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Relationship between Carbon Dioxide/Methane Emissions and the Water Quality/Sediment Characteristics of Taiwan's Main Rivers

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ABSTRACT

River and sediment have unique carbon dynamics and are important sources of the dominant greenhouse gases (GHG), carbon dioxide (CO_2) and methane (CH_4). To understand the relationship between CO_2/CH_4 emissions and water quality/sediment characteristics, we have investigated critical parameters in the river water. Eight parameters of water quality (dissolved oxygen, oxidation-reduction potential [ORP], chemical oxygen demand, biochemical oxygen demand [BOD_5], suspended solid, nitrate [NO_3^-], NH_4^+, and bacteria) and four sediment characteristics (total organic carbon [TOC], total nitrogen [T-N], NO_3^-, and ammonium [NH_4^+]) were measured in two of the larger rivers in Taiwan, and relevant environmental conditions were recorded. The experimental results indicated that CO_2 emissions from the river were mainly affected by BOD_5 concentrations and the levels of bacteria. CH_4 emissions, on the other hand, were greatly affected by the ORP in the river. The correlation between CO_2 emissions and sediment characteristics was insignificant ($R^2 < 0.3$). However, TOC and T-N in the sediment may lead to increases in CH_4 emissions into the atmosphere. A deeper analysis of the relationship between the different parameters and GHG emissions by ANOVA and the multiple regression method revealed that CO_2 emission (y) was significantly related to bacteria number (x_1) and BOD concentration (x_2). The regression equation takes the form $y = 0.00032x_1 + 3.18089x_2 + 25.37304$. Also, the regression relationship between CH_4 emission (y) and ORP (x) in the river can be described as $y = -0.825216x + 169.02257$. The relationship between CH_4 emission and sediment characteristics may be described as $y = 5.073962x_{1(\mathrm{TOC})} + 2.871245x_{2(\mathrm{T\text{-}N})} - 12.3262$. Extra sampling data were collected to examine the feasibility of the developed multiple regression equations. The experimental results suggest that the emissions of such GHGs as CO_2 and CH_4 from rivers can be predicted using the regression equations developed here. Moreover, the emissions may be reduced by manipulating the proper factors.

IMPLICATIONS

The relationships between CO_2/CH_4 emitted from rivers and the water quality/sediment characteristics of those rivers were first demonstrated and established. A biostatistic analysis of the critical parameters affecting CO_2 and CH_4 emissions was then presented. Preliminary results indicate that the developed regression equations have the potential to predict the amount of the GHGs produced from a river and that they can play a major role in reducing emissions by controlling the emitted factors.

INTRODUCTION

Greenhouse gases (GHGs) are gaseous components of the atmosphere that contribute to the greenhouse effect. Carbon dioxide (CO_2) and methane (CH_4) are two major GHGs, and their emission into the atmosphere is detrimental to the environment.[1] Although the amount of CO_2 accumulating in the atmosphere each year is several orders of magnitude higher than that of CH_4, CH_4 is more effective (22 times) at potentially warming the Earth's surface than CO_2.[2] CH_4 has accumulated rapidly in the past century, currently reaching a concentration unprecedented in human history.[3] Atmospheric concentrations of CH_4 and CO_2 have increased from 1.50 to 1.72 and 337 to 360 ppmv, respectively, during last decade.[4] As for CO_2 accumulation, in the mid-1990s, annual CO_2 emissions to the atmosphere amounted to 7.4 billion t of carbon (GtC),[5] but it will rise to

Table 1. Physical environmental conditions in the Danshuei River and Gaoping River.

Sampling Site	Danshuei River: Ganyuan Bridge (upstream)	Danshuei River: Dahan Bridge (midstream)	Danshuei River: Guandu Bridge (downstream)	Gaoping River: Sandimen Bridge (upstream)	Gaoping River: Gaoping Bridge (midstream)	Gaoping River: Shuangyuan Bridge (downstream)
Location	25°07′N/121°27′E	24°57′N/121°23′E	25°02′N/121°27′E	22°42′N/120°38′E	22°37′N/120°26′E	22°29′N/120°25′E
Pollution source (type)	Domestic sewage	Livestock wastewater (major); industrial wastewater (minor)	Industrial wastewater (major); domestic sewage (minor)	Domestic sewage	Domestic sewage	Industrial wastewater
Wind speed (m sec^{-1})	3.57 ± 0.28	5.36 ± 1.36	3.31 ± 0.64	1.73 ± 0.32	2.65 ± 1.42	2.57 ± 1.14
Air temperature (°C)	28.1 ± 2.3	28.9 ± 3.6	31.3 ± 2.8	26.8 ± 1.8	30.7 ± 2.9	31.2 ± 2.1
Water temperature (°C)	25.7 ± 1.8	23.9 ± 1.5	25.9 ± 2.4	22.7 ± 1.6	28.1 ± 2.0	29.4 ± 1.8
Flow rate (m^3 sec^{-1})	1.91 ± 0.36	18.32 ± 3.15	42.38 ± 5.26	3.57 ± 1.23	8.89 ± 2.05	20.58 ± 3.61
Light intensity (lux)	63,533 ± 7842	46,483 ± 3216	62,625 ± 5230	44,508 ± 2810	48,780 ± 3002	55,900 ± 4380

26 GtC in the year 2100 according to the forecast of the Intergovernmental Panel on Climate Change.[6]

The realization that GHG emissions may be contributing to climate change, with all the deleterious connotations that are implied, has led to research into their source, impact, production, and reduction.[7] Approximately 80% of all CH_4 is produced biologically, and the major source sites include rice paddies, wetlands, sediments, enteric fermentation sites, animal waste treatment sites, and landfills under potential low redox conditions by obligate anaerobes.[8,9] CO_2 is emitted mainly from fuel use, industrial activity, and transportation appliances. The CH_4 and CO_2 emissions from the world's freshwater reservoirs have been estimated to be equivalent to 18% and 4% of other anthropogenic CH_4 and CO_2 emissions, respectively.[10]

