Available online at www.sciencedirect.com

SCIENCE DIRECT

Environment International 31 (2005) 1133 – 1140

ENVIRONMENT INTERNATIONAL

www.elsevier.com/locate/envint

Chemical tracers as indicator of human fecal coliforms at storm water outfalls

Nalini Sankararamakrishnan*, Qizhong Guo

Department of Civil and Environmental Engineering, Rutgers, The State University of New Jersey, 623 Bowser Road, Piscataway, NJ 08854, USA

Received 4 November 2004; accepted 3 March 2005
Available online 1 June 2005

Abstract

Indicators to distinguish between fecal coliforms of human and animal origin were investigated in water from storm sewer outfalls to a coastal lake during wet and dry weather. The ratio of fecal coliform relative to fecal streptococci count was used as the microbiological indicator. Concentrations of human-activities originated caffeine, anionic surfactant, fluoride, and fluorescence whitening agent (FWA) were used as chemical indicators. The ratio of fecal coliform to fecal streptococci ranged from 0.2 to 3.0, during wet weather making it difficult to interpret the origin of fecal pollution. However, concentrations of caffeine, anionic surfactant, fluoride, and FWA in storm water outflow during wet weather were much higher than those in the lake water during dry weather, indicating the presence of human waste at storm water outfall. Strong correlation between fecal coliform counts and chemical parameter values further indicated the human contribution to the fecal coliform count. In addition, a strong correlation among the chemical parameters suggested that only one of them is needed as chemical tracer to detect the presence of human input.

Keywords: Chemical tracer; Storm drainage; Fecal pollution; Chemical analysis; Coastal lake

1. Introduction

To protect public health, regulations on pathogen contamination have been developed for water bodies such as streams, lakes, and coastal waters that are used for swimming and fishing. Presence of fecal coliform is typically used as an indicator for the presence of pathogen. For instance, in the State of New Jersey, USA, the surface water quality standards stipulate that fecal coliform levels should neither exceed a geometric average of 200 counts per 100 ml of water nor should 10% of the total sample taken during any 30-day period should exceed 400 counts per 100 ml of water.

Information on human and/or animal origin of fecal pollution was found necessary for proper source control and treatment that would be required. Sinton et al. (1998) have thoroughly reviewed the methods to distinguish human and animal fecal contamination. Commonly used indicators of pathogen contamination such as fecal coliform could not distinguish the difference between human and animal origin (Feacham, 1975). The ratio of fecal coliform to fecal streptococci (FC/FS), the most frequently used method for determining whether pollution is of human or of animal origin is not an unambiguous indicator of fecal sources. This ratio has been shown to be suitable for relatively fresh samples and sample age dramatically shifts the ratio (Geldreich et al., 1968; Geldreich and Kenner, 1969). Pitt et al. (1993) produced a report for the EPA regarding the detection of inappropriate pollutant entries into storm drainage system. High concentrations of fluoride, ammonia, surfactant, fluorescence, and other constituents were suggested as potential indicators for the presence of sanitary sewage. Hence, it was felt worthwhile to evaluate caffeine, anionic surfactants, and fluorescence whitening agent (FWA) as chemical indicators in the present study.

* Corresponding author. Present Address: Facility for Ecological and Analytical Testing, Indian Institute of Technology, Kanpur, U.P., 208016, India. Tel.: +91 512 2597844; fax: +91 512 2597844.
E-mail address: nalini@iitk.ac.in (N. Sankararamakrishnan).

0160-4120/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envint.2005.04.002

Caffeine is a potential indicator of domestic wastewater because it is clearly of anthropogenic origin and often has been detected in wastewater, surface water, and groundwater. Caffeine concentrations of 37 μg/l in sewage effluent (Paxeus and Schroder, 1996), 3.2 μg/l in well water (Buszka et al., 1994), 0.23 μg/l in ground water (Seiler et al., 1999), and 0.14–1.6 μg/l in Boston Harbor (Siegener and Chen, 2002) have already been reported in the literature. These studies indicate that caffeine should be readily detectable in aquatic systems.

Linear alkyl benzene sulfonate commonly referred to as LAS is a major household anionic surfactant used in detergents. Since domestic wastewater contains used detergents, LAS can be monitored to detect human wastewater contamination. The potential of using LAS as molecular tracers for domestic wastewater was earlier reported (Egan et al., 1983).

Another chemical tracer, which was included in the present study, was fluorescence whitening agent (FWA). FWAs contribute to about 0.15% of the laundry agents. FWAs bound to the fabric and its intense blue fluorescence compensates for the yellowish cast of cotton. Although these FWAs are partly bound to the fabric during the washing process, a considerable fraction (5–80%) remains in the washing liquor and is discharged to the sewers. Several studies have evaluated the use of optical brighteners as indicators of septic tank or sewerage discharge, with varying results (Thrailkill, 1988; Close et al., 1989; Poiger et al., 1998).

