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Assessment of sampling designs to measure riverine fluxes from the Pearl River Delta, China to the South China Sea

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Abstract The Pearl River Delta (PRD), located in South China and adjacent to the South China Sea, is comprised of a complicated hydrological system; therefore, it was a great challenge to sample adequately to measure fluxes of organic and inorganic materials to the coastal ocean. In this study, several sampling designs, including five-point (the number of sampling points along the river cross-section and three samples collected at the upper, middle, and bottom parts at each vertical line), three-point (at the middle and two other profiles), one-point (at the middle profile), and single-point (upper, middle, or bottom sub-sampling point at the middle profile) methods, were assessed using total organic carbon (TOC) and suspended particulate matter (SPM) as the measurables. Statistical analysis showed that the three- and five-point designs were consistent with one another for TOC measurements ($p>0.05$). The three- and one-point sampling methods also yielded similar TOC results (95% of the differences within 10%). Single-point sampling yielded considerably larger errors than the three- and one-point designs, relative to the results from the five-point design, but sampling at the middle sub-point from the middle profile of a river achieved a relatively smaller error than sampling at the upper or bottom sub-point. Comparison of the sampling frequencies of 12 times a year, four times a year, and twice a year indicated that the frequency of twice a year was sufficient to acquire representative TOC data, but larger sample size and higher sampling frequency were deemed necessary to characterize SPM.

Keywords Sampling design · Statistical analysis · Riverine flux · Total organic carbon · Suspended particulate matter · Pearl River Delta

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Introduction

The Pearl River Delta (PRD) is one of the leading economic zones and most urbanized areas in China and

houses several densely populated cities such as Guangzhou, Shenzhen, Hong Kong and Macao (Fig. 1). The PRD cities accounted for 95% of the exports, 76% of the gross domestic product, and 38% of the population of Guangdong Province in 2004 (http://www.teamone.com.hk/prd_glance_big5.php?s#). The PRD receives 64% of the industrial sewage and 74% of the domestic sewage of the entire Guangdong Province (Ma et al. 2005). Because of the large number of rivers and streams and frequent precipitations in the PRD region, surface runoff is a major source of contaminant loads to the coastal ocean. Runoff contains contaminants that pose risks to human health as well as to indigenous plants and animals. These risks are compounded in the PRD because most cities where the rivers and streams run through have been under rapid development with large amounts of waste continuously generated, resulting in a substantial increase in the number of contamination sources and substantial accumulation of pollutants.

In the last 20 years, numerous studies have acquired much information on the levels and distri-