The total length of Taiwan's main rivers is ~2904.21 km. In 2004, 59.44%, or 1726.16 km, were classified as excellent. Approximately 389.95 km (13.43%) were classified as slightly polluted, and 328.94 km (11.33%) and 459.16 km (15.81%) were classified as moderately and heavily polluted, respectively.[11] Also, the proportion (length) of the rivers classified as polluted is increasing at a rate of 1.1%/yr. Thus, the CO_2 and CH_4 emissions from freshwater, especially those from seriously polluted rivers in Taiwan, are worthy of attention. These emissions are mainly dependent on the aquatic environment in the freshwater,[12] and land-use changes resulting in nutrient input into the water body also affect their emissions.[13] The existence of easily degradable organic matter in water stimulates microbial activity and further enhances oxygen consumption. Aerobic conditions usually produce large CO_2 emissions, but anoxic conditions increase CH_4 emissions by enhancing CH_4 production and/or decreasing CH_4 oxidation. In addition, the production and emission of CO_2 and CH_4 involve aquatic plants and their complex physiological processes, which are regulated by climatic and environmental factors.[14] Many studies have focused on the assessment of GHG emissions from natural or artificial ecosystems in Taiwan, such as paddy fields, uplands, peatlands, wetlands, river sediments, lake sediments, and orchard and forest soils,[8,14–16] whereas detailed investigations of aquatic ecosystems have been largely neglected. In particular, little data are to be found on the relationship between GHG emissions and the water quality/sediment characteristics in the rivers.

The temperature in Taiwan shows regular seasonal variations throughout the year. We have, therefore, focused on the seasonal changes in CO_2 and CH_4 emissions from two main rivers in Taiwan: the Danshuei and Gaoping rivers. To understand the relationship between GHG emissions and the aquatic environment in these rivers and to be able to predict or reduce CO_2 and CH_4 production, we have developed multivariable equations by which to accurately estimate CO_2 and CH_4 emissions. The development of such equations is vital for future manipulation and control of GHG emissions.

EXPERIMENTAL WORK

Sampling Location, Frequency, and Environmental Conditions

The Danshuei River (total length, 159 km; drainage area, 2726 km^2) and the Gaoping River (total length, 171 km; drainage area, 3625 km^2), the two largest rivers in Northern and Southern Taiwan, respectively, were selected for investigation. The Danshuei River system is composed of the largest estuarine system in Taiwan. The downstream reaches of its tributaries are influenced by tide and subject to seawater intrusion. It flows in a northwesterly direction, past Taipei City into the Taiwan Strait at Danshuei. The Gaoping River originates in the Central Mountain Range, flowing in a southwesterly direction through the southwestern counties of Taiwan to flow into the Taiwan Strait. It has the largest basin of any river in Taiwan. A number of upstream, midstream, and downstream sites in these rivers, containing or representing various polluted stretches, were sampled regularly. Each site was sampled 10 times between August 2003 and May 2005. In total, 180 water samples (triplicate) and 360 air samples (hexaplicate) were collected. The sampling sites were first positioned by global positioning system (GPS) units. Flow rates in the rivers were measured using a propeller-type flow meter at a depth of 0.6 m and a distance of 1 m from the river bank. Physical environmental conditions (including wind speed, air and water temperature, and light intensity) were recorded simultaneously. The wind speed, air temperature, and light intensity were measured 1.5 m above ground level, whereas water temperature was measured under the same conditions as flow rate. Table 1 shows the average values of the 10 samplings. A 27-hr semicontinuous sampling procedure was carried out at the midstream sampling site (Dahan Bridge), and the

Danshuei River was selected as a check for differences among the discontinuous sampling. Moreover, data including water parameters and GHG emissions from the upstream, midstream, and downstream in the Donggang and Erren River were collected to assess the feasibility of the developed GHG emissions model. The Erren River (length, 63 km; drainage area, 350 km^2) and the Donggang River (length, 44 km; drainage area, 472 km^2) also flow in a westward direction into the Taiwan Strait. The relative geographical location of these four rivers to each other is, from north to south, the Danshuei, Erren, Gaoping, and Donggang rivers. The distance between the mouths of each of these rivers is 300, 55, and 45 km, respectively, with a total distance of 400 km between the mouths of the Danshuei and Donggang rivers.

Gas Sampling Method

An acrylic barrel-type chamber (top diameter, 25 cm; bottom diameter, 28.5 cm; height, 32 cm; capacity: ~18 L) equipped with an electronic fan, a thermometer, and a sampling hole on the top was used to collect the gas samples. A 24-in. life buoy surrounded the chamber as a buoyancy apparatus. For CO_2 and CH_4 emission measurements, the chamber was installed on the river surface (1.5 m from the river bank), and three chambers were used in each measurement. Both CO_2 and CH_4 emission rates were measured at 0.5-hr intervals for 1 hr by examining the changes of the gas concentrations in the chamber. Gas samples (50 mL) were collected from the headspace of the chamber and injected into a 13-mL serum bottle sealed by a butyl rubber stopper and flushed with oxygen-free nitrogen gas.[17]

Emission Estimation

CH_4 and CO_2 emissions from the rivers were calculated using the experimental data and estimated by the following equation[18]: $f = (V/A) \times (\Delta C/\Delta t)$, where f is the CH_4 or CO_2 emission flux (mg m^{-2} hr^{-1}); V is the volume of the chamber (m^3); A is the cross section of the chamber (m^2); ΔC is the concentration difference (mg m^{-3}); and Δt is the time duration between two sampling periods (hr).