The drinking water supplied to the surrounding areas of the study site (Deal Lake, New Jersey, USA), contained 0.8–1.0 ppm of fluoride. The drinking water, after human consumption, ends up in the sanitary sewer. Hence, the ability of fluoride as a chemical tracer to detect human input was also evaluated.

Though individual studies have been reported with one of the chemical tracer to distinguish between human and animal contamination, a combined study on the evaluation of both chemical (caffeine, surfactants, fluoride and FWA) and biological (fecal coliform, fecal streptococci and enterococci) tracers has not been reported so far. Thus, the present study was focused on the evaluation of the combination of chemical and biological tracers including fecal coliform, fecal streptococci, caffeine, surfactant, FWA, and fluoride to detect the presence of sanitary sewage at storm water outfall. Other water quality parameters were also included as a subsidiary part of the study and for the reference purposes. These parameters include enterococci, biochemical oxygen

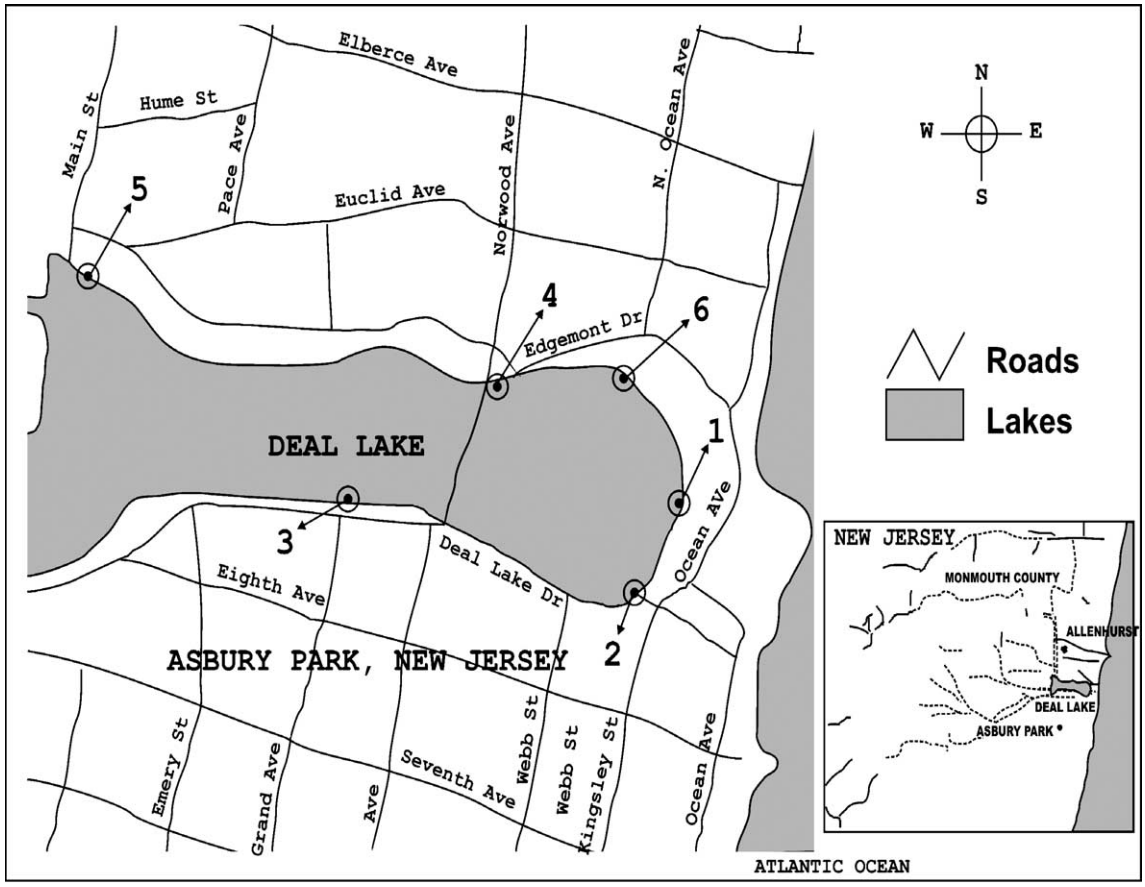

Fig. 1. Sampling locations at Deal Lake, NJ.

Table 1
Water quality parameters analyzed using standard methods

Parameter	Method	Section
Fecal coliform	Fecal coliform procedure	9221 E
Fecal streptococci	Multiple-tube technique	9230 B
Enterococci	Multiple-tube technique	9230 B
Biochemical oxygen demand	5-day BOD test	5210 B
Chemical oxygen demand	Closed reflux, titrimetric	5220 C
Fluoride	SPADNS method	4550-F D
Surfactant	Anionic surfactant as MBAs	5540 C
Nitrate	Automated cadmium reduction	4500-NO_3 F
Orthophosphate	Automated ascorbic acid reduction	4500-P F
Ammonium	Automated phenate method	4500-NH_3 H
Total suspended solids	Total suspended solids method	2540 D

demand, chemical oxygen demand, total suspended solids, nitrate, ammonia, particulate nitrogen, orthophosphate, and salinity.

