane production of sediments had good correlations with Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and organic matter contents (Yang, 1998). Thus, it is worth paying attention to the CO_2 and CH_4 emissions from freshwater, especially from heavily polluted rivers in Taiwan. Until now, however, there have been limited studies on the annual fluxes of GHGs in rivers of subtropical regions, and the data available are not sufficient to evaluate the potential contribution of water CO_2 and CH_4 to the global carbon budget (Hirota et al., 2007; Colwell et al., 2008; Butman and Raymond, 2011; Han et al., 2012). Based on the indexes of pollution, such as Dissolved Oxygen (DO), BOD_5, suspended solids, and NH_4–N, the extent of river pollution (river pollution index) would normally be classified into four classes in Taiwan: (1) class A indicates little or no contamination; (2) class B is slight contamination; (3) class C is medium contamination; and (4) class D is heavy contamination. In this study, three sites at classes B, D and C were selected for the aquatic CO_2/CH_4 emissions at the up–, mid– and down–stream areas of Tanswei River in northern Taiwan. The major factors of water qualities/sediment characteristics were determined. Richey et al. (2002) showed that the outgassing of CO_2 from the Amazon River network was roughly equivalent to terrestrial sequestration and over ten times greater than fluvial CO_2 export. Cole et al. (2007) reported that inland waters received roughly 1.9 Pg C y^{-1} from anthropogenic and natural sources, which was roughly twice as much C that was exported from land to the sea. This implies that there are major losses of CO_2 to the atmosphere during transit. Therefore, we estimated the annual carbon deposited amount from Tanswei River to ocean with annual flow amounts and COD. CO_2 and CH_4 concentrations and emission rates were measured with homemade apparatus to offer the information for environmental protection and GHGs emissions from fresh water.

2. Materials and Methods

2.1. Sampling sites

Up–stream (site I, Guan–Yuan Bridge, N24°57′58.4″, E121°23′37.7″), mid–stream (site II, Ta–Han Bridge, N25°02′14.8″, E121°27′40.0″) and down–stream (site III, Kung–Du Bridge, N25°07′32.0″, E121°27′15.3″) areas that contained or represented the various extents of pollution in Tanswei River were chosen (Figure 1). The Tanswei River has an area of 2 726 km^2 and is 323.4 km in length. It is one of the most important water resources in northern Taiwan, especially for Taipei City and New Taipei City. The up–, mid– and down–stream areas can be classified as classes B, D and C, respectively; and three sites were selected for the aquatic CO_2 and CH_4 emissions determinations. The water samples, sediments and air samples of each measurement sites were collected around 200 m in length and 20 m in width.

2.2. Gas sampling method

CO_2 and CH_4 across the air–water interface were collected with floating acrylic barrel–type static chambers (top diameter 25 cm, bottom diameter 28 cm, height 32 cm and volume 18 L) that were equipped with a dry battery driven fan, a thermometer and a sampling hole on the top. A life buoy of 61 cm diameter surrounded the chamber as a buoyancy apparatus and three replicate chambers were deployed every 50 m alone the bank. For CO_2 and CH_4 emission measurements, the chamber was installed at the water surface (at least 1.5 m away from the riverside) and three replicate chambers were deployed in each measurement. Gas samples from the chamber were manually withdrawn with 50 mL syringes at 0 and 30 min after deployment, and injected by the replacement method into glass serum bottles (13 mL), which had been sealed by butyl rubber stoppers and flushed with oxygen–free nitrogen gas (Chang and Yang, 2003; Wu et al., 2007).

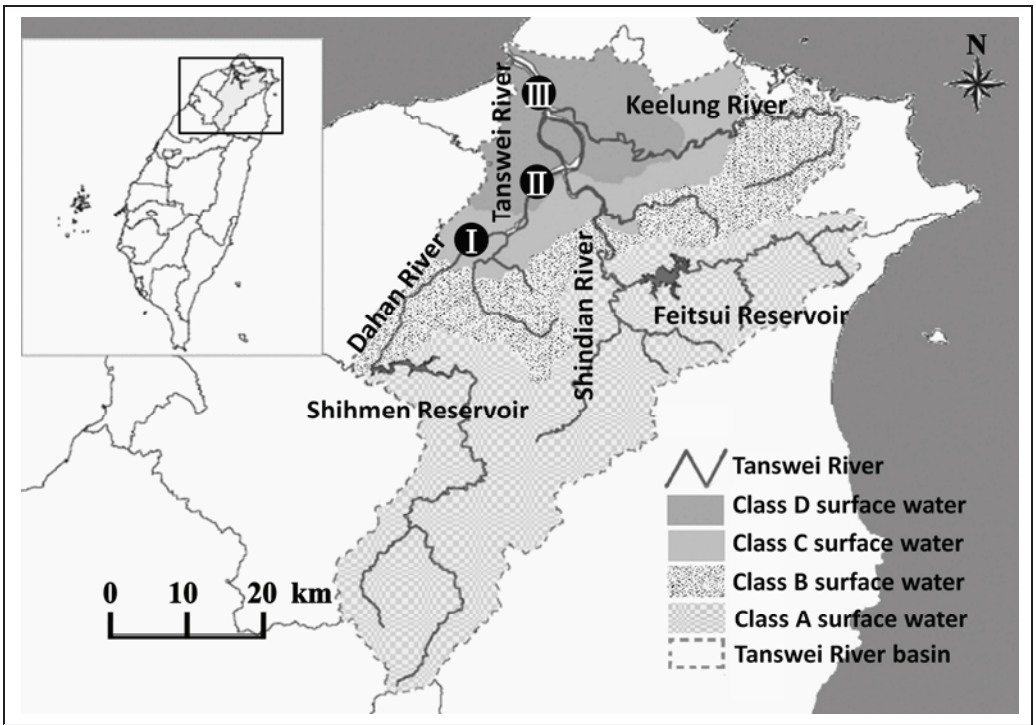

Figure 1. *The Tanswei River basin includes Tanswei, Keelung, Shindian, and Dahan Rivers. Sampling site I: up–stream area; site II: mid–stream area; site III: down–stream area.*