Analytical Methods

Ambient and water temperature were determined with a thermometer (the maximum error was ±1%). Light intensity was measured with a photometer (SPI-5, Toshiba). Wind speed was measured with a weathercock. Water samples were taken at a depth of 0.6 m and 1 m from the river bank. Conductivity, pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO) were determined in situ with a portable multiparameter instrument (Multi 350i, WTW). Turbidity was measured in situ with a turbidity meter (WTW). Other water quality parameters and sediment characteristics were measured in the laboratory within 48 hr of being collected. These water and sediment samples were put into plastic bottles and stored at 4 °C in an ice bucket. Ammonium (NH_4^+), nitrate (NO_3^-), and chemical oxygen demand (COD) were analyzed in the laboratory using a multiparameter instrument (PhotoLab S12, WTW). Biochemical oxygen demand (BOD_5) was determined by azide modification of the iodometric method.[19] Bacteria number was determined by a commercial Millipore kit: bacteria were cultured in the kit at 35 °C in an aerobic incubator for 48 hr and the number of bacteria counted. The total organic carbon (TOC) content of the sediment was analyzed by wet oxidation using the Walkey-Black method.[20] The total nitrogen content of the sediment was measured by the modified Kjeldahl method.[21] CH_4 concentration was analyzed by a Shimadzu gas chromatography-14B gas chromatograph (Shimadzu Co.) with a Porapak Q glass column (2.6 mm × 2 m) and a flame-ionization detector. The column temperature was set at 100 °C, and the injection and detector temperatures were set at 130 °C.[17] For CO_2 analysis, a TCD detector was used. The column, injection, and detector temperatures were 100 °C, 120 °C, and 120 °C, respectively. Experiments were carried out in duplicate at the very least. The relationship between gas emission and water quality was analyzed using the Statistical Analysis System.

RESULTS AND DISCUSSION

Environmental Conditions Related to CO_2/CH_4 Emission

To evaluate the effect of environmental conditions on CO_2/CH_4 emission, a fixed sampling site was carefully selected. All of the sampling sites were positioned by GPS units, and sampling operations were conducted during the day. The weather conditions throughout the sampling period were sunny, with the exception of 8 cloudy days. The wind speed was in the range of 1.02–8.45 m sec^{-1} at the Danshuei River sites and 0.25–6.27 m sec^{-1} at the Gaoping River sites. No significantly high wind speeds affected the sampling or experimental procedures. The air temperature was in the range of 13.8–44.2 °C at the Danshuei River sites and 23.5–39 °C at the Gaoping River sites. The flow rate was in the range of 0.16–82.6 m^3 s^{-1} in the Danshuei River and 0.08–36.3 m^3 s^{-1} in the Gaoping River. The dramatic variation in flow rate was mainly caused by a typhoon. The light intensity fluctuated from 2 to 125,000 lux at the sampling sites, primarily because of the weather conditions.

Table 1 shows the average readings of 10 samplings at each site. All of the data on gas emissions, with the exception of the four negative values, were then analyzed to identify the relationship between CO_2/CH_4 emissions and environmental conditions. Unexpectedly, four negative CO_2 emission values (−25.69, −36.21, −45.82, and −87.52 mg m^{-2} h^{-1}) were collected from the Guandu Bridge site (downstream) in the Danshuei River. However, previous research on the lakes in the state of Wisconsin[22] and in Finland.[12,22] has suggested that the occurrence of photosynthesis by large aquatic plants in the river at noon usually causes the same result. Based on the experimental data, regression analysis on all of the parameters revealed an insignificant correlation ($R^2 < 0.3$) between CO_2/CH_4 emissions and environmental conditions. This finding corresponds with results obtained at a landfill site in Taiwan.[23] However, the results for the effect of temperature on CH_4 emission were the opposite of those obtained in a simulated serum bottle system.[15] Accordingly, we concluded that an evaluation of CO_2 or CH_4 emissions by field measurement was more appropriate than creating a simulated environment for measurement.

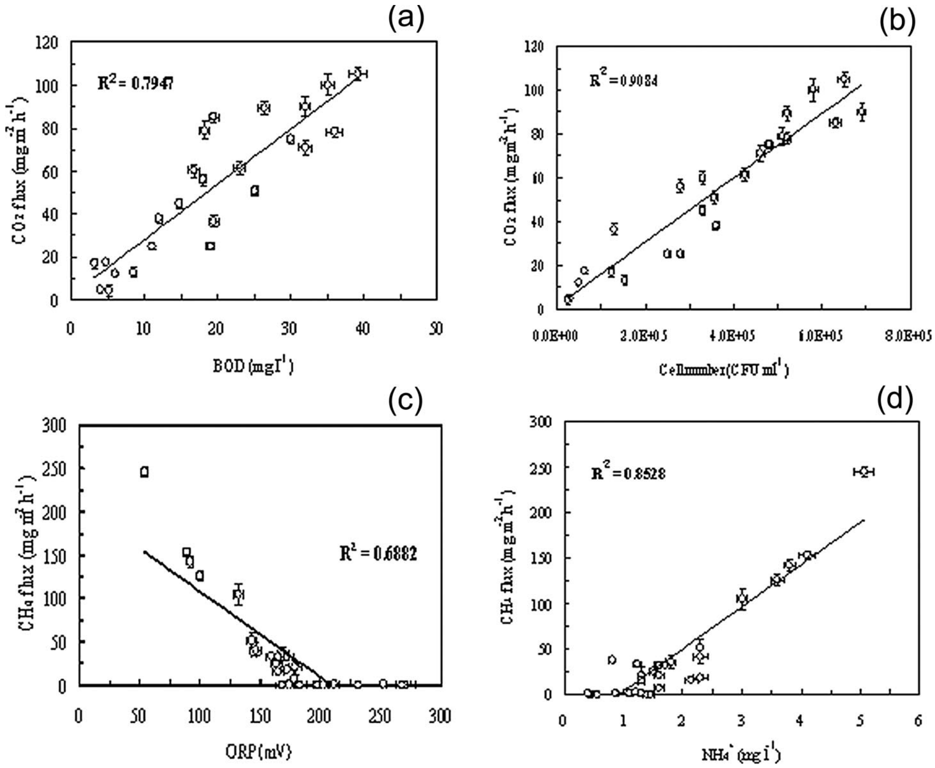

Figure 1. Relationship between CO_2/CH_4 flux and water quality in the Danshuei River. (A) CO_2 flux and BOD; (B) CO_2 flux ad cell number; (C) CH_4 flux and ORP; (D) CH_4 flux and NH_4^+. The error bars shown represent the standard deviation of replicate measurements.