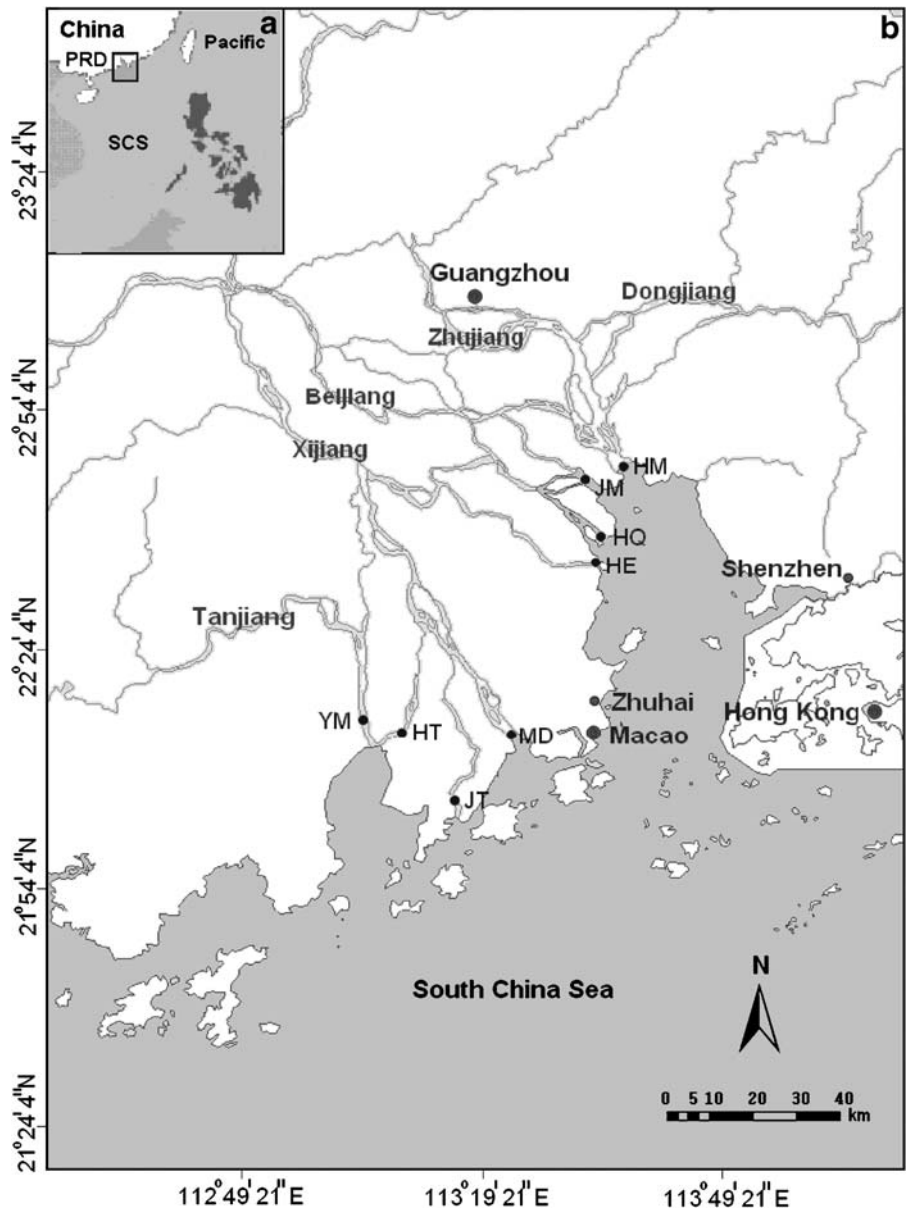

Fig. 1 (**a**) Schematic showing the geographical locality of the Pearl River Delta in China. (**b**) Map of the general study area and sampling sites symbolized by dot (•). The eight major runoff outlets are labeled with HM (Humen), JM (Jiaomen), HQ (Honqimen), HE (Hengmen), MD (Modaomen), JT (Jitimen), HT (Hutiaomen), and YM (Yamen)

bution of contaminants in the aquatic environments within the PRD (Chen and Gao 1993; Yeh and Li 1999; Zhang et al. 1999, 2002a,b; Zheng et al. 2001, 2004; Callahana et al., 2004; Hunga et al. 2005; Mai et al. 2005a,b; Ye et al. 2005; Chau 2006; Chen et al. 2006). On the other hand, no systematic study has been conducted to gauge the mass emissions of contaminants from the PRD to the coastal ocean. Such information is important for assessing the biogeochemical processes of contaminants on a regional and global scale. The main reason for lack of data on contaminant fluxes is perhaps the challenge to sample adequately because there are eight major outlets connecting the PRD to the ocean (Fig. 1). The fact that the PRD system is a tidal watercourse simply adds to the sampling difficulty. A successful sampling program must consider all eight runoff outlets simultaneously and minimize the tidal influences.

To determine the requirements for an adequate sampling strategy, the present study was initiated to introduce, evaluate, and compare several sampling designs. Total organic carbon (TOC) and suspended particulate matter (SPM) were used as evaluation parameters. Consistency among various sampling designs was evaluated based on the results of TOC. Statistical analyses were further conducted to compare the results from different sample sizes and sampling frequencies, as to elucidate the best sampling strategy in terms of measurement precision and cost effectiveness. The present study was part of our ongoing efforts to measure the mass emissions of a suite of organic and inorganic constituents from the PRD to the South China Sea (SCS) via riverine runoff, and the assessment results therefore are useful for interpretation of other related data. In addition, the information presented herein should also benefit similar studies conducted in other complicated coastal systems.

Methods

Sampling areas

The PRD, located at 111°30′E–116°E and 21°30′N–23°40′N, is an alluvial plain covering approximately 26,820 km^2. The watershed around the PRD has a total area of 453,690 km^2, with an annual mean runoff volume of 333.8 billion m^3. The PRD situates in a transitional zone of the East Asian monsoon system, where the southwesterly summer monsoon comes from the SCS and tropical Pacific oceans, while the northeasterly winter monsoon comes from mainland China (Cao et al. 2004). The PRD locates in the subtropical zone with an annual mean temperature of 14–22°C and an annual mean precipitation of 1,200–2,200 mm. Precipitations are distributed unevenly over the year, i.e., 80% of them occur in the April–September period (wet weather season) and only 20% in October–March (dry weather season) (Zhao 1990). Mean evaporation can be as much as 1,720 mm; as a result, drought remains a frequent threat to the local communities.

