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Research Article

Distributions and Sources of Sedimentary Sterols as well as Their Indications of Sewage Contamination in the Guanting Reservoir, Beijing

Xin Wen,[1] Yijuan Bai,[1] Shurong Zhang,[1,2] Aizhong Ding,[1,2] Lei Zheng,[1,2] and Jian Li[1,2]

[1]*College of Water Sciences, Beijing Normal University, Beijing 100875, China*
[2]*Beijing Key Laboratory of Urban Hydrological Cycle and Sponge City Technology, Beijing 100875, China*

Correspondence should be addressed to Shurong Zhang; srzhang@bnu.edu.cn

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In this study, domestic sewage contamination in the Guanting Reservoir, one of the major water source reservoirs of Beijing, was examined using sterols as tracing molecular markers. Nineteen sediment samples in seven cross-sections in the Guanting Reservoir were collected, extracted, and analyzed by gas chromatography-mass spectrometry (GC-MS). Seven different sterols were identified and quantified from the surface sediment samples in the Guanting Reservoir. The total sterols in sediments of the reservoir ranged from 2.78 $\mu g\ g^{-1}$ to 40.31 $\mu g\ g^{-1}$ with the average concentration of 13.53 $\mu g\ g^{-1}$. Concentrations of fecal sterols, coprostanol and epicoprostanol in the Guishui River reservoir area were generally higher than in the Yongding River reservoir area. The average concentrations of coprostanol and epicoprostanol in the Yongding River reservoir area were 0.41 $\mu g\ g^{-1}$ and 0.34 $\mu g\ g^{-1}$, respectively. The average concentrations of coprostanol and epicoprostanol in the Guishui River reservoir area were 0.72 $\mu g\ g^{-1}$ and 0.70 $\mu g\ g^{-1}$, respectively. Ratios of sterols indicated higher sewage pollution in regions close to river mouths and reservoir banks. Principal component analysis (PCA) indicated three distinct sources of sterols from domestic sewage, phytoplankton, and terrestrial higher plants. This article identified the current situation of sewage contamination in sediments of the Guanting Reservoir, which could provide important references for further implementation of pollution control and basin management in the region.

1. Introduction

With strict industrial pollution control, domestic sewage discharge has increasingly become the main concern of water quality issues in many populated regions [1–4]. Sterols have been widely used as a typical biochemical marker to indicate the source of organic matter, such as domestic sewage, marine, and terrestrial source [5–7]. Compared with other microbial source tracking markers such as microorganisms (such as *E. coli*) and molecular markers (such as DNA), sterol markers have high sensitivity, high specificity, and high stability [8, 9]. Especially, with their hydrophobic properties and high persistence in the sediment, sterols are prone to be attached to particles and accumulate in sediments, and they are considered as good markers for tracing sewage contamination in sediments [10–12].

Sterols can be originated from animals, plants, and fungi. Based on their specific structures, sterols provide useful information for source specification in the aquatic environment. Animal sterols are mostly synthesized in the intestines of animals, and the precursor substances are mostly cholesterol [13]. Various types of sterols are formed by cholesterol under the action of the intestinal flora. This "fecal sterol fingerprint" can be used to evaluate the pollution of domestic sewage and trace the source of pollutants [14–16]. Particularly, coprostanol is considered as a major sign of fecal contamination, and a positive connection has been found between levels of coprostanol and abundance of fecal bacteria in previous studies [17, 18]. Moreover, various thresholds of coprostanol concentrations (such as 0.1, 0.5, or 0.7 $\mu g\ g^{-1}$) were proposed to indicate sewage contamination in aquatic sediments [19–21]. Phytosterols are mainly found

in the seeds of plants, including sitosterol, stigmasterol, and campesterol. Among them, sitosterol and stigmasterol are important markers of terrestrial organic matter, mainly from higher plants, while campesterol is mainly derived from phytoplankton [22, 23]. Fungal sterols are mainly found in molds and mushrooms, and the most common one is ergosterol [24].