Relationship of CO_2/CH_4 Emissions and Water Quality in the Danshuei and Gaoping Rivers

Based on the concentrations of pollutants, such as DO, BOD_5, suspended solid, and NH_4^+-N, the extent of river pollution (river pollution index) would normally be classified into four levels in Taiwan: (1) level 1 indicates little or no contamination; (2) level 2, slight contamination; (3) level 3, medium contamination; and (4) level, 4 heavy contamination. Consequently, on the basis of currently available data on the pollution parameters for water quality, the upstream, midstream, and downstream sections of the Danshuei River can be classified as levels 2, 4, and 3, respectively, and the upstream, midstream, and downstream sections of the Gaoping River can be classified as levels 2, 3, and 3, respectively. The variation in the degree of pollution in the rivers increases the reliability of the equation established in this study. All of the data, excluding the four removed negative data on CO_2 caused mainly by the photosynthetic adsorption of the water plants from the Guandu Bridge site in the Danshuei River, were used to identify the relationship between CO_2 emission and water quality.

The results indicate that there was an insignificant negative correlation ($R^2 < 0.3$) between ORP/nitrate content and CO_2 emission; all of the other parameters presented a positive correlation with CO_2 emission. BOD_5, for example, favored CO_2 emission ($R^2 = 0.7947$), and bacteria number had the highest correlation coefficient with it ($R^2 = 0.9084$), as indicated in Figure 1, A and B. ORP showed a significant negative correlation with CH_4 emission ($R^2 = 0.6882$). In addition, a high amount of CH_4 was produced when ORP in the river was <159 mV (Figure 1C). COD, BOD_5, and bacteria number in the river did not cause an increase in the CH_4 emission flux. Conversely, NH_4^+ was the major source favored for CH_4 emission (Figure 1D), and NO_3^- was the second with $R^2 = 0.654$ (data not shown). A similar tendency was observed in the Gaoping River. CO_2 emission was independent of NH_4^+, NO_3^-, and suspended solids, but all of the other parameters demonstrated positive correlations. BOD_5 and bacteria number had the highest correlation coefficients with CO_2 emission compared with the other parameters (Figure 2, A and B). NH_4^+ and NO_3^- were more favorable to CH_4 emission than the other parameters (Figure 2, C and D). The ORP had little influence on CH_4 emission, with $R^2 = 0.4308$. Other parameters, including BOD_5, COD, and bacteria count, were independent of CH_4 emission. Because a higher ORP was found in the Gaoping River than in the Danshuei River, it exhibited a different impact on CH_4 emission. As mentioned above, a river with an ORP <159 mV would produce a high amount of CH_4. Consequently, a close correlation was hardly observed between ORP and CH_4 emission in the Gaoping River.

Relationship of CO_2/CH_4 Emissions and Sediment Characteristics in the Danshuei and Gaoping Rivers

To determine the relationship between CO_2/CH_4 emissions and the sediment characteristics in the river, we selected four critical sediment characteristics (TOC, total nitrogen [T-N], NO_3^-, and NH_4^+) for further investigation. The effect of the parameters on the transfer of CO_2/CH_4 from the sediment to the water phase was also taken into careful consideration. Our results show that the relationship between CO_2 emission and sediment characteristics is different between the Danshuei and Gaoping

