Methane production in river and lake sediments in Taiwan

Shang-Shyng Yang

Department of Agricultural Chemistry and Global Change Center, National Taiwan University, Taipei, Taiwan 10617, Republic of China
E-mail: ssyang@ccms.ntu.edu.tw

To investigate the relationship between methane production in the sediments and pollution of the river and lake, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the water sample, organic matter content and methane production of the sediment were measured. Experimental results indicated that BOD, COD and organic matter contents were low in Bei-tan Lake, the I-lan River and reservoirs; and methane production of these sediments ranged from 0.24 to 1.06 mg L^{-1}. However, BOD, COD and organic matter contents were high in the Hsin-dan River, Keelung River, drainage river of Taoyuan County, park pond and fishery pond. Methane production of these sediments was between 11.75 and 54.54 mg L^{-1}. Sediments of drain river and fishery pond had high methane production, at 25.41 to 54.54 mg methane L. Methane production of sediments had a good correlation with BOD, COD and organic matter contents. Methane production was proportional to the increment in incubation temperature from 12 to 40°C.

Keywords: BOD, COD, methane production, organic matter, sediment

Introduction

Although methane is a minor component of the global carbon cycle, its increased concentration in the atmosphere has recently received increasing attention (Cicerone and Shetter, 1981; Seiler, 1984). Methane concentrations have been increasing from 1.50 to 1.72 ppm during the last decade (Seiler, 1984; Ehhalt, 1985). The major contributing sources of methane production are found in wetlands, rice paddies, and sediments (Ehhalt, 1985; Conrad, 1989).

The total length of the major rivers in Taiwan is 2934.0 km. For 1857.2 km (63.3%) there was no pollution, for 361.1 km (12.3%) there was slight pollution, for 326.4 km (11.1%) there was moderate pollution, and for 389.3 km (13.3%) there was heavy pollution (EPA-ROC, 1996). In addition, there were 62 943 ha of ponds for fishery cultivation in 1994. Most fishery feeds contained high protein and organic matter, and the residue of feeds polluted the ponds. In this work, the relationship between water pollution (such as BOD, COD and organic matter content) and the methane production of sediment was investigated to assess the feasibility of using the methane production of sediment as the index of water pollution of river and lake.

Materials and Methods

Sediment collection

The sediments from lakes or rivers were collected with a home-made stainless steel cylinder (id 6 cm, od 10 cm, and length 30 cm). The cylinder was lowered to the bottom of lake or river where it scraped the sediment, slowly. After sampling, the sediment was put in an anaerobic glove bag and sampled immediately with a home-made acrylic tube (id 2.15 cm, od 2.50 cm, and height 50.00 cm), put into a serum bottle which was previously flushed with oxygen-free nitrogen gas and sealed with a butyl rubber stopper. Hsin-dan River, Keelung River and Tai-hu Park are located in Taipei City; Wan-chang-chuen Bridge and Bridge No. 9 (I-lan River) are located in I-lan County (northeastern Taiwan); fish pond, reservoir and drain river are located in Taoyuan County (northern Taiwan). Bei-tan is located at the entrance of the Hsin-dan River to Taipei City where tourists go boating during holiday and at weekends. Yung-hu Bridge and Tung-an Street are located in the central Taipei City of Hsin-dan River. Nan-kang-chi and Chuen-mei Bridge are located in the central Taipei City of Keelung River.

Biochemical oxygen demand (BOD)

Dissolved oxygen (DO) is determined by azide modification of the iodometric method and measured by 0.025N $Na_2S_2O_3$ with 2 mL of starch solution as indicator. Biochemical oxygen demand was calculated as (Rand *et al.*, 1976):

$$\mathrm{BOD}(\mathrm{mg\,L^{-1}}) = \frac{D_5 - D_0}{P}$$

where D_0 = DO of diluted sample prior to incubation, D_5 = DO of diluted sample after 5 days incubation, and P = decimal fraction of sample used.

Chemical oxygen demand (COD)

The COD value of sample was titrated by 0.25N $Fe(NH_4)_2(SO_4)_2$ with ferron as the indicator (S mL). The blank was also titrated with 0.25N $Fe(NH_4)_2(SO_4)_2$ as described above (B mL). The COD was calculated as follow (Rand *et al.*, 1976):

$$\text{COD (mg L}^{-1}) = \frac{(B - S) \times N \times 8000}{V}$$

where B = volume (mL) of blank titrated, S = volume (mL) of sample titrated, V = volume (mL) of sample, and N = normality of $Fe(NH_4)_2(SO_4)_2$.

Organic matter content

The organic carbon content was determined by wet oxidation using the Walkey–Black method and organic matter content was calculated as 1.724 times the organic carbon (Nelson and Sommers, 1982).