2. Materials and methods

2.1. Sampling site

Deal Lake is located in eastern Monmouth County, New Jersey. The lake extends 58 hectares (143 acres) with a watershed area of 496 hectares (1228 acres). During storm events on December 6, 1999 and during dry conditions on December 28, 1999, water samples were collected from various sites around Deal Lake, New Jersey, USA as shown in Fig. 1. Location 1 is where the lake water and ocean water are exchanged through a flume and a weir. Water samples were taken at the lake outlet during both storm events and dry conditions. At locations 2 through 6, water samples were collected directly from storm water outfalls during storm events and from the lake adjacent to the outfalls during dry conditions.

2.2. Sampling method

Three storm water samples were collected during three different storm events on December 6, 1999 and one lake water sample during the dry weather on December 28, 1999 at each location. Samples were collected in sterilized one-l polythene bottles and stored in ice. Samples for the bacterial analysis were immediately transported to QC Laboratories, Pennsylvania. Samples for the analysis of nitrate–N, ammonium, and orthophosphate were immediately filtered using Whatman 0.45 μm syringe filters and stored in sterilized polyethylene test tubes in ice. After transportation to the lab, analysis of biochemical oxygen demand was carried out immediately and all the other samples were stored at −20 °C until analyzed. Duplicate analyses were carried out on all the chemical parameters.

2.3. Analytical methods

Standard Methods (APHA, 1995) were used to analyze samples for the parameters listed in Table 1. The methodologies for other chemical parameters are described below.

2.3.1. Measurement of salinity

Salinity was measured using ATAGO hand refractometer.

2.3.2. Determination of caffeine in water samples

Caffeine was analyzed by Varian 3400 GC interfaced to a Finnigan MAT 8230 high resolution, magnetic sector, double focusing mass spectrometer GC/MS. Caffeine-trimethyl-$^{13}C_3$ was used as an internal standard. The detection limit of the method was found to be 20 ng/l in the final solution. One milliliter of 10 mg/l of Caffeine-trimethyl-$^{13}C_3$ was added to 1 l of water sample. The solution was extracted three times with 200 ml of methylene chloride. After extraction, the combined organic layers were evaporated in a Kuderna–Danish evaporator to ~5 ml. Nitrogen gas was purged to reduce the volume further to ~1

Table 2
Counts of microorganisms in storm water samples at Deal Lake during storm event on December 6, 1999

Storm event	Parameter	Loc. 1	Loc. 2	Loc. 3	Loc. 4	Loc. 5	Loc. 6
End of first storm (11:30 AM)	Enterococci (mpn/100 ml)	800	>160,000	5000	13,000	N/A[a]	8000
	Fecal coliform (mpn/100 ml)	23,000	>160,000	5000	8000		24,000
	Fecal streptococci (mpn/100 ml)	800	>160,000	8000	24,000		8000
	Fecal coliform/fecal streptococci	28.7	1.0	0.6	0.3		3.0
During second storm (1:30 PM)	Enterococci (mpn/100 ml)	80	24,000	24,000	2300	5000	13,000
	Fecal coliform (mpn/100 ml)	400	50,000	24,000	8000	5000	5000
	Fecal streptococci (mpn/100 ml)	400	24,000	24,000	24,000	24,000	24,000
	Fecal coliform/fecal streptococci	1.0	2.1	1.0	0.3	0.2	0.2
End of second storm (3:45 PM)	Enterococci (mpn/100 ml)	1400	13,000	24,000	3400	8000	5000
	Fecal coliform (mpn/100 ml)	8000	5000	24,000	24,000	24,000	8000
	Fecal streptococci (mpn/100 ml)	5000	24,000	24,000	24,000	8000	5000
	Fecal coliform/fecal streptococci	1.6	0.2	1.0	1.0	3.0	1.6

[a] Water was not flowing from this storm water outlet during outfall storm.

Table 3
Concentrations of water quality parameters in storm water samples at deal lake during storm event on December 6, 1999