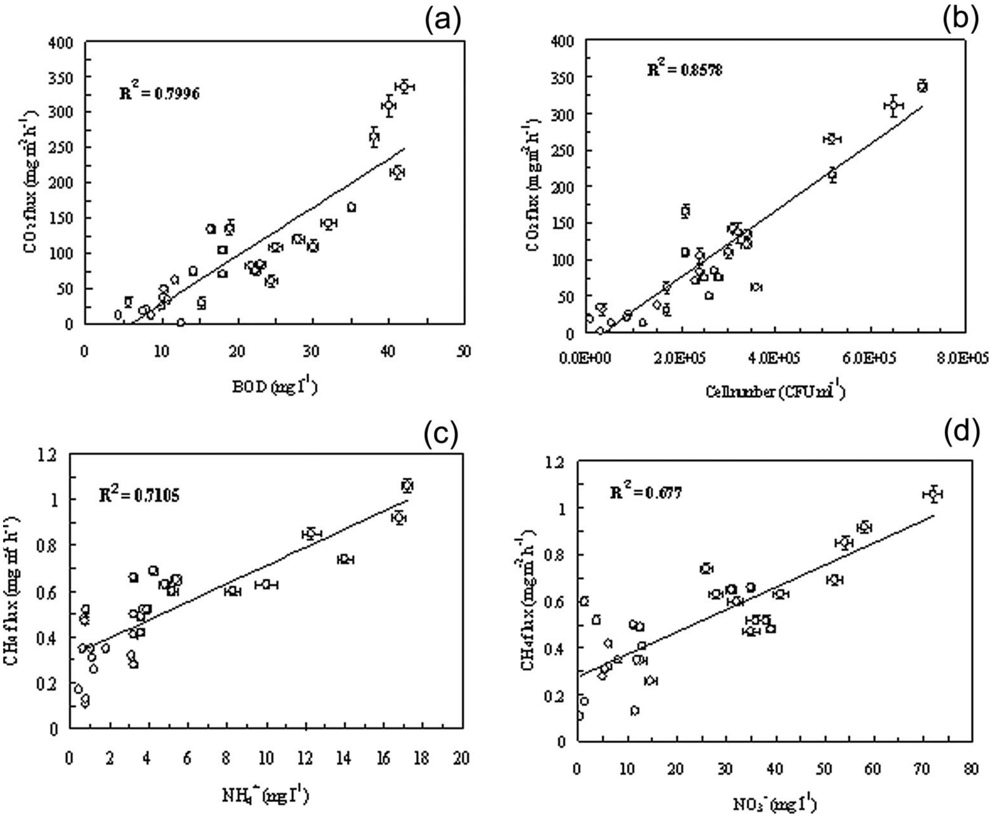

Figure 2. Relationship between CO_2/CH_4 flux and water quality in the Gaoping River. (A) CO_2 flux and BOD; (B) CO_2 flux and cell number; (C) CH_4 flux and NH_4^+; (D) CH_4 flux and NO_3^-. The error bars shown represent the standard deviation of replicate measurements.

rivers; however, similar relationships were observed in both rivers between CH_4 emission and sediment characteristics. In the Danshuei River, an insignificant negative correlation ($R^2 < 0.3$) between NO_3^- concentration and CO_2 emission was found, but T-N showed a positive correlation ($R^2 = 0.3085$) with CO_2 emission. Other parameters in the sediment were independent of CO_2 emission. In the Gaoping River, four parameters in the sediment were all independent of CO_2 emission. TOC and T-N in the sediment favored CH_4 emission under the conditions of the sources from both the Danshuei (Figure 3, A and B) and Gaoping rivers (Figure 3, C and D), and other parameters were independent of CH_4 emission. Because the amount of CH_4 was limited by the ORP in the river, it would be easier for the deeper water layer to emit more CH_4. Also, the organic compounds and nitrogen are two vital sources for bacteria growth, both favoring the production of CH_4. Accordingly, the impact of TOC and T-N in the sediment on CH_4 emission is superior to that of organic compounds (e.g., BOD and COD) with higher ORP in the water layer. A similar effect of TOC and T-N on CH_4 emission was also observed in wetlands and anaerobic soil.[14,24]

Relationship between CO_2/CH_4 Emissions and Water Quality/Sediment Characteristics in Both the Danshuei and Gaoping Rivers

In the previous section we discussed the relationship between CO_2/CH_4 emissions and water quality/sediment characteristics in the Danshuei and Gaoping rivers, respectively, using selected critical parameters. Although these results may suggest a general relationship, the research would be more cogent if the specific local parameters involved were added. Hence, the relationship between gas emissions and water quality (sediment characteristics) was eventually established, whereas data collected from various areas were properly taken into account. The results indicate that the BOD_5 and bacteria number in the rivers are closely related to the amount of CO_2 emission (Figure 4, A and C), whereas ORP is the most important factor affecting CH_4 emission (Figure 4B). If the range of ORP fell <200 mV, the R^2 would increase from 0.6763 to 0.8923. With respect to the sediment characteristics in the rivers, the TOC and T-N parameters are positively correlated with CH_4 emission (Figure 5), but none of the sediment characteristics showed any significant correlation ($R^2 > 0.3$) with CO_2 emission.

Relationship between CO_2/CH_4 Emissions and Water Quality in the Danshuei River during a 27-hr Semicontinuous Investigation

To evaluate the relationship between CO_2/CH_4 emissions and water quality in a short but continuous cycle, the variations in gas emission rates and water quality at the midstream sampling site (Dahan Bridge) of Danshuei River on February 16 and 17, 2004, were measured at 3-hr intervals daily. The environmental conditions and water qualities are presented in Table 2. The results show that temperature, light intensity, pH value, DO, ORP, COD, and bacteria number were in the range of 16.3–34.6 °C, 0–78,420 lux, 7.31–9.57, 0.41–3.76 mg L^{-1}, 23–170 mV,