The general study area is depicted in Fig. 1 and the geographical information and morphology of the eight sampling sites are listed in Table 1. The PRD system consists of three main tributaries, i.e., Beijiang River, Xijiang River, and Dongjiang River. Eight major outlets can be geographically divided into two groups, i.e., the eastern and western outlets. Beijiang and Dongjiang flow into the SCS mainly via the eastern outlets, including Humen (HM), Jiaomen (JM), Hongqimen (HQ), and Hengmen (HE), while

Table 1 Geographic information about the sampling sites

Site[a]	Cross section	R.W. (m)[b]	R.L.L. (m)[c]	Station locations
YM	Guanchong	1,083	350, 480	22°16′58.6″(N), 113° 04′29.8″(E)
HT	Xipaotai	470	320	22°13′18″(N), 113°07′ 19.7″(E)
JT	Huangjin	362	110, 230	22°8′10.4″(N), 113° 17′08.5″(E)
MD	Denglongshan	612	480	22°13′45″(N), 113°23′ 50″(E)
HE	Hengmen	684	190, 500	22°34′28″(N), 113°31′ 08″(E)
HQ	Fengmamiao	535	270	22°42′00″(N), 113°29′ 42″(E)
JM	Nansha	1300	563	22°44′38″(N), 113°33′ 52″(E)
HM	Dahu	3017	605, 1,885	22°48′10″(N),113°35′ 04″(E)

[a] *YM*, Yanmen; *HT*, Hutiaomen; *JT*, Jitimen; *MD*, Modaomen; *HE*, Hengmen; *HQ*, Hongqilimen; *JM*, Jiaomen; and *HM*, Humen.

[b] River width.

[c] Representative line location.

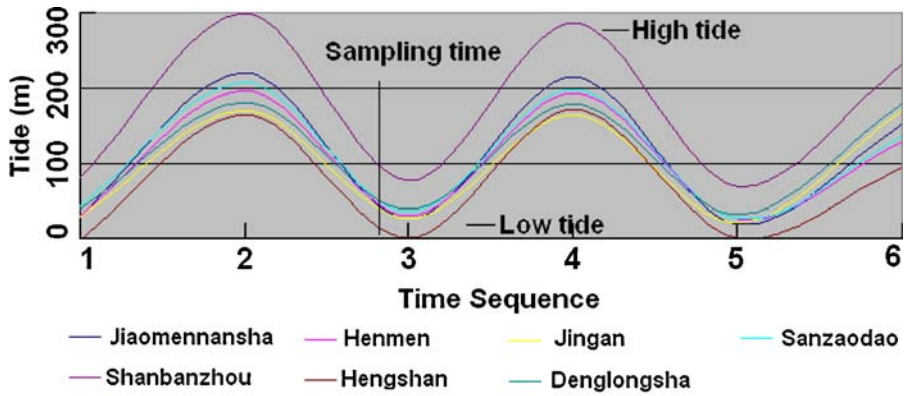

Fig. 2 A sketch to illuminate the variation of tides and the sampling time. The tide profiles were acquired from the government-owned hydrologic stations

Xijiang mostly discharges through the western outlets, including Modaomen (MD), Jitimen (JT), Hutiao (HT), and Yamen (YM). Besides, one western outlet (YM) receive most of the runoff from the Tanjiang River, a different source than those in the PRD.

Sampling protocols

Sampling was conducted during neap tides to avoid tidal influences. Because the PRD is subject to subtropical monsoon climates resulting in seasonal variation of precipitation, it was decided that sampling every month was appropriate to collect representative samples for the entire year. Furthermore, sampling was conducted approximately one hour before the intra-day lower tides (Fig. 2), but at slightly different times for the eight outlets to account for different tidal cycles. This allowed the final results to be comparable for different runoff streams. The actual sampling times at JM are listed in Table 2 and those at other outlets were approximate to JM.

Samples were collected adjacent to a government-owned hydrologic station for each outlet so that the hydrologic data acquired at the station could be used to gauge the tidal variation. At each sampling site, three sampling points were chosen vertically and three (<1,500 m) or five (>1,500 m) horizontal points were selected depending on the river width (Fig. 3). Vertically, the three sampling points were placed at the upper (1 m from the air–water surface), middle (at the middle of the water depth), and bottom (1 m from the river bed) parts of the water column. The horizontal sampling points were evenly distributed along the river cross section (Fig. 3). Overall, 15 samples were collected from HM and MD each month whereas nine were collected from the other six outlets.

Sample collection and pretreatment

Sampling was conducted once a month from March 2005 to February 2006, and a total of 1,008 water samples were taken. Before sampling, water depth, flow rate, and salinity were measured and the vertical sampling points were determined as well. Water was pumped with a stainless-steel submersible pump. After pumping for the first 5 min (water was discarded), water was collected into pre-cleaned glass containers with 1 L of water for each sample. All the samples were placed into foam boxes filled with ice during transportation to the laboratory.