2.3. Gas emission from water using head–space method

A 100 mL water sample was collected with a 110 mL colorless or brown color serum bottle, and 100 µL of saturated $HgCl_2$ solution was added to retard microbial activity. The bottle was sealed immediately after collection and stored at room temperature. After equilibrium between the gas and water phases for more than 24 h, the gas phase was analyzed for CO_2 and CH_4 concentrations (Yang et al., 2008; Chen et al., 2011a; Chen et al., 2011b).

2.4. Analysis with gas chromatography

CO_2 concentrations in the gas samples were analyzed by a Shimadzu GC–14B gas chromatograph (Shimadzu Co., Japan), fitted with a thermal conductivity detector and a glass column (2.6 mm× 2.0 m) packed with Porapak Q (80/100 mesh). The column temperature was set at 100 °C and the injector and detector temperatures were both set at 120 °C. The carrier gas was N_2 at a flow rate of 20 mL min^{-1}. For CH_4 analysis, a flame ionization detector was used. The column temperature was set at 100 °C. The injector and detector temperatures were set at 130 °C. Hydrogen gas was used as the carrier gas and the flow rate was maintained at 20 mL min^{-1}. A 0.5 mL aliquot of each gas sample was injected directly into the gas chromatographic column via a 1.0 mL gas–tight syringe (Hamilton Co., USA). CO_2 and CH_4 concentrations were calculated with their standard curves (Chang and Yang, 2003; Chen et al., 2008).

2.5. Gas emission rate

CO_2 and CH_4 emission rates from water were calculated by using the experimental data and estimated by the following equation: $F=(V/A)(\Delta C/\Delta t)$ (Rolston, 1986; Chen et al., 2008). Where, F is the CO_2 or CH_4 emission rate (mg m^{-2} h^{-1}), V is the volume of chamber above water (m^3), A is the cross–section of chamber (m^2), ΔC is the concentration difference between zero and t times (mg m^{-3}), and Δt is the time duration between two sampling periods (h).

2.6. Suspended solute, total organic matter and total inorganic substance determinations

Water samples were filtered with Whatman GF/F glass filter (pore size 0.7 µm and diameter 25 mm). The residue was dried at 105 °C for 3 h as the suspended solute. After incineration at 450 °C for 3 h, the weight loss was determined as the total organic matter, while the residue was the total inorganic substance (Wu et al., 2007).

2.7. Analysis methods

Water temperature was determined with thermometer in the pale area, and air temperature was measured at 1 m height. Flow rate was measured with flow meter in the middle of river. Light intensity was detected with a Toshiba SPI–5 photometer (Tsai et al., 2007). Wind speed was measured with a weathercock (Weather link 4.0, USA). The pH was determined directly or in a 1:1 soil to water suspension (w v^{-1}) using a pH meter (Horiba pH meter F–21, USA). Turbidity was measured with a turbidity meter (WTW, Germany) in situ; while conductivity and DO were determined with a hand–held multiple–parameter instrument Multi 350i (WTW, Germany). Redox potential (Eh) was measured with a Hanna potentiometer (model no. 081–854) (Yang and Chang, 1997). Moisture and ash contents of sediments were determined gravimetrically at 105 °C overnight and at 600 °C for 6 h, respectively. Total Organic Carbon (TOC) was estimated using a TOC–5000A total organic carbon analyzer (Shimadzu, Japan). Organic matter content was calculated as C×1.724 (Nelson and Sommers, 1982). Total Nitrogen (TN) was determined by the modified Kjeldahl method (Yang et al., 1991). Ammonia, nitrate and COD were measured with a multi–parameter instrument PhotoLab S12 (WTW, Germany) at a specific wavelength. Total alkalinity was determined with a titration of 0.1 N HCl and methyl orange as the indicator. BOD was measured by azide modification of the iodometric method (Rand et al., 1976). Bacterial count was determined with Millipore Kit MHPC 10025 (Millipore, USA).

2.8. Statistical analysis

Experiments were carried out in triplicates. Statistical analysis was performed according to the SAS User's Guide (SAS Institute, 2002). Analysis of variance was performed by one–way analysis of variance (ANOVA), and the difference between specific means was tested for significance by Duncan's multiple–range test (Steel and Torrie, 1960). The difference between two means was considered statistically significant when $p<0.05$.

3. Results

3.1. Environmental conditions

The environmental conditions of Tanswei River during measurements are shown in Figure 2. Air and water temperatures were low in the winter season and high in the summer season. In most cases, air temperatures were higher than those of water temperatures. The water flow rate was also the highest in the summer season and the lowest in the winter season. The flow rate was the highest in the down–stream area, followed by the mid–stream area, and the up–stream area was the lowest. High flow rates on July 14, July 31 and November 5, 2004 were due to the typhoons and heavy rain. The wind speeds were 1.24–7.77, 0.06–8.45 and 1.02–5.36 m sec^{-1} in the up–, mid– and down–stream areas, respectively. There was no significant strong wind flow that could interfere with the monitoring of GHGs during measurement. The light intensity was between 3 and 125 000 lux during the sampling period. The pressure ranged from 727.0 to 766.2 mm Hg.