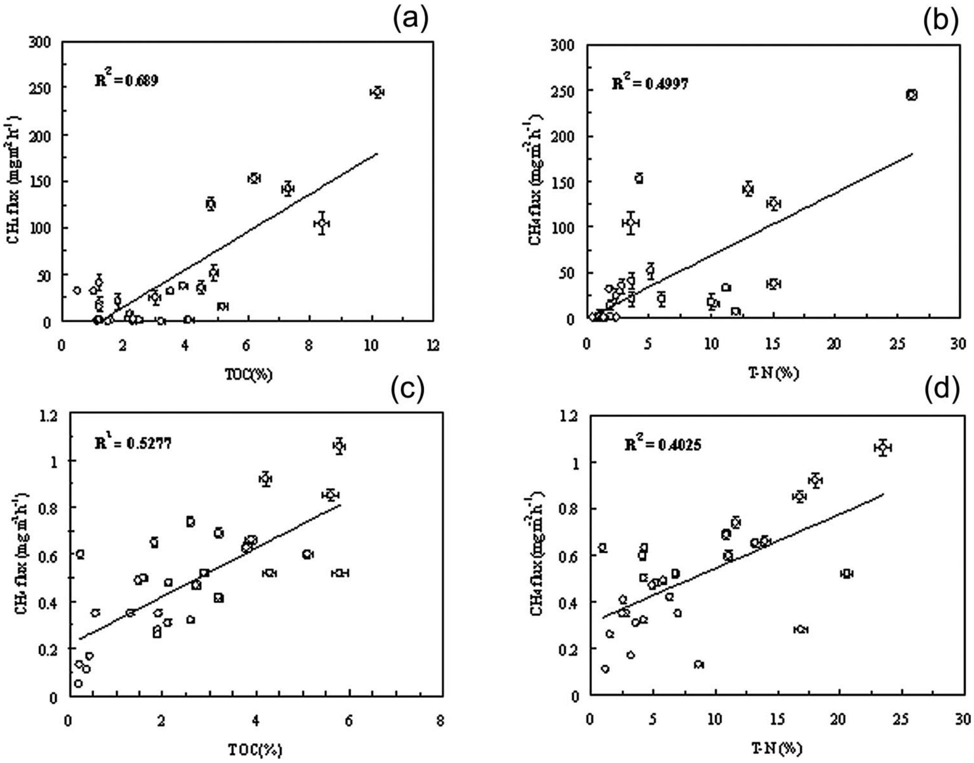

Figure 3. Relationship between CH_4 flux and sediment characteristics in rivers. (A) CH_4 flux and TOC in the Danshuei River; (B) CH_4 flux and T-N in the Danshuei River; (C) CH_4 flux and TOC in the Gaoping River; (D) CH_4 flux and T-N in the Gaoping River. The error bars shown represent the standard deviation of replicate measurements.

10–201 mg L^{-1}, and $1.5 \times 10^{5-6} \times 10^5$ colony-forming units mL^{-1}, respectively. The dramatic change in environmental conditions and quality parameters during a 27-hr semicontinuous investigation can be used to evaluate the relationship between selected parameters and CO_2/CH_4 emissions. Figure 6 indicates the positive

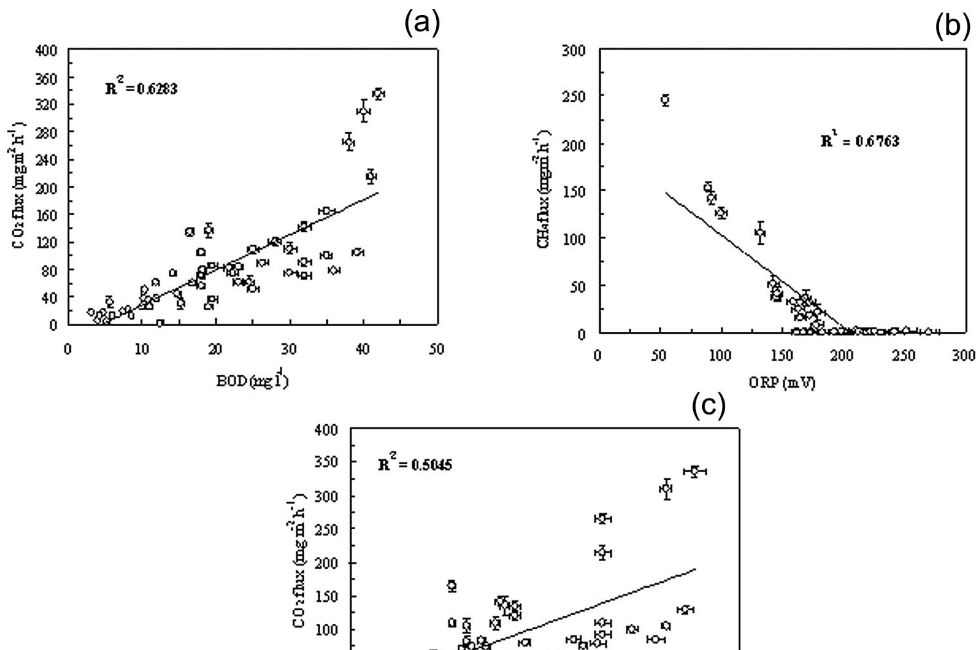

Figure 4. Relationship between CO_2/CH_4 flux and water quality in both the Danshuei and Gaoping rivers. (A) CO_2 flux and BOD; (B) CH_4 flux and ORP; (C) CO_2 flux and cell number. The error bars shown represent the standard deviation of replicate measurements.

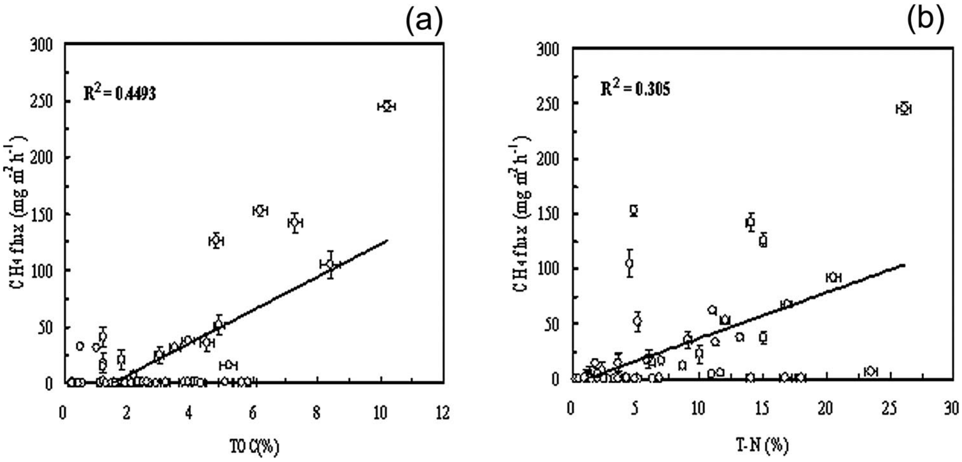

Figure 5. Relationship between CH_4 flux and sediment characteristics in both the Danshuei and Gaoping rivers. (A) CH_4 flux and TOC; (B) CH_4 flux and T-N. The error bars shown represent the standard deviation of replicate measurements.

correlation (R^2 = 0.8784) between bacteria number and CO_2 emission, which is consistent with the previous results. No regular correlation was observed between other parameters and CO_2/CH_4.