Methane production

Sediment was placed in a 50 mL serum bottle which had previously been flushed with oxygen-free nitrogen gas. After shaking, the gases (1.0 mL) in the head-space were withdrawn and analysed using a Shimadzu 14A gas chromatograph (Shimadzu Co., Tokyo, Japan) equipped with a flame-ionization detector. The gas sample was separated by a glass column (0.26 mm × 2 m) packed with Porapak Q (80/100 mesh). The column temperature was 55°C, and injection and detector temperatures were 80°C. The methane concentration was estimated by the head-space volume, the amounts of sediment and the water content of sediment (Yang *et al.*, 1994).

Methane-production rate

The methane production rate was measured at 0.5 hour intervals for 1.5 hours, then examined by the change in methane concentrations in the head-space after the bottle was flushed with oxygen-free nitrogen gas.

Effect of temperature on methane production rate

Twenty grams of sediment was placed into a 125-mL flask and flushed with oxygen-free nitrogen gas. The flask was incubated at 25°C for 1 hour to yield a steady state of methane production, then changed to 10°C to 40°C for 1.5 hours and the methane production rate was measured.

Chemical analysis

The pH of the water or sediment was directly measured with a pH meter, and total nitrogen was measured by the modified Kjeldahl method (Yang *et al.*, 1991).

Results

Methane production in sediment from the Hsin-dan River and the Keelung River in Taipei City

In the Hsin-dan River, the BOD and COD of Bei-tan (located at the entrance of Taipei City) was 18.1 to 24.3 and 108 to 138 mg L^{-1}, respectively. The BOD and COD of Yuan-hu Bridge and Tung-an Street (located in the central Taipei City) was 154 to 399 mg L^{-1} and 1262 to 2479 mg L^{-1}, respectively. The organic matter content of sediment ranged from 1.10 to 1.24% in Bei-tan, while it was 2.88 to 3.85% in Yuan-hu bridge and Tung-an Street. Methane production was between 0.49 and 0.63 mg L^{-1} in Bei-tan, and between 11.75 and 37.39 mg L^{-1} in Yuan-hu Bridge and Tung-an Street. The methane production rate was undetectable in Bei-tan, while it ranged from 0.06 to 0.48 mg L^{-1} $hour^{-1}$ in Yuan-hu Bridge and Tung-an Street. In the Keelung River, the BOD and COD of Nan-kang-chi and Chuen-mei

Table 1 *Methane production and properties of the water and sediment of river and lake.*

Sampling site	BOD (mg L^{-1})	COD (mg L^{-1})	Organic matter (%)	Methane production (mg L^{-1})	Methane production rate (mg L^{-1} $hour^{-1}$)
Bei-tan (Hsin-dan River)	18.1–24.3	107.6–138.0	1.10–1.24	0.49–0.63	–
Tai-tan (Taoyuan County)	10.1–15.0	49.3–86.2	0.75–0.93	0.24–0.63	0.00–0.01
Wan-chang-chuen Bridge (I-lan River)	2.0–5.0	30.1–70.0	0.30–0.75	0.24–0.61	0.00–0.02
Bridge No. 9 (I-lan River)	2.5–15.1	73.3–120.0	0.66–1.50	0.56–1.03	0.02–0.05
Reservoir (Taoyuan County)	12.1–29.7	106.7–173.3	0.70–1.76	0.93–1.06	0.03–0.18
Tung-an Street (Hsin-dan River)	306.4–399.0	1415.0–2479.0	3.17–3.85	30.71–37.39	0.06–0.10
Yuan-hu Bridge (Hsin-dan River)	153.5–260.0	1262.0–1837.0	2.88–3.25	11.75–35.15	0.15–0.48
Nan-kang-chi (Keelung River)	160.4–180.7	1215.0–1637.0	3.57–4.33	25.26–29.61	0.62–0.75
Chuen-mei Bridge (Keelung River)	144.9–169.5	606.6–839.2	2.09–3.21	22.35–27.46	0.06–0.10
Drain river(Taoyuan County)	486.0–570.0	1000.0–1683.0	3.51–5.96	26.92–54.54	0.17–0.36
Fish pond (Taoyuan County)	128.3–130.0	250.0–268.0	4.85–5.64	25.41–29.33	2.75–3.20
Tai-hu Park (Taipei City)	92.0–132.0	232.0–296.0	1.77–2.03	20.01–21.40	0.02–0.63

All the data were in triplicate except for drain river and reservoir which were four samples.

Bridge ranged from 181 to 245 mg L^{-1} and 607 to 1637 mg L^{-1}, respectively. Methane production was 22.35 to 29.61 mg L^{-1}, and the methane production rate was 0.06 to 0.75 mg L^{-1} $hour^{-1}$ (Table 1). The BOD, COD and organic matter contents were low in Bei-tan, while they were high in Yuan-hu Bridge, Tung-an Street, Nan-kang-chi and Chuen-mei Bridge. Methane production was low in Bei-tan, and the values were high in other locations.