Upon returning to the laboratory, water samples were filtered immediately to collect SPM with preweighed GF/F glass fiber filters (47-mm diameter; pore size 0.7 μm; Whatman International, Maidstone, England) pre-combusted at 450 °C for at least 5 h. The filters loaded with SPM were wrapped with aluminum foil and stored in plastic bags at −20°C until analysis. Filtrates of 1 L for each sample were collected for dissolved organic carbon (DOC) measurements within 48 h.

Table 2 Low tide times and sampling times at Jiaomen (JM) from March 2005 to February 2006

Sampling date	Mar 7	Apr 3	May 15	Jun 19	Jul 11	Aug 15	Sep 13	Oct 12	Nov 11	Dec 12	Jan 7	Feb18
Low tide time	6:00	2:45	0:30	18:00	23:00	15:55	15:40	15:00	14:55	11:45	13:00	10:45
Sampling time	5:00	2:30	0:30	16:00	22:15	15:25	14:30	14:40	14:00	11:30	12:30	10:10

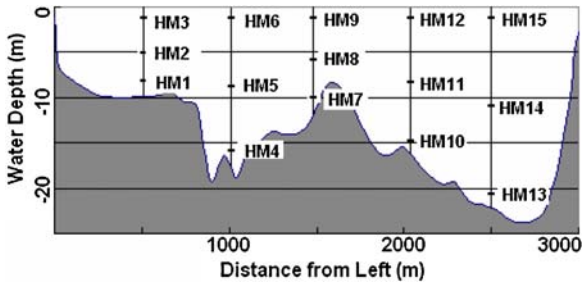

Fig. 3 Schematic showing the five-point sampling design employed at the Humen (HM) outlet and the distribution of sampling points

Total organic carbon measurements

Prior to TOC measurements, filtrate and filter samples were treated with 1 mol L^{-1} HCl to remove carbonate residues. DOC was assayed using a total organic carbon analyzer (Shimadzu TOC-VCPH, Kyoto, Japan). Carbon concentrations were determined against potassium hydrogen pthalate standards. Organic carbon standards were analyzed every 15 field samples to monitor possible instrument shifts. Samples, standards and blanks were measured in triplicate. The detection limit was 0.5 mg L^{-1} and the relative standard deviation was approximately 10%. The filters were dried at 60°C overnight, re-weighed to obtain SPM contents. Blank filters were processed the same way. Particulate organic carbon (POC) was determined by high temperature oxidation using an elemental analyzer (Elementar, Vario, EL III, Germany). Samples were analyzed in duplicate. Detection limit (calculated as three times the standard deviation of the blank for carbon) was 30 μg for carbon, and the precision for the measurement of C was under 0.1% as estimated by repeated analyses. The sum of DOC and POC concentrations was defined as TOC content.

Sampling design assessment

In the present study, one-, three-, or five-point sampling design was defined corresponding to the number of sampling points horizontally along the river cross-section. The objective of the assessment was to compare the results from different combinations (samples from different sampling designs). For HM and MD, results from one-, three-, and five-point sampling designs, representing composites of three, nine, and 15 samples, respectively, were compared with each other. For the three-point design with HM and MD, the two sampling profiles near the river banks (furthest from the middle profile) were used in addition to the middle profile. Results from one- and three-point sampling designs for the other outlets were assessed. In addition, results from the three vertical samples (each and average) at the middle profile (one-point sampling design) of each outlet were also compared with the three- and five-point sampling results. Finally, sampling frequencies of 12 (monthly), four (quarterly), and two (wet and dry weather seasons) times a year were compared. Statistical analyses were conducted with the SPSS v13.0 package.

Result and discussion

Consistency of sampling designs

The three sampling designs described in the preceding section were examined using TOC concentration as the measurable. There were two reasons for selecting TOC to discuss the consistency of the sampling designs. First, TOC was defined as the sum of POC and DOC. As a result, TOC could mimic the characteristics of organic pollutants in the particulate and dissolved phases in riverine systems. Second, using the concentration instead of the mass emission of TOC could minimize the impact of water discharge that largely regulates the TOC mass emission. Figure 4 shows that the concentrations of TOC were similar in all the samples collected from the same sampling site at the same time. The TOC contents ranged mostly within 2–4 mg L^{-1}, with 85% of all relative standard deviation (RSD) values under 20% and only 14 RSD values over 20%. The comparability among the concentrations of TOC in all individual samples collected from each river cross section confirmed the consistency of the sampling designs employed in the present study. The moderate variability in a few samples was probably resulted from various water flow rates at the sub-sampling points. As expected, the irregular shapes of the river cross-sections would cause uneven distribution of flow velocity across a river, resulting in unequal amounts of organic matter distributing throughout the river cross-section.