In the study of source analysis using sterols, the researchers have found that besides concentrations of individual sterols, the ratios of sterols can be used as more robust indicators to assess the sewage contamination, such as sources of pollution and treatment of sewage [25–30]. The most common ratio parameters are the ratios between coprostanol, epicoprostanol, cholesterol, and cholestanol. Coprostanol/cholesterol can indicate the pollution of domestic sewage and its pollution level. Coprostanol can be converted into epicoprostanol in the process of anaerobic treatment of domestic sewage. Hence, whether the sewage has been treated or not can be indicated by epicoprostanol/coprostanol [31]. In addition, some researchers have found that, in an uncontaminated environment, cholesterol is more likely to form cholestanol through hydrogenation [32]. Coprostanol/(coprostanol + cholestanol) can determine whether domestic sewage exist or not on water bodies.

Guanting Reservoir, an important water source of Beijing, plays a crucial role for water resources allocation and water security of Beijing city. However, human activities, such as farming and wastewater discharge in the upstream basin, are imposing a great pressure for water source protection in the Guanting Reservoir [33, 34]. Hence, it is of great significance to detect the pollution and identify the pollution sources for the protection of the Guanting Reservoir. Although studies have been widely carried out for examining water and sediment chemistry in the Guanting Reservoir, such as nutrients, persistent organic pollutants, and emerging pollutants [35–37], our current knowledge about sewage input and fecal contamination is limited. This study aims to (1) investigate the spatial distributions and sources of sedimentary sterols by combining biomarkers and statistical methods and (2) assess sewage contamination in the surface sediments of the Guanting Reservoir for providing important references for future basin management.

2. Materials and Methods

2.1. Study Area and Sampling. Guanting Reservoir is located between Beijing and Hebei province (115.43°–115.97°E, 40.19°–40.50°N), with the drainage area of 43,402 km^2 spanning the Inner Mongolia Autonomous Region, Shanxi province, Hebei province, and Beijing Municipality. It belongs to temperate continental monsoon climate zone, with the average annual rainfall amount of 350–500 mm, and majority of rainfall occurring in summer. In the basin, agriculture is the main land-use type. There are two rivers, Yongding River and Guishui River, discharging into the Guanting Reservoir.

In this study, there are 19 sampling points in total located in 7 cross sections in the Guanting Reservoir (Figure 1). Section S1 is located close to the dam, and sections S4 and S7 are river mouth sections of the Yongding River and the Guishui River, respectively. Table 1 shows the specific information of sampling points.

Nineteen surface sediment samples (0–10 cm depth) were collected in the Guanting Reservoir using a stainless-steel dredge sampler. Once collected, sediment samples were immediately stored on ice during transportation to the laboratory and then stored at −20°C until further analysis.

2.2. Chemicals. (3β, 24R)-Ergost-5-en-3-ol (campesterol, >65% purity), (3β)-stigmast-5-en-3-ol (β-sitosterol, >95% purity), and (3β, 22E)-stigmasta-5, 22-dien-3-ol (stigmasterol, >95% purity) were purchased from Sigma-Aldrich (St. Louis, MO USA). (3β)-Cholest-5-en-3-ol (cholesterol, >98% purity), (3β, 5α)-cholestan-3-ol (cholestanol, >98% purity), (3β, 5β)- cholestan-3-ol (coprostanol, >98% purity), and (3α, 5β)- cholestan-3-ol (epicoprostanol, >98% purity) were purchased from Steraloids Inc (Newport, RI, USA). 5α-Androstan-3β-ol (>98% purity) was obtained from Chiron Inc (Trondheim, Norway). N,O-Bis (trimethylsilyl) trifluoro acetamide (BSTFA) was obtained from TCI Inc (Tokyo, Japan). Ultra resi-analyzed n-hexane and dichloromethane were purchased from J. T. Baker Inc (Center Valley, PA, USA).

2.3. Sample Pretreatment. Prior to sterol analysis, all samples were freeze-dried, ground in a mortar, sieved at 100 μm, and extracted.

Sterol extraction procedures were described in the previous paper by Bataglion et al. [38]. In brief, 25 g of sediment samples were spiked with a known amount of the surrogate standard (5α-androstan-3β-ol) and extracted by a microwave extraction system (MarsX, CEM, USA) using the mixture of n-hexane and dichloromethane (1 : 1, v/v). The extracts were concentrated to 0.5 ml using a rotary evaporator and nitrogen blowing instrument and then cleaned up by solid phase extraction (SPE) on C18 cartridges with 10 ml dichloromethane. Extracts were concentrated to near dryness under gentle nitrogen flow and derivatized with BSTFA under 70°C for 1 h.