Methane production in sediment from I-lan River

The BOD and COD values at Wan-chang-chuen Bridge and Bridge No. 9 in I-lan River were 2.0 to 15.1 mg L^{-1}, and 30.1 to 120 mg L^{-1}, respectively. The organic matter content ranged from 0.30 to 1.50%. Methane production was between 0.24 and 1.03 mg L^{-1}, and the methane production rate ranged from 0.00 to 0.05 mg L^{-1} $hours^{-1}$ (Table 1). The BOD, COD and organic matter contents were low in these locations, as were methane production and the methane production rate.

Methane production in sediment from drain river in Taoyuan County

The river in Taiwan has two functions – irrigation and drainage – so pollution of the drainage river will contaminate irrigation. The BOD and COD ranged from 486 to 570 mg L^{-1} and 1000 to 1683 mg L^{-1} for the drain rivers in Taoyuan County, respectively. The organic matter content was between 3.51 and 5.96%. Methane production ranged from 26.92 to 54.54 mg L^{-1}, and the methane production rate was between 0.17 and 0.36 mg L^{-1} $hour^{-1}$ (Table 1). Since the water pollution of drainage river is very heavy, methane production and the methane production rate are also very high in these sediments.

Methane production in sediments from lakes, ponds and reservoirs

There were 62 943 ha of fish ponds in Taiwan for the cultivation of milk fish, eels, shrimps, mussels, algae, and other fishery products, in 1994. The feed, which contained high protein and organic matter, enhanced methane production in the sediments of fish ponds. The BOD was between 12.1 and 29.7 mg L^{-1} in reservoirs, between 128 and 130 mg L^{-1} in fish ponds and between 92.1 and 132 mg L^{-1} in park ponds. The COD ranged from 107 to 173 mg L^{-1} in reservoirs, 250 to 268 mg L^{-1} in fish ponds and 232 to 296 mg L^{-1} in park ponds. The organic matter content ranged from 0.70 to 1.76% in reservoirs, 4.85 to 5.64% in fish ponds, and 1.77 to 2.03% in park ponds. Methane production was between 0.93 and 1.06 mg L^{-1} in reservoirs, between 25.41 and 29.33 mg L^{-1} in fish ponds, and between 20.01 and 21.40 mg L^{-1} in park ponds, and the methane production rate ranged from 0.03 to 0.18 mg L^{-1} $hour^{-1}$ in reservoirs, 2.75 to 3.20 mg L^{-1} $hour^{-1}$ in fish ponds, and 0.02 to 0.63 mg L^{-1} $hour^{-1}$ in park ponds (Table 1). The sediment of fish ponds and park ponds contained a higher level of organic matter and had a higher methane concentration and methane production rate than that of reservoirs.

Correlation between BOD, COD, organic matter content and methane production

From the results cited, it is clear that Bei-tan, the reservoir and I-lan River had low BOD, COD and organic matter content and methane production of these locations was low. The relationships between these parameters are presented in Figure 1. The BOD, COD and organic matter content had a linear correlation with methane production: $y = 0.023x + 0.303 (r^2 = 0.713)$ for methane production and BOD value; $y = 0.006x + 0.077 (r^2 = 0.868)$ for methane production and COD value; and $y = 0.524x + 0.112$ $(r^2 = 0.785)$ for methane production and organic matter content.

In Yuan-hu Bridge, Tung-an Street (located in Hsin-dan River), Nan-kang-chi, Chuen-mei Bridge (located in Keelung River), fish pond, park pond and drain river, the relationships between BOD, COD, organic matter content and methane production are shown in Figure 2. The BOD, COD and organic matter content had also linear correlation with methane production. $y = 4.176x + 17.060 (r^2 = 0.672)$ for methane production and BOD value; $y = 0.777x + 19.230 (r^2 = 0.511)$ for methane production and COD value; and $y = 4.101x + 12.500 (r^2 = 0.629)$ for methane production and organic matter content.

It was found that either heavy pollution sediments or low pollution sediments had good correlation between methane production and BOD, COD and organic matter contents. Therefore, methane produc-

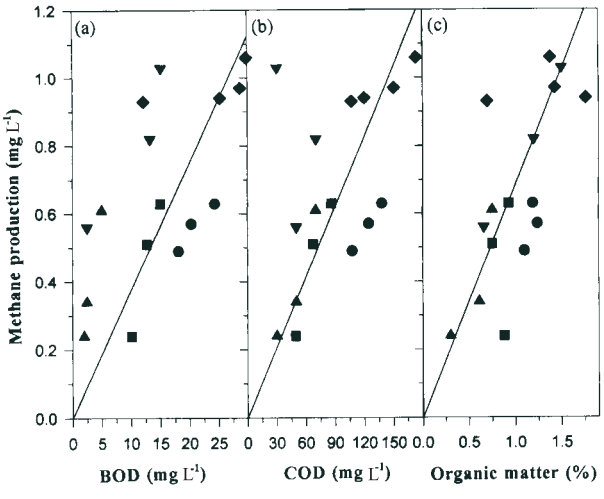

Figure 1 *Correlation between (a) BOD, (b) COD, and (c) organic matter content, and methane production in low pollution areas.* ●, *Bei-tan;* ■, *Tai-tan;* ▲, *Wan-chang-chuen Bridge;* ▼, *Bridge No. 9;* ◆, *Reservoir.*