3.2. Water qualities

The water quality of Tanswei River is presented in Figure 3. The pH values, turbidities and total alkalinities were 6.95–8.34, 16.1–1 190 Nephelometric Turbidity Unit (NTU) and 60–235 mg L^{-1} $CaCO_3$, respectively. The mid–stream area had the highest value, followed by the down–stream area, and the up–stream area was the lowest.

The conductivities were 0.12–44.70 ms cm^{-1}. The down–stream area had a high value due to the charged pollutants in river and the salinity of seawater. The up–stream area had the highest amount of DO, and the mid–stream area had the lowest due to the highest level of pollution in this area. The trend in Eh was similar to that of DO. The BOD and COD values of the mid– and down–stream areas were higher than those in the up–stream area due to the industrial and domestic wastewater pollutions in the down–stream area, and the hog wastewater pollution in the mid–stream area. Therefore, the BOD/COD ratio was high in the mid–stream area (0.11–0.82), while the value was low in the down–stream area (0.03–0.39). The Suspended Organic Matter (SOM) and Suspended Inorganic Matter (SIM) were low, except during typhoon season (e.g. June 14–15 and July 30–31, 2004) when the water contained a large amount of suspended substances, especially mud and sand particles.

The NH_4–N and nitrate nitrogen (NO_3–N) concentrations were 0.06–6.14 and 0.26–59.80 mg L^{-1}, respectively. The NH_4–N concentrations were slightly higher in the mid–stream area than the other stream areas, which might be due to the contamination of hog wastewater. The bacterial counts were between 4.50×10^3 and 5.40×10^4 CFU mL^{-1}. The mid–stream area had the highest value, while the up–stream area was the lowest.

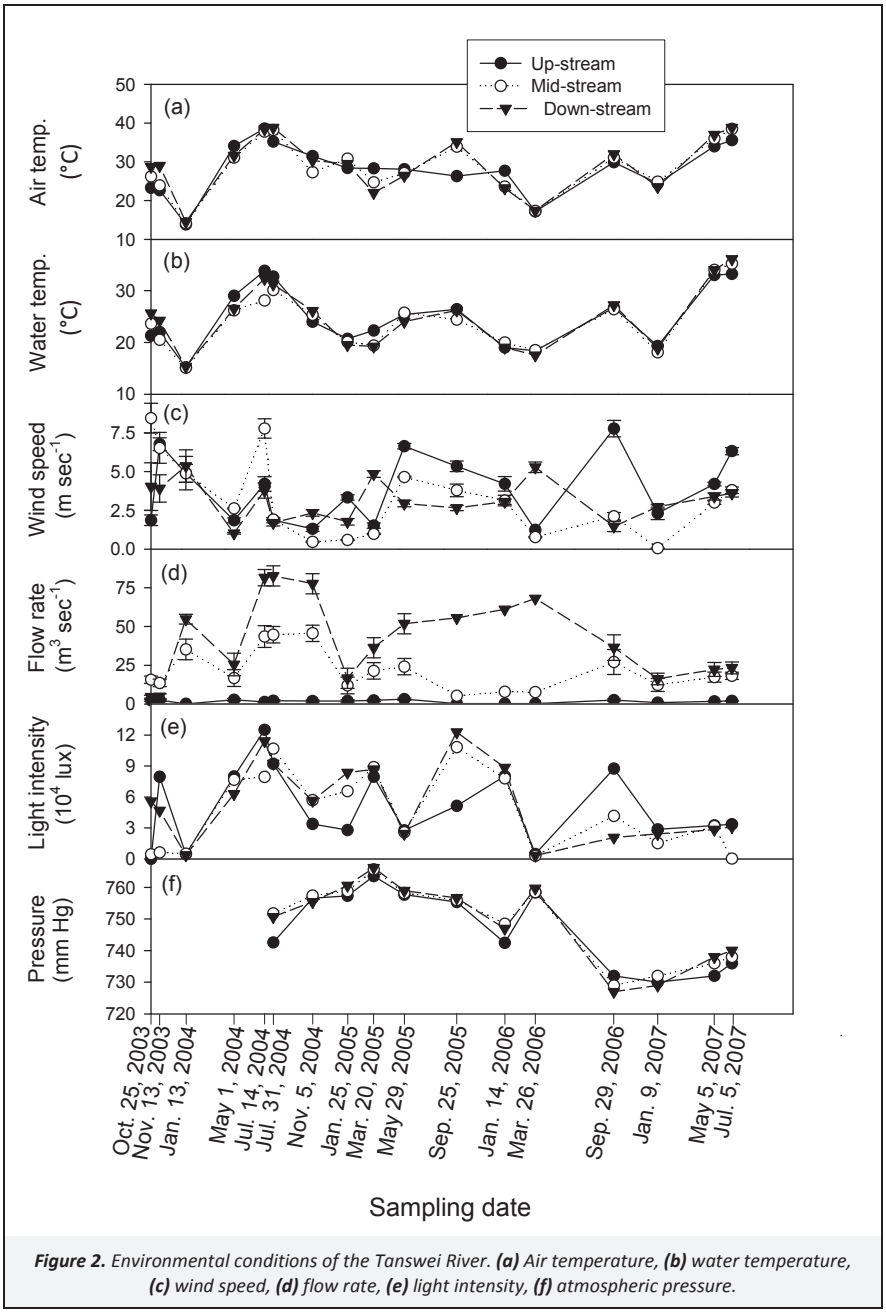

Figure 2. *Environmental conditions of the Tanswei River.* ***(a)*** *Air temperature,* ***(b)*** *water temperature,* ***(c)*** *wind speed,* ***(d)*** *flow rate,* ***(e)*** *light intensity,* ***(f)*** *atmospheric pressure.*

3.3. Ranking of water quality

According to the ranking system of water quality, the River Pollution Index (RPI) includes DO, BOD, suspended solutes and NH_4–N. The up–stream area of Tanswei River received grades of A to C depending upon the seasons; the mid–stream area received grades of C to D; while the down–stream area received grades of B to C.