Storm event	Parameter	Loc. 1	Loc. 2	Loc. 3	Loc. 4	Loc. 5	Loc. 6
End of first storm[a] (11:30 AM)	BOD (mg/l)	5.8±0.2	14.3±0.1	16.9±0.2	9.8±0.1	N/A[b]	19.9±0.2
	COD (mg/l)	160.0±3.5	213.3±4.8	240.0±5.6	106.6±7.5		80.0±2.5
	TSS (mg/l)	14.8±0.2	23.2±0.1	18.9±0.2	15.5±0.3		19.2±0.3
	NO_3–N (mg/l)	0.10±0.02	0.50±0.05	0.30±0.02	0.70±0.05		0.60±0.05
	NH_3–N (mg/l)	0.10±0.01	3.80±0.02	0.70±0.04	0.50±0.02		0.30±0.03
	PN (mg/l)	0.20±0.01	0.30±0.02	0.40±0.04	0.40±0.03		0.20±0.02
	PO_4–P (μg/l)	ND	0.10±0.01	0.20±0.01	0.20±0.01		0.10±0.01
	Salinity (g/l)	18.0±0.5	3.0±0.5	2.0±0.5	7.0±0.5		4.0±0.5
During second storm[a] (1:30PM)	BOD (mg/l)	7.9±0.3	24.1±0.5	17.6±0.2	21.1±0.3	20.3±0.5	18.8±0.2
	COD (mg/l)	120.0±5.5	160.0±6.8	128.0±5.6	240.0±5.9	120.0±4.8	106.6±6.5
	TSS (mg/l)	23.9±0.6	29.3±0.5	20.2±0.2	13.3±0.5	58.0±0.8	24.0±0.3
	NO_3–N (mg/l)	0.10±0.01	0.40±0.02	0.20±0.02	0.30±0.03	0.20±0.04	0.40±0.05
	NH_3–N (mg/l)	0.20±0.03	0.50±0.02	0.40±0.03	0.10±0.02	0.10±0.02	0.20±0.02
	PN (mg/l)	0.20±0.02	0.30±0.02	0.30±0.02	0.30±0.02	0.30±0.02	0.30±0.02
	PO_4–P (mg/l)	ND	0.10±0.01	0.20±0.02	0.10±0.01	0.10±0.01	0.10±0.01
	Salinity (g/l)	11.0±0.5	3.0±0.5	2.0±0.0	2.0±0.0	2.0±0.0	2.0±0.0
End of second storm[a] (3:45 PM)	BOD (mg/l)	6.9±0.5	10.3±0.3	17.6±0.4	19.3±0.5	15.6±0.5	10.6±0.2
	COD (mg/l)	160.0±6.5	106.7±7.2	80.0±2.5	75.0±5.2	80.0±5.5	40.0±0.5
	TSS (mg/l)	20.1±1.0	27.8±1.2	27.8±0.8	15.8±0.5	45.2±1.2	22.5±0.3
	NO_3–N (mg/l)	0.10± 0.01	0.20±0.01	0.10±0.02	0.10±0.01	0.20±0.01	0.10±0.01
	NH_4–N (mg/l)	ND	0.10±0.02	0.30±0.02	0.10±0.01	ND	ND
	PN (mg/l)	0.10±0.02	0.20±0.02	0.30±0.02	0.30±0.02	0.20±0.01	0.30±0.03
	PO_4–P (mg/l)	ND	0.10±0.01	0.20±0.01	0.20±0.02	0.10±0.01	0.10±0.02
	Salinity (g/l)	18.0±0.5	2.0±0.0	2.0±0.0	2.0±0.0	2.0±0.0	2.0±0.0

ND—not detected.
[a] Values indicate the standard deviation between three readings.
[b] Water was not flowing from this storm water outflow during first storm.

ml and analyzed. Mass analysis parameters were set for positive electron impact and selected ion monitoring (SIM) for *m*/*z* 111, 193, 194, and 197 ions. The identity of the caffeine was confirmed by comparing retention times and mass spectral ion ratios with those of a known caffeine standard and those found in the National Institute of Standards and Technology (NIST) MS database. The most abundant molecular ion peak of caffeine at *m*/*z* 194 (99.8) was selected as the quantitation signal. The *m*/*z* 193 (14.3) ion was selected as the confirmation ion. [Trimethyl-$^{13}C_3$] caffeine (quantitation ion *m*/*z* 197(43.2), confirmation ion *m*/*z* 111(22.8)) was used as an isotopic reference for quantitation. The mass spectrum of [trimethyl-$^{13}C_3$] caffeine does not have signal at *m*/*z* 194 or at *m*/*z* 193, and that of caffeine does not have signal at *m*/*z* 197 or at *m*/*z* 111. Thus, there are no contributions between the caffeine and [trimethyl-$^{13}C_3$] caffeine masses.

2.3.3. Determination of fluorescence whitening agent (FWA)

FWA was determined by the method described by other researchers (Close et al., 1989; Uchiyama, 1979). Tinopal CBS-X (Disodium Distyrylbiphenyldisulfonate) provided by the manufacturer (Ciba-Geigy AG) was used as standard. The fluorescence measurements of the samples

Table 4
Microbiological counts and concentrations of water quality parameters in Deal Lake water samples during dry weather on December 28, 1999