In our ongoing efforts to characterize organic pollutants in the riverine runoff of the PRD, an equal

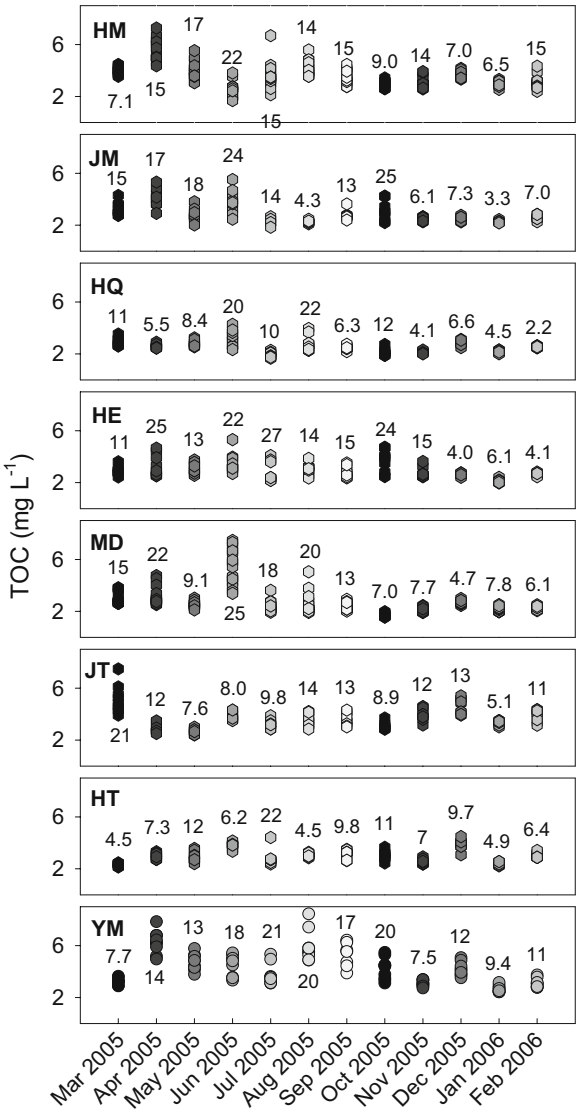

Fig. 4 Distribution of TOC concentrations in all individual samples collected from all the riverine runoff outlets from March 2005 to February 2006. The values of the relative standard deviations (%) at each sampling site were presented on the upper or bottom parts of the corresponding TOC concentrations

amount of water was taken from every sampling subpoint and combined to produce a representative sample for the entire river cross-section. The comparability of TOC concentrations in all individual samples as presented above suggests that such a mixing procedure was adequate to obtain runoff samples for our objective. In another word, the considerably even distribution of TOC indicates that organic matter in the water column may have been well blended before being transported to the sampling sites.

Comparison of sample size effects

Sample size is a critical factor in a large-scale sampling program, as it is always desirable to sample adequately at the lowest cost. To achieve this goal, the number of samples representative of the best situation should be minimized.

Statistical comparison of five- and three-point sampling designs

Among the eight riverine runoff outlets sampled, the five-point sampling design was used in HM and MD only. In this comparison, HM was used as an example. Using the data in Fig. 4, we conducted statistical analyses to examine whether there was any significant difference between the TOC results acquired by the three-point and five-point sampling designs. First, the TOC data were divided into two independent groups, i.e., the data from the three-point sampling design were designated as group 1 and those from the five-point sampling as group 2. In the statistical analysis, the degree of freedom=9 (three-point sampling)+15 (five-point sampling)−2=22. Because the difference in sampling designs was the only factor influencing the statistical results, it was designated as a single variable. Second, the two groups of data were processed separately by descriptive statistics to ensure the data sets could be further analyzed statistically. Finally, the Levene's test for equality of variances and *t*-test for equality of means were conducted.

The statistical results (Table 3) show that all the significance probability (p) values of the F-test were greater than 0.05 (the SPSS default value of significance probability). This indicates that the variances of two sampling designs were not significantly different with a 95% confidence interval(Ma 2004). Moreover, the significance probability values of the t-test were also greater than 0.05, suggesting that the average effects of the two sampling methods were not significantly different. In another word, the three- and five-point sampling designs had the same mean effect on the TOC results. Apparently, the three-point sampling design is more cost-effective and efficient

Table 3 Statistical comparison of the difference between the TOC results acquired by the three- and five-point sampling designs at the Humen (HM) outlet