3.4. Amount of carbon deposited from river into ocean

In the assessment of deposited carbon amount from river into ocean, the annual flow amounts of Tanswei River were estimated as 1.3×10^9, 1.7×10^9, 3.1×10^9, 2.7×10^9 and 4.3×10^9 cm^3 in 2003, 2004, 2005, 2006 and 2007, respectively; while the ranges of COD values were 11.9–37.3, 6.9–22.9, 11.1–74.5, 7.1–29.6 and 5.7–20.3 mg L^{-1} in the Tanswei River Mouth, Tanswei Area, and New Taipei City, respectively. Therefore, the annual carbon flows from Tanswei River into ocean in 2003, 2004, 2005, 2006 and 2007 were estimated 8.9×10^3, 1.8×10^4, 3.9×10^4, 2.7×10^4 and 1.2×10^4 tons by the flow amount and COD in the Tanswei River Mouth, respectively.

3.5. Atmospheric concentrations of carbon dioxide and methane

Carbon dioxide and methane concentrations and emission rates of the Tanswei River were listed in Figure 4. The atmospheric concentrations of CO_2 were 374.7±18.1 (347.4–400.7), 385.8±17.3 (342.8–417.3) and 388.8±20.0 (348.5–417.0 ppm in the up–, mid– and down–stream areas, respectively; while the atmospheric concentrations of CH_4 were 1.75±0.10 (1.59–1.98), 1.89±0.13 (1.74–2.10) and 1.88±0.26 (1.70–2.43) ppm, respectively. The mid– and down–stream areas had higher level of atmospheric CO_2 and CH_4 than those in the up–stream area.