Parameter	Loc. 1[a]	Loc. 2[b]	Loc. 3[b]	Loc. 4[b]	Loc. 5[b]	Loc. 6[b]
Enterococcus (mpn/100 ml)	<20	<20	<20	<20	<20	<20
Fecal coliform (mpn/100 ml)	80	20	40	500	20	40
Fecal streptococci (mpn/100 ml)	20	20	20	20	20	20
Fecal coliform/fecal streptococci	4	1	2	25	1	2
BOD (mg/l)	8.1 (0.5)	7.6 (0.4)	9.6 (0.6)	6.4 (0.4)	7.2 (0.5)	8.9 (0.5)
COD (mg/l)	106.6 (1.5)	160.5 (2.5)	106.6 (5.5)	159.9 (3.5)	54.2 (2.5)	54.2 (2.0)
TSS (mg/l)	40.5 (2.6)	21.8 (1.5)	23.5 (2.0)	20.5 (2.0)	35.9 (2.8)	27.8 (2.9)
Salinity (ppt)	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)
NO_3–N (μg/l)	0.30 (0.02)	0.40 (0.03)	0.30 (0.02)	0.30 (0.02)	0.40 (0.03)	0.30 (0.02)
NH_3–N (μg/l)	0.80 (0.2)	1.00 (0.3)	851.6 (51.6)	824.3 (62.8)	492.0 (35.5)	786.2 (42.8)
PN (μg/l)	81.5 (4.5)	73.2 (5.2)	115.3 (3.5)	133.1 (5.5)	94.1 (4.2)	113.4 (3.8)
PO_4–P (μg/l)	2.4 (0.5)	1.2 (0.3)	3.9 (0.5)	3.1 (0.5)	5.7 (0.5)	5.4 (0.4)

Values in the parentheses indicate the standard deviation between three readings.
[a] Lake outlet.
[b] Lake water near storm water outfall.

were made using Hitachi model F-2000 fluorescence spectrophotometer against the reagent blank. The excitation and emission wavelength used were 330 and 430 nm, respectively. Duplicate analyses were carried out for all the samples and the detection limit of the method was found to be 0.01 μg/l.

2.3.4. Determination of particulate nitrogen

For the analysis of particulate nitrogen, 500 ml to 1 l of the samples were filtered under vacuum, at less than 200 mm Hg, onto glass fiber filters (Whatman GF/F, 24 mm). The glass fiber filters used for the analysis were pre-combusted for 2 h at 475 °C. Filters were then transferred to clean Petri dishes, dried at 80 °C for 2 h, and stored at room temperature. These dried glass fiber filters were then made into pellets using tin cups. Tin cups used for this purpose were pre washed with methylene chloride and combusted at ~450 °C. The pellets were analyzed for nitrogen using Carlo Erba Na-1500 elemental analyzer. Samples were run in duplicate and pre-combusted filters served as blanks. Acetanilide was used as a standard.

2.3.5. Statistical analysis

Relationships between chemical and biological indicators were examined using the Pearson correlation coefficient (r). Variables with ≥ 25% zero values were excluded. Statistical significance was assessed at $\alpha = 0.05$ (i.e. 95% confidence level), a value accepted in most statistical analyses and defined prior to analysis.

3. Results and discussion

The results obtained for the various microbiological and chemical parameters are presented in Tables 2–5 and Figs. 2–5 for wet and dry weather. Ratios of fecal coliform (FC) to fecal streptococci (FS) are also included in Tables 2 and 4. Tables 3 and 4 represent the results of various physical and chemical parameters that were included in the present study. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonium (NH_4–N), nitrate (NO_3–N), particulate nitrogen (PN), total suspended solids (TSS), and salinity are not necessarily solely associated with the sanitary sewage. The Pearson's Statistical correlation among microbiological parameters (fecal coliform, fecal streptococci, and enterococci) and physical parameters (TSS, Salinity) is presented in Table 6 and that of chemical parameters (nitrate–N, ammonia–N, surfactant, fluoride, caffeine, and FWA) for samples taken from the various storm water outlets (locations 2 to 6 in Fig. 1) during the wet weather is shown in Table 7. The values obtained for various chemical and biological parameters obtained during the wet weather from location 2 to 6 were used in the correlation analysis. Figs. 2–4 show comparison of concentrations of Surfactant, Fluoride, and FWA, respectively, around the Deal Lake between wet and dry weather conditions. Concentrations of surfactant, fluoride, caffeine, and FWA at the outlet during wet and dry seasons are shown in Fig. 5. For the wet weather data, arithmetic average value of the three samples collected during the storm event at each location has been presented.

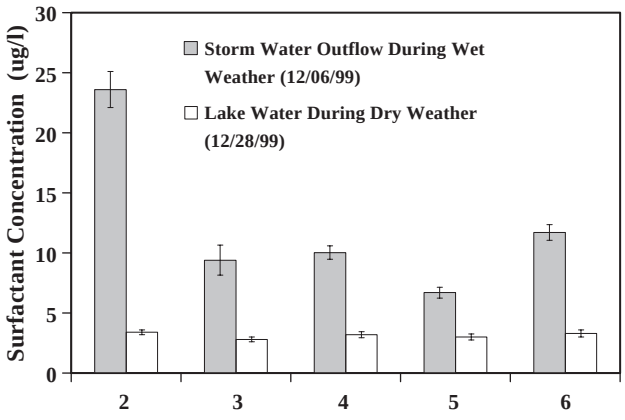

Fig. 2. Surfactant concentration in water samples of Deal Lake.