2.4. Sterols Analysis. The sterols were quantified by gas chromatography-mass spectrometry (GC-MS). The instrument used was Agilent 7890B GC coupled with Agilent 5977A MS on the single ion monitoring (SIM) mode. There were 3 ions selected for particular sterol identification (Table 2). Samples were injected into the injector (250°C) carried by helium at a rate of 1 ml/min. The temperature gradient was with initial temperature 60°C, 15°C/min to 250°C, 1°C/min to 280°C, 5°C/min to 300°C, and hold for 10 min.

For quality assurance and quality control, the external standard method was used for quantitative analysis based on six-point calibration (1, 2, 4, 6, 8, and 10 $\mu g\ ml^{-1}$). The linear regression coefficients for cholesterol, cholestanol, coprostanol, epicoprostanol, campesterol, sitosterol, and stigmasterol were 0.989, 0.979, 0.977, 0.986, 0.941, 0.992, and

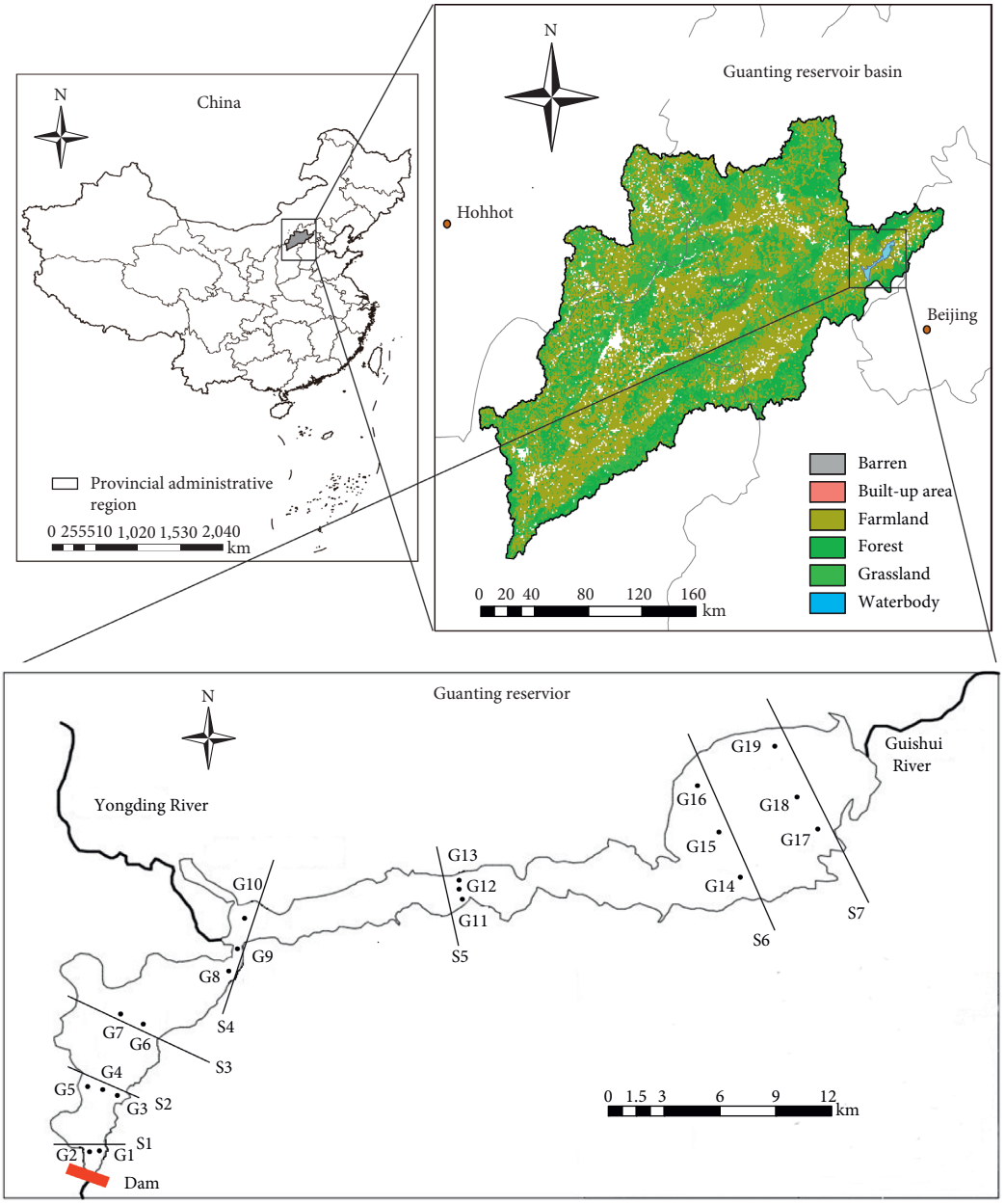

Figure 1: Map of sampling points in the Guanting Reservoir.