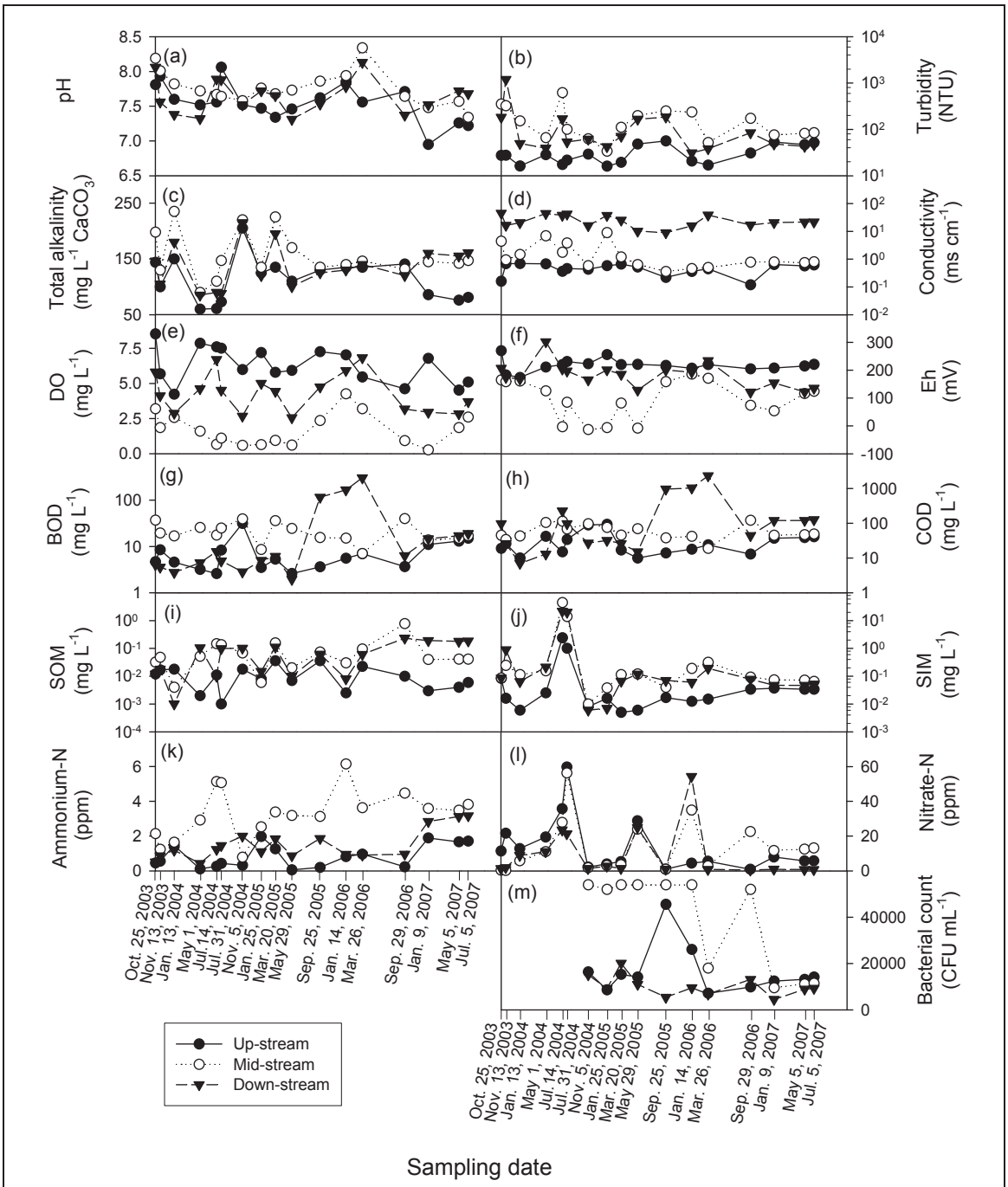

Figure 3. *Water qualities of the Tanswei River.* ***(a)*** *pH,* ***(b)*** *turbidity,* ***(c)*** *total alkalinity,* ***(d)*** *conductivity,* ***(e)*** *DO,* ***(f)*** *Eh,* ***(g)*** *BOD,* ***(h)*** *COD,* ***(i)*** *SOM,* ***(j)*** *SIM,* ***(k)*** *ammonium–N,* ***(l)*** *nitrate–N,* ***(m)*** *bacterial count.*

3.6. Effect of bottle color on carbon dioxide and methane concentrations in headspace of water samples

CO_2 concentrations in the headspace of water samples with colorless bottles were 2 679±1 588 (577–6 750), 4 461±2 146 (1 480–8 814) and 3 154±2 593 (1 510–9 401) ppm in the up–, mid– and down–stream areas, respectively; while the values with brown colored bottles were 3 058±1 666 (665–6 917), 4 795±2 324 (1 485–9 369) and 3 545±2 457 (1 580–9 637) ppm, respectively (Figures 4c and 4e). CO_2 concentrations had higher values in the mid– and down–stream areas than those in the up–stream area.

In the case of CH_4 concentrations, the values were 87.1±90.5 (15.6–312.5), 2 924.8±2 401.1 (65.0–5 868.1) and 616.1±1 156.8 (33.1–4 276.9) ppm with colorless bottles, respectively; while the values were 89.1±93.3 (16.8–319.0), 3 319.1±2 620.1 (66.0–6 288.2) and 641.9±1 236.4 (34.1–4 627.5) ppm with brown colored bottles, respectively (Figures 4d and 4f). CH_4 concentrations also had higher values in the mid– and down–stream areas than those in the up–stream area. The brown colored bottles also had higher CH_4 concentrations than the colorless bottles as were seen for CO_2 concentrations.