It is evident that there was a significant amount of fecal contamination ($p < 0.001$) present in the storm drain outflow compared to the lake water during dry weather (Table 2 vs. Table 4). Especially, at location 2, the values of fecal coliform, fecal streptococci, and enterococci were greater than 160,000 mpn/100 ml at the end of the first storm on that day. In comparison, counts of these three microbiological parameters were 20 mpn/100 ml at location 2 during the dry weather. At the lake outlet (location 1 in Fig. 1), arithmetic average fecal coliform count during wet weather was 10,500 mpn/100 ml, which was much higher than 80 mpn/100 ml during dry weather. The fecal coliform criteria were not exceeded during dry weather neither in the lake nor in the coastal waters into which the lake waters were discharged. However, coastal beach outside Deal Lake was commonly closed, after heavy rainfall due to a high fecal coliform count.

Table 5
Concentrations of caffeine in water samples from Deal Lake during wet and dry weather

Location	1	2	3	4	5	6
Caffeine conc. in μg/l during wet weather (12/6/1999)[a]	0.248 (0.050)	44.666 (2.850)	1.912 (0.085)	0.602 (0.050)	0.416 (0.056)	0.398 (0.045)
Caffeine conc. in μg/l during dry weather (12/28/99)	0.213 (0.035)	0.215 (0.025)	0.221 (0.050)	0.157 (0.025)	0.267 (0.030)	0.144 (0.030)

Values in the parentheses indicate the standard deviation between three readings.
[a] Average values of the three storm events during wet weather.

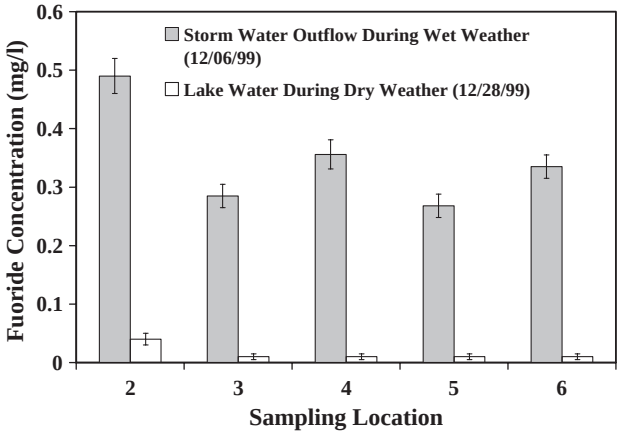

Fig. 3. Fluoride concentration in water samples of Deal Lake.

It is generally accepted that the FC/FS ratio larger than 4.0 indicates fecal contamination of human origin, and the FC/FS ratio less than 0.7 of animal origin. The FC/FS ratios between 0.7 and 4.0 are difficult to interpret (Geldreich et al., 1968; Geldreich and Kenner, 1969; Feacham, 1975). The results from Table 2 indicate that the FC/FS ratio ranges from 0.2 to 3 with the exception of location 1 (lake outlet, not storm water outfall) where it is found to be 28.7 at the end of the first storm. In the case of dry weather, the values ranged between 1.0 and 25.0 highest being at location 4. Nevertheless, due to the differential survival rates and other factors, this ratio is not reliable if the fecal contamination is not fresh, or if the concentrations of fecal streptococci are less than 100 cfu/100 ml (APHA, 1995). This was demonstrated in a study in South Africa where the addition of human fecal material into an agriculturally impacted river showed a rise in the FC/FS ratios, but farther down stream, the ratio fell to levels that would not indicate the presence of domestic sewage (Jagals and Grabow, 1996). Hence, based on this ratio alone, it is difficult to interpret the origin of fecal contamination.

Since a clear distinction cannot be made with the origin of the fecal contamination using microbiological indicators

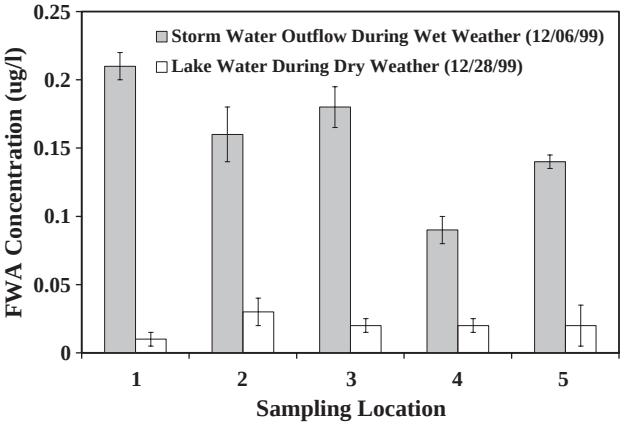

Fig. 4. Fluorescence whitening agent concentration in water samples of Deal Lake.