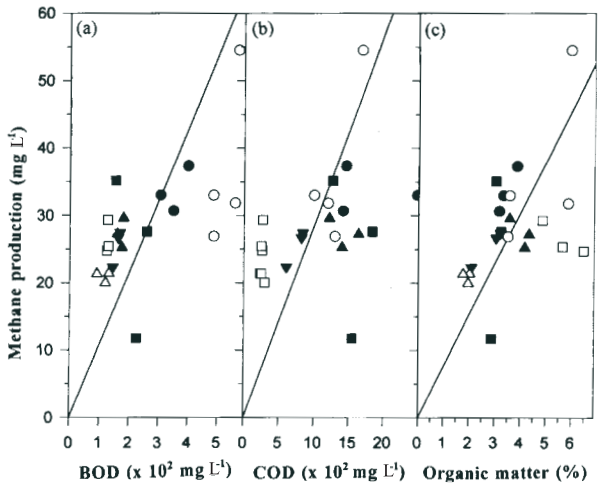

Figure 2 *Correlation between (a) BOD, (b) COD, (c) organic matter content and methane production in heavy pollution areas.* □, *Fish pond;* △, *Park pond;* ●, *Tung-an Street;* ■, *Yuan-hu Bridge;* ▲, *Nan-kang-chi;* ▼, *Chuen-mei Bridge;* ○, *Drain river.*

tion of sediment can be used as the index of water pollution of river and lake.

Effect of temperature on methane production rate

When the incubation temperature was lower than 12°C, the methane production rate was significantly inhibited. The methane production rate increased with incubation temperature from 12°C to 40°C, and a linear correlation was found between incubation temperature and methane production rate ($r^2 = 0.99$).

Discussion

BOD, COD and organic matter contents are the parameters used as the index of water pollution. The BOD values of Bei-tan, reservoirs and I-lan River (i.e. low pollution areas) were below the BOD upper limit for rivers, reservoirs and lakes of our country. The BOD values downstream of the Hsin-dan River, Keelung River and drain river of Taoyuan County (i.e. heavy pollution areas) were higher than the BOD upper limit of wastewater effluent of cities and counties (EPA-ROC, 1985). Cultivation of fish, eels, shrimps, algae and mussels is important for fisheries in Taiwan. Total cultivation areas of fish ponds was 62 943 ha in 1994, and the annual production was 254 780 tons (costing 1097 million US dollars). The total length of major rivers in Taiwan is 2934.0 km, and 13.3% of them were heavily polluted in 1994. Twenty-five public reservoirs are available for drinking water supply and some of them suffered eutrophication in 1994 (EPA-ROC, 1996).

BOD and COD of water, organic matter contents of the sediment in Bei-tan, I-lan River and reservoir were low, while the values were high in fishery ponds, park ponds, the downstream of Hsin-dan River and Keelung River, and drain river of Taoyuan County. The methane production of the sediments had good correlation with BOD and COD of water, and organic matter content of sediments. Methane production of paddy soils also increased with organic matter content of test soils (Yagi and Minami, 1990; Wang *et al.,* 1992; Yang *et al.*, 1994). In addition, methane production and production rate of the sediment were not only affected by organic matter content, but also determined by the component of organic matter. The methane production rate of sediments from fishery ponds was higher than that from rivers or park ponds; these results indicated that high protein feed residue favoured methane production. Most of the organic matter in the sediment of river was resistant to decomposition by the microbes for methane production. A similar effect was also found in the fresh green manure supplement to the paddy soil which had a higher stimulating effect for methane production than xylan, rice straw or corncob supplement (Chang, 1996).

Methane production depended on the incubation temperature (Koyama, 1963; Zeikus and Winfrey, 1976). When the incubation temperature was higher than 12°C, methane production rate increased with temperature. Methane production of sediment by methanogenic bacteria depended on incubation temperature. The same phenomena were observed in the paddy soils (Khalil *et al.*, 1991; Yang *et al.*, 1994; Chang, 1996).

From the above results, BOD and COD of water sample, and the organic matter content of sediment had a linear relation with methane production of sediments of rivers and lakes. Thus, methane production of the sediment could be used as the index for water pollution in river and lake.

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