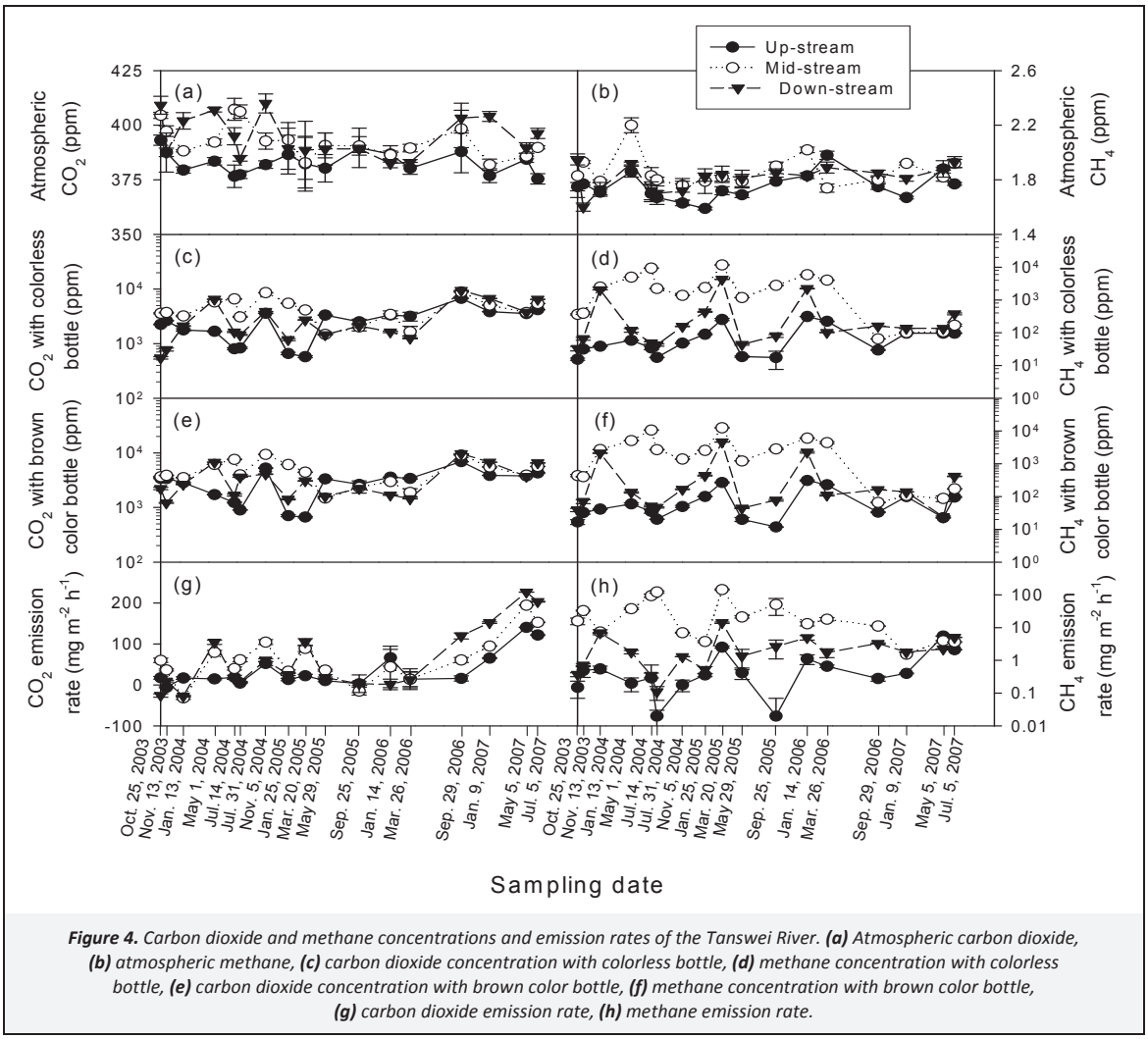

Figure 4. *Carbon dioxide and methane concentrations and emission rates of the Tanswei River.* ***(a)*** *Atmospheric carbon dioxide,* ***(b)*** *atmospheric methane,* ***(c)*** *carbon dioxide concentration with colorless bottle,* ***(d)*** *methane concentration with colorless bottle,* ***(e)*** *carbon dioxide concentration with brown color bottle,* ***(f)*** *methane concentration with brown color bottle,* ***(g)*** *carbon dioxide emission rate,* ***(h)*** *methane emission rate.*

3.7. Carbon dioxide and methane emission rates

CO_2 emission rates from river in the up–, mid– and down–stream areas were –22.3–140.5, –31.7–194.7 and –27.5–252.6 mg m^{-2} h^{-1}, respectively; while CH_4 emission rates were 0.02–5.52, 1.55–289.09 and 0.11–14.10 mg m^{-2} h^{-1}, respectively. CO_2 and CH_4 emission rates had higher values in the mid– and down–stream areas than those in the up–stream area (Figures 4g and 4h).

3.8. Correlations between water qualities and carbon dioxide and methane emissions

The fluctuations of air and water temperatures in the up–, mid– and down–stream areas of Tanswei River were not significant (Figure 2). CO_2 emission rates were negative in the down–stream area on October 25, 2003 (–25.69 mg m^{-2} h^{-1}) and January 13, 2004 (–27.52 mg m^{-2} h^{-1}); in the mid–stream area on January 13, 2004 (–31.70 mg m^{-2} h^{-1}) and September 25, 2005 (–15.24 mg m^{-2} h^{-1}); and in the up–stream area on November 13, 2003 (–5.69 mg m^{-2} h^{-1}) and March 20, 2005 (–22.33 mg m^{-2} h^{-1}). These phenomena might be because of the measurement times were at noon and some photosynthetic microbes and microalgae in the water were undergoing active photosynthesis.

The main items of water quality and GHG concentrations/emissions were selected for further correlation analysis. DO, Eh, BOD, SOM, SIM and NH_4–N were the major factors that affected CO_2 and CH_4 emissions from water. CO_2 emissions had very significant positive correlations with BOD and NH_4–N; significant positive correlation with SOM; and significant negative correlations with pH and DO. CH_4 emissions had very significant positive correlations with SIM and NH_4–N; and very significant negative correlations with DO and Eh (Table 1). CO_2 and CH_4 emissions had the highest correlations with water quality in the down–stream area, followed by the mid–stream area, and the up–stream area had the lowest.

The multiple regression method was selected to simulate and predict the GHG fluxes of Tanswei River. The results indicated that turbidity, SOM, SIM and NO_3–N in all of the parameters and the constant (equation intercept) was significant. The regression equation between CO_2 concentration in the headspace of water (y), turbidity (x_1), SOM (x_2), SIM (x_3) and NO_3–N (x_4) is:

$$y = 1.884x_1 + 10\,160.507x_2 + 71.930x_3 - 46.157x_4 + 3\,705.831 \quad (1)$$

The regression equation between CH_4 concentration in the headspace of water (y'), SIM (x_1) and NH_4–N (x_2) is:

$$y' = 84.463x_1 + 864.274x_2 - 456.171 \quad (2)$$

Table 1. *Correlation coefficients between carbon dioxide and methane fluxes and water quality parameters*

Parameters	CO_2 Emis.	CH_4 Emis.	CO_2 Conc.	CH_4 Conc.	pH	Turbid.	Alkali.	Conduct.	DO	Eh	BOD	COD	SOM	SIM	NH_4–N	NO_3–N
CH_4 emis.	0.207	1														
CO_2 conc.	0.258	0.237	1													
CH_4 conc.	0.296 [a]	0.174	0.229	1												
pH	–0.391 [a]	0.117	0.157	0.158	1											
Turbidity	0.144	0.212	0.223	0.107	0.107	1										
Alkalinity	0.116	0.227	0.281 [a]	0.104	0.188	–0.030	1									
Conduct.	0.021	–0.035	0.375 [b]	0.116	0.153	0.015	–0.066	1								
DO	–0.337 [a]	–0.478 [b]	–0.410 [b]	–0.311 [a]	0.008	–0.246	–0.430 [a]	–0.172	1							
Eh	–0.271	–0.432 [b]	–0.279 [a]	–0.223	–0.026	–0.221	–0.351 [a]	–0.187	0.854 [b]	1						
BOD	0.236	0.230	0.231	0.165	0.252	0.201	0.090	0.227	–0.248	–0.146	1					
COD	0.134	0.104	0.116	0.132	0.241	0.175	–0.003	0.327 [a]	–0.181	–0.127	0.577 [b]	1				
SOM	0.295 [a]	0.200	0.346 [a]	0.107	–0.005	0.050	0.116	0.054	–0.381 [b]	–0.320 [a]	0.057	0.006	1			
SIM	0.161	0.416 [b]	0.277 [a]	0.113	0.104	0.320 [a]	–0.200	0.160	–0.143	–0.259	–0.054	–0.006	0.086	1		
NH_4–N	0.374 [b]	0.528 [b]	0.245	0.344 [a]	0.089	0.182	0.215	–0.198	–0.647 [b]	–0.574 [b]	–0.020	–0.080	0.421 [b]	0.294 [a]	1	
NO_3–N	–0.217	–0.207	–0.145	–0.099	0.087	–0.044	–0.368 [b]	–0.138	0.096	–0.045	0.053	0.023	–0.001	0.326 [a]	0.152	1