0.991, respectively. The minimum concentration of the standard curve was defined as the detection limit. According to the quantitative calibration curve, the minimum concentration was 1 μg ml^{-1}, and the mass of the sediment was 25 g, so the corresponding limit of quantification for sediment samples was 0.04 μg g^{-1}. The analysis precision was less than 10% for individual sterols based on three replicate analysis of a sediment sample.

2.5. Statistical Analysis. In this study, we used cluster analysis (CA) to identify the spatial distribution pattern of sterol compounds in surface sediments of the Guanting Reservoir based on various sterol concentrations of sediment samples. Also, we used Pearson correlation analysis and principal component analysis (PCA) to examine the association between sterol compounds and identify sources of organic matter using sterols. The adaptability of PCA in our study was tested using the Kaiser–Meyer–Olkin (KMO) test. All the statistical analysis were performed by SPSS software, version 16.0 (Chicago, Illinois, US).

3. Results and Discussion

3.1. Sterol Contents and Composition Characteristics. Concentrations of the sterols in sediments of the Guanting Reservoir are shown in Table 3. The total sterols in sediments of the reservoir ranged from 2.78 μg g^{-1} to 40.31 μg g^{-1} with the average concentration of 13.53 μg g^{-1}. The most abundant sterol observed was sitosterol, followed by stigmasterol

Table 1: General information of sampling points in the Guanting Reservoir.

Sampling area	Sampling section	Sampling point	Latitude	Altitude
Yongding River reservo\ir area	S1	G1	40°14.7′	115°36.12′
		G2	40°14.7′	115°35.25
	S2	G3	40°14.5′	115°36.18′
		G4	40°14.57′	115°35.55′
		G5	40°14.58′	115°35.31′
	S3	G6	40°16.16′	115°36.31′
		G7	40°16.11′	115°35.46′
		G8	40°17.43′	115°37.20′
	S4	G9	40°18.57′	115°37.4′
		G10	40°18.16′	115°37.28′
	S5	G11	40°21.7′	115°41.33′
		G12	40°21.11′	115°41.21′
		G13	40°20.22′	115°41.2′
Guishui River reservoir area	S6	G14	40°20.49′	115°43.43′
		G15	40°20.55′	115°43.31′
		G16	40°21.6′	115°43.17′
		G17	40°21.17′	115°45.19′
	S7	G18	40°21.28′	115°45.11′
		G19	40°21.35′	115°45.13′

Table 2: Peak time and characteristic ions of sterols for GC-MS.

Sterols	Systematic name	Number of carbon	Molecular weight	Retention time/min	m/z for quantification and identification
Cholesterol	(3β)-Cholest-5-en-3-ol	27	386.65	29.60	73,129,329
Cholestanol	(3β, 5α)-Cholestan-3-ol	27	388.67	29.91	75,129,215
Coprostanol	(3β, 5β)-Cholestan-3-ol	27	388.67	26.89	73.75,370
Epicoprostanol	(3α, 5β)-Cholestan-3-ol	27	388.67	27.19	75,215,370
Campesterol	(3β, 24R)-Ergost-5-en-3-ol	28	400.68	28.34	43,73,129
Sitosterol	(3β)-Stigmast-5-en-3-ol	29	412.69	36.04	57,73,129
Stigmasterol	(3β, 22E)-Stigmasta-5,22-dien-3-ol	29	414.71	34.03	55,83,370
5α-Androstan-3β-ol		19	276.46	14.831	75,258,333

Table 3: Sterol concentrations in sediments of the Guanting Reservoir (μg g^{-1}).