Multiple Regression Equations between CO_2/CH_4 Emissions and Water Quality in Both the Danshuei and Gaoping Rivers

The emission of CO_2 and CH_4 is normally affected by certain water quality parameters.[25] The multiple regression method was selected to simulate and predict the GHG fluxes. In this analysis, the analysis of variance (ANOVA) table was used to obtain these multiple regression equations. A coefficient of multiple determination (R^2), 0.384, suggested that an insignificant difference existed between the water quality parameters in the Danshuei and Gaoping rivers and the CO_2 flux. The significant level (0.0238) of the F test in the ANOVA table was lower than α of 0.05, which indicated that the water quality parameters should have a regressive correlation with the CO_2 flux. The *t* tests were also used to assess the significance of the coefficients between the means of two independent samples. A common rule of thumb is to drop the variable from the equation if its significant level (*P* value) is at $\geq$0.05. The results indicated that both the bacteria count (x_1) and BOD (x_2) in all of the parameters passed muster and that the constant (equation intercept) was significant. The multiple regression equation was estimated as $y = 0.00032x_1 + 3.18089x_2 + 25.37304$. The BOD($x_2$) was the most significant factor, with its coefficient effect being the most pronounced. The same method was also applied to uncover the relationship between water quality parameters and CH_4 fluxes. The results indicate a significant difference between water quality parameters and CH_4 flux, with a high R^2 (0.883). The significance level (0.0003) was <0.05 (α), indicating that some parameters existed in a significant regressive correlation with CH_4 flux. The *t* tests indicate that ORP and the constant were significant. The regression equation between the ORP value and CH_4 flux was estimated as $y = -0.825216x + 169.02257$, and this was near to the regression equation of Figure 1C.

Multiple Regression Equations between CO_2/CH_4 Emissions and Sediment Characteristics in Both the Danshuei and Gaoping Rivers

The fluxes of CO_2 and CH_4 are normally affected by some sediment characteristics. To evaluate the multifactor effect on gas emission, the multiple regression method, ANOVA analysis, and *t* test checks were applied to uncover their correlation. A relatively low coefficient of multiple determination (R^2 = 0.298) revealed that a very

Table 2. Environmental conditions and water qualities at the midstream sampling site (Dahan Bridge) of the Danshuei River during a 27-hr semicontinuous investigation.

Sampling Time	Light Intensity (lux)	Air Temperature (°C)	Water Temperature (°C)	Conductivity (μs cm^{-1})	pH	DO (mg L^{-1})	ORP (mV)	COD (mg L^{-1})	Bacteria Count (colony-forming units mL^{-1})
12:00 p.m.	64,200	32.3	23.2	1177	7.31	1.42	96	101	1.5×10^4
3:00 p.m.	53,580	31.9	23.7	919	9.13	3.76	98	10	2.0×10^4
6:00 p.m.	15,600	25.4	20.2	1015	7.88	3.51	120	86	1.7×10^4
9:00 p.m.	26	21.5	19.5	1704	8.10	0.45	170	58	3.6×10^4
12:00 a.m.	0	18.5	19.4	1033	9.37	2.06	119	113	4.2×10^4
3:00 a.m.	0	16.3	18.6	1063	9.57	3.13	122	102	5.4×10^4
6:00 a.m.	4500	17.6	18.1	926	8.96	0.93	23	131	6.0×10^4
9:00 a.m.	35,300	26.3	19.5	5680	7.99	0.44	105	201	3.2×10^4
12:00 p.m.	78,420	34.6	23.7	5360	8.01	0.54	121	97	2.4×10^4
3:00 p.m.	48,600	34.4	22.5	3270	8.18	0.41	71	102	1.9×10^4

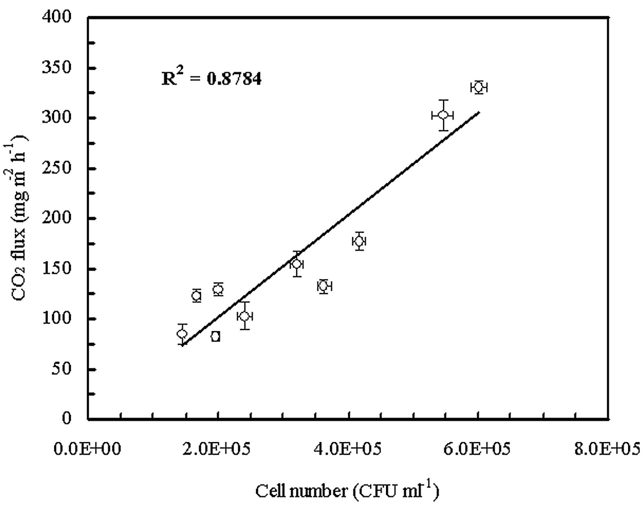

Figure 6. Relationship between CO_2 flux and cell number in the midstream (Dahan Bridge) of the Danshuei River during a 27-hr semicontinuous investigation. The error bars shown represent the standard deviation of replicate measurements.