[a] *p<0.05,* [b] *p<0.01, n=51*

4. Discussion

The world CH_4 budget is becoming more concerning in recent years. Freshwater ecosystems have been estimated to contribute over 70% the natural sources of CH_4 and over 20% of the total CH_4 sources to the atmosphere (Kortelainen et al., 2004). CO_2 and CH_4 emissions from the world's freshwater reservoirs make up 4% and 18% of other anthropogenic CO_2 and CH_4 emissions, respectively (St. Louis et al., 2000). But, there is little systematic data in time and space to evaluate the impact of groundwater and streams on large regional riverine carbon balances (100 s–1 000 s km). Only organic matter dissolved in water and flow rate were estimated to calculate the annual carbon flux in general condition, without considering extreme storms such as typhoons and heavy rain. Because typhoons and heavy rain wash away huge amounts of sediment and a lot of carbon was carried into the ocean (Goldsmith et al., 2008).

The Tanswei River basin includes Tanswei, Keelung, Shindian, and Dahan Rivers. They are the most important water resources in northern Taiwan. 192.7 km (59.6%) was classified as fair, 47.3 km (14.6%) was slightly polluted, in 50.9 km (15.8%) there was moderate pollution, and in 32.4 km (10.0%) there was heavy pollution (Environmental Protection Administration/Taiwan, 2012). There are some industrial and hog wastewaters input into the mid–stream area, and some industrial and domestic wastewaters discharge into the down–stream area. On the basis of currently available data on the pollution parameters for water quality, the up–, mid– and down–stream sections of Tanswei River can be classified as classes B, D and C, respectively.

BOD, COD, organic matter content and DO are the parameters used as the index of water pollution (Wu et al., 2007). BOD, COD, SOM, SIM and NH_4–N had positive correlations with CO_2 and CH_4 emissions from water in the Tanswei River (Table 1). CO_2 and CH_4 production of sediments had good correlations with the BOD and COD of water, and the organic matter and above ground biomass contents of sediment (Yang, 1998; Hirota et al., 2007). Most of the organic matter in sediments of rivers and lakes are resistant for decomposition by the microbes that produce CH_4. A similar effect was also found in the fresh green manure used to supplement in paddy soil which had a greater stimulatory effect on CH_4 production than xylan, rice straw or corncob supplements (Yang and Chang, 1998).

The mid– and down–stream areas of Tanswei River had higher atmospheric CO_2 and CH_4 concentrations than those in the up–stream area because of the input of industrial, livestock and domestic wastewaters (Environmental Protection Administration/Taiwan, 2012). While in the up–stream area, the atmospheric concentrations of CO_2 were low due to the presence of many trees and small shrubs undergoing active photosynthesis during the daytime. Therefore, there was a net CO_2 deposition rather than emission during the testing period in the up–stream area (Figure 4g). Similar phenomena were also reported in the Keelung River (Chang and Yang, 2003), Shan–Chu–Ku landfill site (Hegde et al., 2003), Fu–Der–Kan closed landfill (Chen et al., 2008) and Lake Nakaumi (Hirota et al., 2007).

CO_2 and CH_4 concentrations in the headspace of water samples from Tanswei River with brown colored bottles were higher than those with colorless bottles. This might be due to the use of penetrating light for photosynthesis by microbes, and decreased CO_2 emission. Same phenomenon was also observed in the Lake Nakaumi, Japan. CO_2 emission rates in an opaque chamber were higher than those in transparent chamber, and the values in daytime were also lower than those at nighttime (Hirota et al., 2007).

Light might also affect the oxygen distribution and penetration in the water–air interface, and enhance the CH_4 oxidation. CH_4 emission from the Tanswei River was slightly affected at low light intensity in comparison with high light intensity in paddy soils under anaerobic conditions, but the effect became significant in aerobic conditions (Yang and Chang, 1998).

CO_2 and CH_4 emissions from Tanswei River were high in the summer season and low in the winter season. Temperature is one of the most important factors affecting the CH_4 emission from lake littorals, paddy soils and wetlands (Yang and Chang, 1998; Yang and Chang, 2001a; Yang and Chang, 2001b; Freeman et al., 2002; Chang and Yang, 2003; Huttunen et al., 2003; Xing et al., 2005; Hirota et al., 2007). There was a positive linear correlation between CH_4 production and temperature between 15 and 37 °C (Yang and Chang, 1998). The increasing availability of easily degradable organic matter input into rivers and lakes increases the bacterial decomposition, oxygen consumption, and promote the oxygen depletion in waters (Carpenter et al., 1998). In water ecosystem, CH_4 is produced in anoxic sediment via methanogenesis and

aerobically oxidized by methanotrophic bacteria if oxygen is available in water. Oxygen depletion can stimulate CH_4 production and decrease CH_4 oxidation, leading to increase CH_4 emissions from water to atmosphere.