Sample date	Levene's test[a]		*t*-test for equality of means			
	F[b]	p[c]	t[d]	p (2-tailed)	MD[e]	SED[f]
01/2006	0.442	0.513	−0.054	0.957	−0.0049	0.090
02/2006	0.589	0.451	−0.011	0.991	−0.0013	0.116
03/2005	0.230	0.637	0.542	0.593	0.0620	0.114
04/2005	0.195	0.195	0.663	0.767	−0.1118	0.373
05/2005	0.371	0.549	0.004	0.997	0.0013	0.311
06/2005	0.442	0.513	−0.054	0.957	−0.0049	0.090
07/2005	0.604	0.445	−0.585	0.565	−0.2211	0.378
08/2005	0.725	0.404	−0.176	0.862	−0.3978	0.226
09/2005	0.040	0.843	−0.244	0.810	−0.0556	0.228
10/2005	0.006	0.941	0.321	0.758	0.0362	0.116
11/2005	0.100	0.755	−0.062	0.951	−0.0116	0.186
12/2005	0.576	0.456	−0.009	0.993	−0.0011	0.116

[a] Levene's test for equality of variances.

[b] Parameter for Levene's test for equality of variance, $F = S_1^2/S_2^2$.

[c] Probability of significance; the SPSS default value is 0.05.

[d] Parameter of *t*-test for equality of means; $t = (\overline{X} - \mu)\sqrt{n}/S$.

[e] Mean difference.

[f] Standard error difference.

than the five-point sampling design, and should be considered more favorable over the five-point sampling design in future sampling programs.

Difference between one- and three-point sampling designs

Using the data from JM, HQ, HE, JT, HT and YM, we compared one- and three- point sampling designs. As one-point sampling design obtained only three data points, no reliable statistical analysis could be performed. Therefore the average concentrations of TOC from one- and three-point sampling designs used in the above-mentioned runoff outlets were calculated and compared with each other (Fig. 5):

$$[\mathrm{TOC}]_T = K \cdot [\mathrm{TOC}]_O \quad (1)$$

where $[\mathrm{TOC}]_T$ and $[\mathrm{TOC}]_O$ are the average concentrations of TOC from the three-point and one-point sampling designs, respectively, and K is the proportionality constant, indicative of the difference between the three- and one-point sampling strategies. Figure 5 shows that most K values (~95% of the total) are with the range of 0.9−1.1, i.e., most of the differences between the TOC results acquired from the two methods are less than 10%. The remaining 5% of the K values are within the range of 0.8−1.2. These results indicate that the errors arising from the three- and one-point sampling methods should not exceed 20% in the worst-case scenario. In addition, the TOC concentrations from the one-point sampling design were consistently lower than those from the three-point sampling design. Therefore, the one-point sampling design is regarded acceptable if the sampling error allowed is approximately 10%.

Effectiveness of minimum sample size

The minimum sample size means one sample collected from one sampling point (such as HM_7, HM_8 or HM_9 in Fig. 3) at the middle profile of each runoff outlet. If the mean concentrations of TOC and SPM from the five-point sampling design are treated as the "true" values, the effectiveness of the minimum sample size can be assessed. To generalize the assessment, the three- and one-point sampling strate-