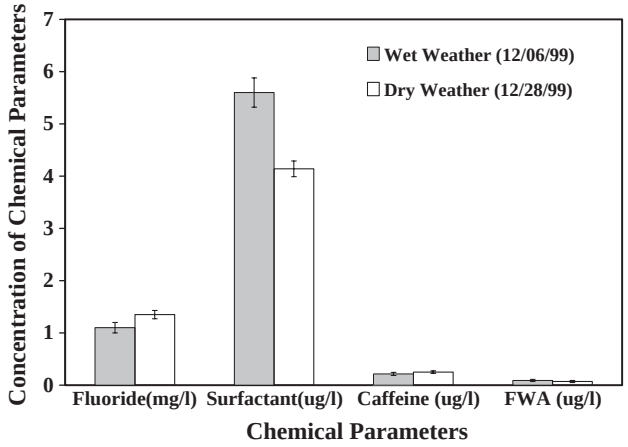

Fig. 5. Concentrations of fluoride, surfactant, caffeine, and FWA in water samples at the outlet of the Deal Lake.

alone, other water quality parameters were also evaluated. The concentrations of other water quality parameters namely, BOD, COD, nitrate–N, phosphate–P, ammonia–N, particulate–N in wet weather samples (Table 3) and dry weather samples (Table 4) are not clearly or consistently different either. They are discounted as tracers of the human waste in this study. However, concentrations of Surfactant, FWA, and Fluoride were found to be consistently higher in storm water outflow during wet weather than that of lake water during dry weather.

From Table 5, it is evident that Caffeine concentration is very high at location 2 during the storm event. It is also evident from Table 5 that there exists a steady background concentration of caffeine during dry weather. This could be due to the effect of long term and steady contamination from storm water samples to the lake. It is clear from Fig. 2 that higher concentrations of anionic surfactants were found during the wet weather. However, the background value during the dry weather was significant ($p<0.01$) and it could be attributed to the interference from humic substances such as phenols, chloride, and nitrate in natural water (Hennes and Rapaport, 1989).

Due to the mixing of lake water and ocean waters at the lake outlet and a relatively higher concentration of fluoride in the ocean water, a high concentration of fluoride was found at the lake outlet during both wet weather and dry weather (Fig 5). This also explains the increased salinity values at the outlet (Tables 3 and 4). It is also evident from Fig. 5 that

Table 6
Pearson's correlation coefficient (r) among microbiological and physico-chemical parameters

Parameter	Enterococci	Fecal coliform	Fecal streptococci
BOD	0.84[a]	0.87[a]	0.83[a]
COD	0.87[a]	0.71[a]	0.78[a]
TSS	−0.19[b]	−0.13[b]	−0.21[b]
Salinity	−0.04[b]	0.01[b]	0.16[b]

[a] p value<0.01.
[b] Non-significant.

Table 7
Pearson's correlation (r) among microbiological and chemical indicators

Parameter	Enterococci	Fecal coliform	Fecal streptococci	Fluoride	Caffeine	Anionic surfactant	FWA
Enterococci	1.00						
Fecal coliform	0.98	1.00					
Fecal streptococci	0.93	0.97	1.00				
Fluoride	0.77	0.79	0.85	1.00			
Caffeine	0.97	1.00	0.97	0.83	1.00		
Anionic surfactant	0.91	0.90	0.88	0.93	0.92	1.00	
FWA	0.55	0.50	0.59	0.74	0.51	0.67	1.00

$p<0.001$; results correspond to 45 samples collected during the wet season.

concentrations of surfactant, caffeine, and FWA at the lake outlet were not much higher during wet weather compared to those in the lake water during the dry weather. This again could be attributed to the mixing of ocean and Lake Waters at the outlet. The background concentrations of surfactant, caffeine, and FWA in the ocean water might reflect the presence of the wastewater treatment plant effluent that was discharged into the near shore coastal waters.

None of the indicator microorganisms used showed significant correlation with the physicochemical parameters like TSS and salinity during the wet weather (Table 6). Relationships were similar for each indicator organism. As expected, strong positive correlations were observed among BOD and microbiological parameters ($p<0.01$; $r>0.8$). Strong positive correlation between COD and microbiological indicators ($p<0.01$; $r>0.7$) suggests the presence of sewage at the storm water outfalls.

Significant positive correlations ($r>0.9$) were established among the three microbiological parameters as shown in Table 7, with a p value<0.001. This strong correlation indicates a recent fecal contamination. With the knowledge that the chemical tracers were derived from the human activities rather than the animal activities, a generally good correlation between the microbiological and chemical parameters ($r>0.7$, $p<0.001$) indicates contribution of the human source to the fecal coliform count.

Strong correlation among caffeine, anionic surfactant, fluoride, and FWA (Table 7) with $r>0.5$ and p value<0.001 suggests that any of these four chemical parameters could be used to detect the presence of sanitary sewage. However, in the surfactant determination, there was a high background value due to the interference of humic substances and the instability of FWA to sunlight (Wong-Wah-Chung et al., 2001) makes caffeine and fluoride to be better chemical indicators.