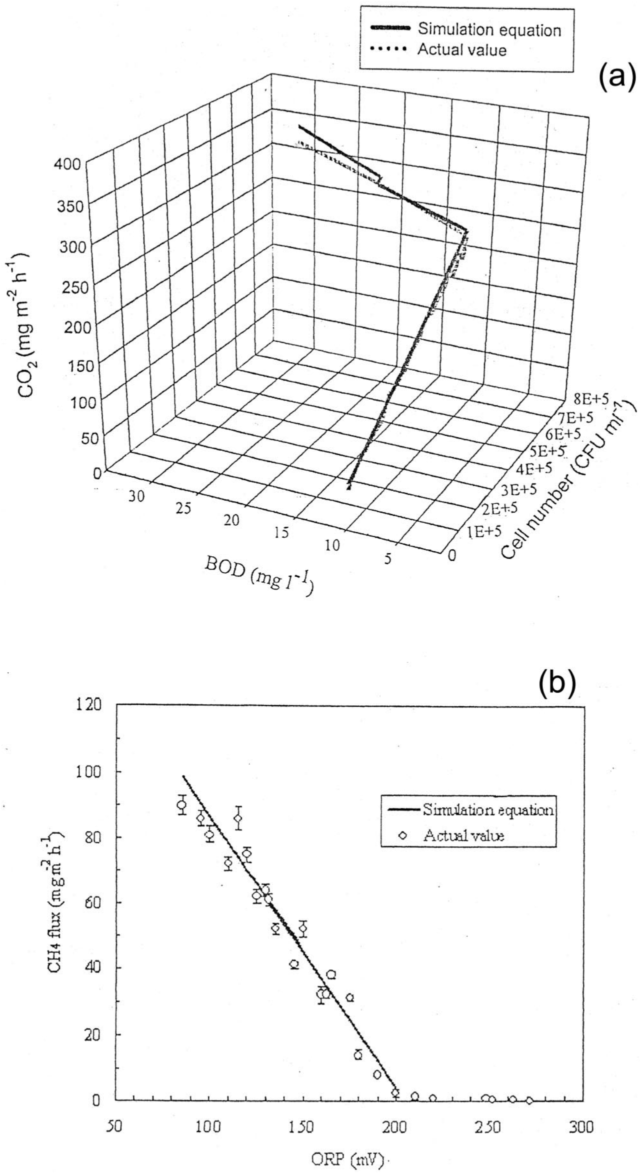

Figure 7. Verification of correlation between gases flux and water quality. (A) Predicted CO_2 flux and actual CO_2 flux in the different rivers; (B) Predicted CH_4 flux and actual CH_4 flux in the different rivers.

insignificant difference existed between sediment characteristics in the Danshuei and Gaoping rivers and CO_2 flux. The significance level (0.6418) was >0.05 (α), indicating that none of the sediment characteristics was related to CO_2 flux. For the CH_4 emission study, a relatively high R^2 (0.636) revealed significant differences between some sediment characteristics and CH_4 flux. The significance level (0.0177) was <0.05 (α), indicating that a regressive correlation should exist between sediment characteristics and CH_4 flux. Using the *t* tests check, we determined that TOC (x_1), T-N (x_2), and the constant were significant; their multiple regression equation can be expressed as $y = 5.073962x_1 + 2.871245x_2 - 12.3262$.

Model Verification and Gas Emissions Reduction

The feasibility and reliability of the developed multiple regression equations in this study were determined by focusing on a cross-check of additional data collected from the Danshuei and Gaoping rivers. Data obtained from the upstream, midstream, and downstream segments of the Donggang River and Erren River in Southern Taiwan were also included in testing the validity of the developed equations. Twenty-four sets of measured data originating from 12 sampling sites were used to evaluate the aptness of the regression equations. The results indicate that the actual CO_2 flux from various sampling sites was consistent with the simulation equation, with a maximal deviation of 14.3% (Figure 7A). Similarly, the actual CH_4 flux from various sampling sites also fitted the simulation equation ($y = -0.825216x + 169.02257$), with a maximal deviation of 11.2% (Figure 7B). Figure 8 indicates the results of model verification for CH_4 flux combined with the TOC and T-N parameters of sediment characteristics. A satisfactory relationship was observed between actual and simulation data derived from the equation $y = 5.073962x_1 + 2.871245x_2 - 12.3262$, with a maximal deviation of 17.5%. The results mentioned above confirm that CO_2 emissions are closely related to BOD_5 concentration and bacteria number. Also, CH_4 emissions are highly dependent on ORP in the river, and CH_4 emissions maintain a strong connection with TOC and T-N contents in the sediment. TOC in the sediment is normally derived from organic matter (e.g., BOD) in the river. Both BOD_5 in the river and TOC in the sediment separately play a decisive role in CO_2 and CH_4 emissions. Therefore, BOD reduction/removal should be the best means of preventing the production of GHG in the river.

CONCLUSIONS

The results of this study demonstrate that an insignificant relationship exists between CO_2/CH_4 gas emissions and environmental conditions. For the relationship between water quality parameters and gas emissions, BOD_5 concentration and bacteria number in the rivers are closely related to CO_2 emission, and ORP is the main factor affecting CH_4 emission, especially when ORP is <159 mV. For the relationship between sediment characteristics and

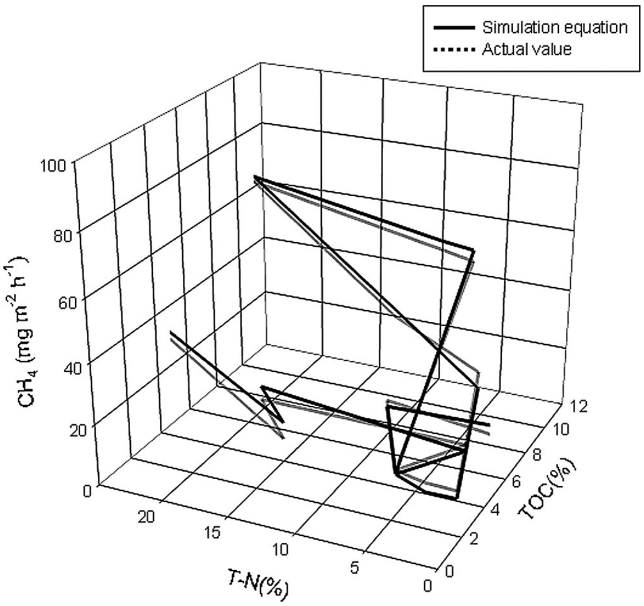

Figure 8. Verification of correlation between CH_4 flux and sediment characteristics.

gas emissions, TOC and T-N concentrations are positively correlated with CH_4 emission, but none of the sediment characteristics are significantly correlated with CO_2 emission. These relationships are described by several multiple regression equations, and their reliability is verified by actual data, with a <18% maximal deviation. Because CO_2 and CH_4 emissions are mainly affected by BOD_5 concentrations in the river and by TOC contents in the sediment, reducing the discharge of organic matter into rivers is the best way to reduce GHG emission.

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