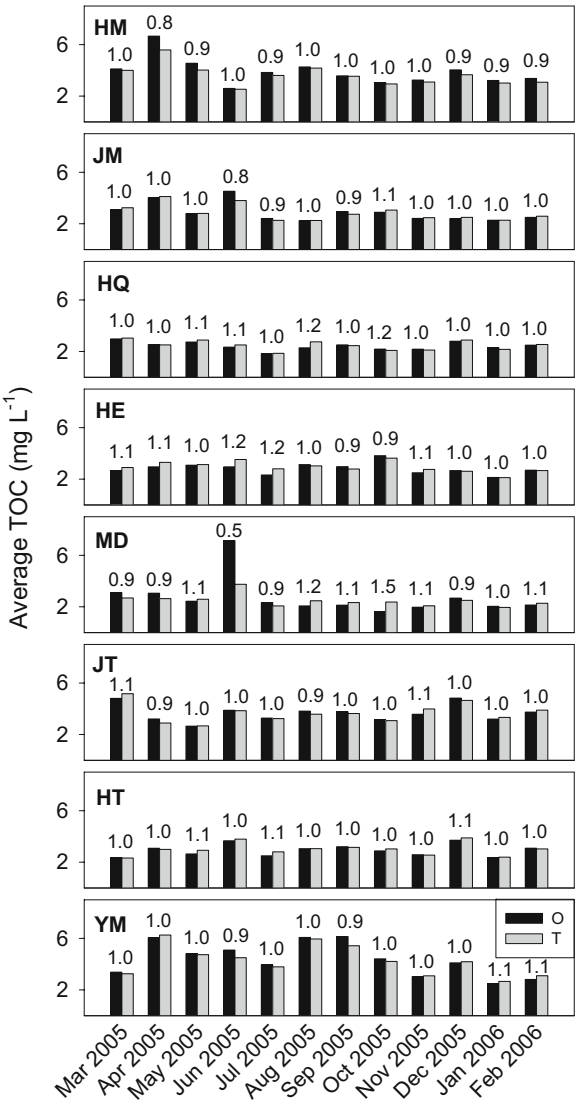

Fig. 5 Comparison of the average concentrations of TOC from the three-and one-point sampling designs within the same sampling sites: JM (Jiaomen), HQ (Honqimen), HE (Hengmen), JT (Jitimen), HT (Hutiaomen), and YM (Yamen). *O* designates the one-point sampling design (black bar) and *T* denotes the three-point sampling design (gray bar). The numbers on the bars are $[TOC]_T/[TOC]_O$

gies discussed above were also included for comparison. Again, the HM data were used for comparison.

Figure 6 shows that the three-point sampling method obtained a smaller error than those from all other sampling methods. This well corroborates the statistical analysis results for the three- and five-point sampling designs (Table 3). On the other hand, the errors associated with sampling from just one point at the middle profile (HM_7, HM_8 or HM_9 in Fig. 3) were considerably larger, with the error from the bottom sampling point (HM_7 in Figure 3) being the largest. Both the TOC and SPM data show that the relative errors with HM_8 were smaller than those with either HM_9 or HM_7. Additionally, the relative deviation with the one-point sampling design was greater than that with the three-point sampling design but smaller than those with single-point samplings (HM_7, HM_8 or HM_9). Figure 6a also shows that the relative deviation with the sampling at HM_8 for TOC was less than 10%. A comparison of the relative deviations with the TOC results from different sampling designs indicates that sampling from HM_8 and the other three sampling designs (one-, three- and five-point) were able to obtain the same sampling efficacy with a relative deviation of less than 15% (Fig. 6a).

It should be noted that the relative deviation for SPM with HM_8 was greater than 20% compared to the "true" value (Fig. 6b). The relative deviations for SPM with other sampling strategies were also larger than those for TOC. Even the one-point sampling design was not acceptable because the error of SPM was greater than 20% relative to the five-point sampling design (Fig. 6b). This seems to suggest that assessment on a specific sampling design using these two measurement parameters would not result in similar conclusions. This dissimilarity between the two parameters may be due to the transport process that would mix long-transported suspended particles with some denser materials such as sandy soil containing lower organic matter contents. Furthermore, sediment on the riverbed can be easily turbinated, resuspended into the water column, and be available for sampling. This may explain why sampling at HM_7 resulted in the largest errors for both TOC and SPM compared to other sampling methods (Fig. 6). All these results indicate that TOC was more appropriate than SPM as a measure for assessment of the effectiveness of riverine runoff sampling designs. Moreover, TOC can reflect the true distribution of organic pollutants in the water column because of the strong affiliation of hydrophobic chemicals with organic matter. As a result, the effectiveness of sampling designs seems to be better assessed by TOC than SPM, although SPM was also used to examine the efficiency of sampling designs elsewhere (Leecaster et al. 2002).

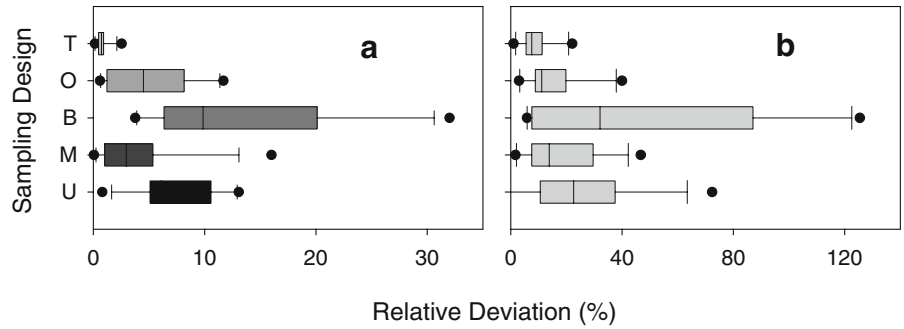

Fig. 6 Comparison of the standard deviations associated with the one- and three-point sampling strategies relative to the five-point strategy using (**a**) TOC and (**b**) SPM data from Humen (HM). *T*: three-point sampling design; *O*: one-point sampling strategy; *U*: Upper point at the middle profile (Fig. 3); *M*: Middle point of at the middle profile; *B*: Bottom point at the middle profile

Comparison of sampling frequency

All the previous assessments of the efficacy of different sampling designs were based on a sampling cycle of 12 times a year (once a month). To examine whether the sampling frequency would affect the concentration or flux data, we compared the annual fluxes and mean concentrations of TOC and SPM using the simulated sampling frequencies of 12 times a year (monthly), four times a year (quarterly), and twice a year (wet and dry weather seasons) (Table 4). In this comparison, two types of sampling designs were used, i.e., the five-point (for HM and MD) or the three-point (for the remaining six outlets) design and the one-point design for all the outlets.