From the comparison of chemical tracer concentrations in storm water outflow during wet weather and those of lake water during dry weather, it is evident that the storm water outflow around the Deal Lake contains sanitary sewage, which might be due to leakage, cross connection, or overflow of the sanitary sewer pipes. The worst affected site is location 2, which is a storm drainage outlet from Asbury Park, New Jersey where one of the oldest public sewers in the U.S. were placed.

4. Conclusions

The presence of even low levels of caffeine along with elevated counts of fecal coliform and its strong correlation with various chemical and biological parameters is clear, unambiguous evidence of human contribution to fecal coliform count at the storm water outfall. High concentration of fluoride during wet weather is also an indication of human contribution. The higher concentration observed in wet weather for surfactant and fluorescence whitening agent (FWA) than in dry weather further indicates the presence of human influence. Assertion of the human contribution to fecal coliform count in storm water outflow was supported by a strong correlation between concentrations of human-activities derived chemical tracers and counts of fecal coliform in water samples taken from storm water outfalls, the worst affected being location 2. In addition, the strong correlation among caffeine, anionic surfactant and fluoride, and FWA ($r>0.5$; $p<0.001$) also suggests that any one of these four chemical parameters could be used as the indicator of the presence of human waste. However, due to higher stability, low background values caffeine and fluoride serve as better chemical tracers.

Acknowledgements

This study was financially supported by the Brookdale Rutgers Ocean Center (BROC), a partnership between Rutgers University Institute of Marine and Coastal Sciences (IMCS) and Brookdale Community College. Jeffery Pace assisted in water sampling. Laboratory personnel in IMCS and Advanced Food Technology Center at Rutgers University assisted in chemical analysis.

References

APHA. Standard methods for the examination of water and wastewater. 18th ed. Washington, DC: American Public Health Association; 1995.

Buszka PM, Barber II LB, Schroeder MP, Becker LD. Organic compounds downstream from a treated-wastewater discharge near Dallas, Texas, March 1987. U.S. Geological Survey Water-Resources Investigations Report 93-4194, Austin, Texas; 1994.

Close M, Hodgson L, Tod G. Field evaluation of fluorescence whitening agents and sodium tripolyphosphate as indicators of septic tank

contamination in domestic wells. NZ J Mar Freshw Res 1989;32: 323–48.
Egan HRP, Bloomfield DL, Kapalan IR. Long chain alkyl benzene as molecular tracers of domestic wastes in marine environment. Environ Sci Technol 1983;17:532–50.
Feacham RG. An improved role for fecal coliform to fecal streptococci ratios in the differentiation of human and non-human pollution sources (note). Water Res 1975;9:689–90.
Geldreich EE, Kenner A. Concepts of fecal streptococci in stream pollution. J Water Pollut Control Fed 1969;41:R336–52.
Geldreich EE, Best LC, Kenner BA, Van Donsel DJ. The bacteriological aspects of storm water pollution. J Water Pollut Control Fed 1968;40:1861–72.
Hennes EC, Rapaport RA. Calculation and analytical verification of LAS concentration in surface water, sediment and soil. Tenside Surfactant Deterg 1989;26:141–7.
Jagals P, Grabow WOK. Indicators of human faecal pollution of environmental water. Water SA 1996;22:235–8.
Paxeus N, Schroder HF. Screening of non-regulated organic compounds in municipal waste water in Goteberg, Sweden. Water Sci Technol 1996;33:9–15.
Poiger T, Field JA, Field TM, Siegrist H, Giger W. Behavior of fluorescent whitening agents during sewage treatment. Water Res 1998;32:1939–47.
Pitt R, Lalor M, Adrian DD, Field R, Barbe D. Investigation of inappropriate pollutant entries into storm drainage systems. EPA/600/R-92/238, United States Environmental Protection Agency 1993.
Siegener R, Chen RF. Caffeine in Boston Sea Harbor. Mar Pollut Bull 2002;44:383–7.
Seiler R, Zaugg S, Thomas J, Howcroft D. Caffeine and pharmaceuticals as indicators of wastewater contamination in wells. Ground Water 1999;37:405–10.
Sinton LW, Finlay RK, Hannah DJ. Distinguishing human and animal fecal contamination in water: a review. NZ J Mar Freshw Res 1998;32:323–48.
Thrailkill J. Flow in a limestone aquifer as determined from well tracing and water levels in well. J Hydrol 1988;78:123–36.
Uchiyama M. Separation and determination of fluorescence whitening agent and anionic surfactant in water. Water Res 1979;13:847–53.
Wong-Wah-Chung P, Mailhot G, Bolte M. 4,4′-Diaminostilbene-2,2′-disulfonate (DSD) behaviour: under irradiation in water Decrease of its activity as a fluorescent whitening agent. J Photochem Photobiol 2001;138:275–80.