The amount of DO was the highest in the up–stream area, followed by the down–stream area, and the mid–stream area had the lowest amount. Rivers or lakes with high primary production have influx of CO_2 from the atmosphere due to the increase in photosynthesis. Additionally, nutrients also affect bacterial metabolism, which contribute to CO_2 and CH_4 production in rivers and lakes (Hirota et al., 2007).

The variation of CH_4 emissions from a polluted, tropical coastal wetland in Madras City, India was found to be based on the degree of pollution (Ramesh et al., 1997). CH_4 emission from the polluted wetland was significantly higher than that reported from similar unpolluted natural wetlands. Wastewaters from domestic sources, factories and livestock feedings are three main sources of pollutants to rivers in Taiwan. Livestock wastes have much higher amount of organic compounds than those from domestic sources and factories. Sun et al. (2002) and Zhu et al. (2005) indicated that fresh penguin droppings had particularly high amount of organic carbon and nitrogen compounds compared with normal tundra soils, and a large amount of animal deposits into the tundra of maritime Antarctica during the breeding period greatly increased CH_4 emissions from the tundra. Hirota et al. (2005) estimated the effect of grazing on global warming potential of the alpine wetlands and found that CO_2 andCH_4 emissions under grazing conditions were 5.6–11.3 folds higher than under non–grazing conditions. The up–stream area with low organic carbon and nitrogen contents had lower CO_2 and CH_4 production than those in the down–stream or mid–stream areas with high organic carbon and nitrogen contents. Same phenomena were also found in the Tungkang and Erren Rivers (data not shown). The oxygen depletion stimulates CH_4 production and decreases CH_4 oxidation, leading to an increase in CH_4 emissions from water to atmosphere.

Methanogenic bacteria are pH sensitive and most of them grow in a relatively narrow pH range of about 6–8 (Yang and Chang, 1998). The tested water samples had pH values between 6.95 and 8.34, and most of them were within the pH range for optimum growth of methanogenic bacteria. Hence, the effect of pH on CH_4 emissions from water was low in the Tanswei River (r=0.117).

Soil mineralogy also has an effect on CH_4 emissions from soil. Conductivity had a negative correlation with CH_4 emissions from water (r=–0.035), and it also had a very low correlation with CO_2 emissions (r=0.021). Irons and electron acceptors, like NH_4^+, Mg^{2+}, Fe^{3+}, NO_3^-, NO_2^- and SO_4^{2-}, also inhibit methanogenesis by stimulating the activity of other bacteria, which compete with methanogens for the reduced substrates (Verma et al., 2002). COD had low correlation with CH_4 emissions (r=0.104) in Tanswei River and it had negative correlation with CH_4 emissions in the down–stream area (r=–0.052). This might be affected by the presence of salt in down–stream area. COD and CH_4 emissions had positive correlation (r=0.075) in the up– and mid–stream areas (r=0.120–0.231) without submerged by tide. In addition, NH_4^+, whose chemical structure resembles that of the CH_4 molecule, can interfere with the oxidation of CH_4 because NH_4^+ competes with CH_4 for CH_4 mono–oxygenase, the key enzyme in CH_4 oxidation. In this study, NH_4–N concentration of water had highly significant positive correlations with CO_2 and CH_4 emissions (r=0.374 vs. r=0.528; p<0.01).

The fluxes of CO_2 and CH_4 from soil and water have shown strong seasonal dynamics in many field studies (Yang, 1998; Yang and Chang, 1998; Yang and Chang, 2001a; Yang and Chang, 2001b; Chang and Yang, 2003). Xing et al. (2005) reported that most of the CH_4 emissions remained low value in a subtropical lake of China when the temperature was below 25 °C, but the emissions dramatically increased when the temperature was above 25 °C in the summer. Seasonal patterns of CO_2 and CH_4 emissions from peatlands in Indonesia were strongly influenced by soil moisture. During the wet season, flooded water on the soil surface caused the soil to become anaerobic and the production of CO_2 decreased, while methanogenic bacteria produced more CH_4. During the dry season, the soil became aerobic and methanogenic activity decreased (Inubushi et al., 2003). Taiwan is located in the subtropical region and the water flow rate varies widely between the dry period (from November to April) and the wet period (from May to October). The highest water flow rate was found in July and the lowest in November, and the highest ratio between the two values was 17.6 in the down–stream area of Tanswei River (Water Resources Agency/Taiwan, 2012). Rivers receive nutrients from their catchment areas via water flow. During the dry period, low flow rate decreased the metabolism of river ecosystem, and increased the precipitation of pollution in the river, which provided more nutrients; during the wet period, organic matter was easily carried away by swift currents. However, the high temperature during the wet period provided better environment for microbial activity producing high concentrations of CO_2 and CH_4 made the measurement become more complex.

In the assessment of carbon flows from Tanswei River into ocean with the annual flow amounts and COD were 9×10^3, 1.8×10^4, 3.9×10^4, 2.7×10^4 and 1.2×10^4 tons in 2003, 2004, 2005, 2006 and 2007, respectively.

5. Conclusions

The atmospheric concentrations and emission rates of CO_2 and CH_4 from Tanswei River were the highest in the mid–stream area, followed by the down–stream area, and the up–stream area had the lowest due to domestic, livestock and industrial wastewater pollutions in the mid– and down–stream areas. DO, Eh, SOM, SIM and NH_4–N were the major factors that affected CO_2 and CH_4 emissions from water.

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