For the five- or three-point sampling design, the sampling frequency of twice a year (June and December, respectively) was strikingly consistent with that of 12 times a year (9.8×10^5 vs. 9.7×10^5 tons year^{-1}) in terms of the annual fluxes of TOC. The frequency of four times a year (February, May, August, and November, respectively), on the other hand, obtained a slightly lower TOC flux value (8.8×10^5 tons year^{-1}) than the other two sampling frequencies (9.7×10^5 and 9.8×10^5 tons year^{-1}; Table 4). For the annual mean TOC concentrations, the sampling frequency of twice a year yielded a slightly larger value (3.6 mg L^{-1}) than the other two sampling frequencies (3.1 and 3.2 mg L^{-1} for quarterly and monthly samplings, respectively). These

Table 4 Annual fluxes and annual mean concentrations of total organic carbon (TOC) and suspended particulate matter (SPM) within the Pear River Delta from different sampling frequencies

Frequency	*TOC*				*SPM*			
	$F_{3/5}$[a]	$C_{3/5}$[b]	F_1[c]	C_1[d]	$F_{3/5}$[a]	$C_{3/5}$[b]	F_1[c]	C_1[d]
12 times year^{-1}[e]	9.7	3.2	10.0	3.2	2.6	51	2.8	51
Four times year^{-1}[f]	8.8	3.1	8.7	3.1	1.3	38	1.1	35
Two times year^{-1}[g]	9.8	3.6	9.7	3.7	4.3	96	5.0	103

[a] Flux in 10^5 (for TOC) or 10^7 (SPM) tons year^{-1} from the five- (for HM and MD) or three-point (for the remaining six outlets) sampling design.

[b] Annual average concentration (mg L^{-1}) from the five- (for HM and MD) or three-point (for the remaining six outlets) sampling design.

[c] Flux in 10^5 tons year^{-1} from the one-point sampling design.

[d] Annual average concentration (mg L^{-1}) from the one-point sampling design.

[e] Sampling once a month.

[f] Sampling once a quarter in February, May, August, and November.

[g] Sampling in June and December, the wet and dry seasons, respectively.

results clearly indicate that the amount of water flow would be the major factor dictating the mass fluxes of organic matter transported from the PRD to the coastal ocean. In this context, the sampling frequency of twice a year should be sufficient if the sampling objective is to gauge the annual flux of organic matter or compounds. It should be noted that, however, one of the sampling times for the twice-a-year frequency must be conducted during the wet weather season when the runoff flow is almost the largest. This is because the TOC concentrations appeared quite constant throughout the entire sampling period (Fig. 4); therefore, the discharge flow becomes a determining factor for flux measurements. On the other hand, the quarterly sampling method obtained better concentration data than the twice a year method (Fig. 4). Table 4 also shows that the results of SPM did not have any clear trend for different sampling frequencies. This may give further evidence that SPM is not a good parameter to assess the effectiveness of sampling designs because too may factors may impact the occurrence and distribution of SPM. Therefore, if SPM is the target analyte, larger sample size and higher sampling frequency become necessary.

For the one-point sampling design, the results were considerably consistent with those from the five- or three-point design (Table 4). Therefore the conclusions about the effectiveness of different sampling frequencies are also applicable to the one-point sampling design. This suggests again that small sample size was able to obtain fairly consistent fluxes and concentrations of organic matter with small errors (less than 10%) relative to the most comprehensive sampling efforts.

Conclusions

The present study thoroughly examined the effectiveness of various sampling designs and frequencies conducted at the eight major riverine runoff outlets connecting the PRD, South China, to the SCS. Several conclusions can be derived from the assessment. First, the three- and five-point sampling designs were not significantly different in acquiring TOC concentrations (or equivalently fluxes) at two larger outlets (HM and MD). Furthermore, the one- and three-point sampling designs were also consistent with one another to determine TOC at the other six smaller outlets. Second, among the single-point sampling methods, sampling at the middle point of the vertical profile (Fig. 3) yielded the best results relative to the five-point sampling design. For TOC measurements, a single-point sampling procedure was adequate with an error of less than 10%. Third, the sampling frequency of twice a year was as effective as the monthly or quarterly sampling frequency in obtaining TOC fluxes or concentrations. Finally, TOC was a better parameter than SPM for the assessment of the sampling designs and frequencies.

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