Sampling point	Cholesterol	Cholestanol	Coprostanol	Epicoprostanol	Campesterol	Sitosterol	Stigmasterol	Total sterols
G1	2.93	1.00	0.28	0.44	0.09	2.88	2.04	9.66
G2	8.41	1.66	0.35	0.34	0.08	7.88	6.29	25.01
G3	0.80	0.50	0.20	0.19	0.06	0.80	0.48	3.03
G4	0.84	0.48	0.11	0.10	0.06	1.40	0.61	3.60
G5	2.63	0.83	0.57	0.33	0.15	8.03	4.69	17.23
G6	2.20	1.14	0.90	0.85	0.22	28.48	6.52	40.31
G7	1.16	0.63	0.39	0.29	0.17	2.68	2.09	7.41
G8	1.24	0.77	0.51	0.29	0.16	5.03	2.44	10.44
G9	1.35	0.57	0.71	0.41	0.17	3.08	1.06	7.35
G10	1.73	0.53	0.40	0.20	0.10	2.21	1.15	6.32
G11	1.16	0.57	0.18	0.32	0.07	1.41	0.64	4.35
G12	1.84	0.70	0.36	0.38	0.11	2.11	0.89	6.39
G13	3.22	0.71	0.37	0.32	0.11	1.73	1.19	7.65
G14	0.59	0.46	0.23	0.17	0.07	0.79	0.47	2.78
G15	7.32	2.00	1.22	1.49	0.21	1.58	1.32	15.14
G16	2.89	1.04	1.24	0.97	0.14	12.29	9.06	27.63
G17	3.01	1.26	0.55	0.67	0.11	19.50	10.58	35.68
G18	5.71	1.51	0.62	0.58	0.11	4.56	3.35	16.44
G19	2.06	0.65	0.45	0.34	0.09	4.67	2.42	10.68
Mean	2.69	0.90	0.51	0.46	0.12	5.85	3.02	13.53

and cholesterol. Concentrations of sitosterol ranged from 0.79 μg g^{-1} to 28.48 μg g^{-1}, with the average concentration of 5.85 μg g^{-1}. Concentrations of stigmasterol ranged from 0.47 μg g^{-1} to 10.58 μg g^{-1}, with the average concentration of 3.02 μg g^{-1}. As seen from Figure 2, the sum proportions of these two sterols in the total sterols were higher than 50% at most sampling points, with the maximum reaching 86.8% of the total sterols. Among phytosterols, concentrations of campesterol were very low, ranging from 0.06 μg g^{-1} to 0.22 μg g^{-1}, with an average concentration of 0.12 μg g^{-1}.

Cholesterol was the most abundant animal sterol, ranging from 0.59 μg g^{-1} to 8.41 μg g^{-1} with the average concentration of 2.69 μg g^{-1}. The concentrations of cholestanol ranged from 0.46 μg g^{-1} to 2.00 μg g^{-1}, and the average value of cholestanol was 0.90 μg g^{-1}. Coprostanol was widely distributed in sediments of the reservoir, ranging from 0.11 μg g^{-1} to 1.24 μg g^{-1}, with the average concentration of 0.51 μg g^{-1}, which was similar to the concentrations of coprostanol in sediments of rivers of Serbia and Ulungur Lake in northern Xinjiang [39, 40]. Generally, the concentration of coprostanol has been used to assess the sewage pollution level, and the maximum threshold of sewage contamination used in previous studies was 0.7 μg g^{-1} [20, 30]. Hence, we considered 0.7 μg g^{-1} as the threshold of sewage contamination in our study. Sampling points with concentrations of coprostanol larger than 0.7 μg g^{-1} in the Guanting Reservoir were G6 (0.90 μg g^{-1}), G9 (0.71 μg g^{-1}), G15 (1.22 μg g^{-1}), and G16 (1.24 μg g^{-1}), suggesting serious sewage contamination in these regions. These sampling points were located close to river mouth regions or close to reservoir banks with leisure resorts. However, the proportion of coprostanol in the total sterol content was comparatively low, ranging from 1.4% to 9.7% with the average proportion of 4.8%. The highest coprostanol concentration detected in this study (1.24 μg g^{-1}) was much lower than that observed in some heavily polluted rivers, such as the Xiaoqing River close to Laizhou Bay in eastern China (63.2 μg g^{-1}) and the Pearl River (53 μg g^{-1} TOC) [30, 41]. The concentrations of epicoprostanol ranged from 0.10 μg g^{-1} to 1.49 μg g^{-1}, with an average of 0.46 μg g^{-1}. The ubiquitous existence of epicoprostanol in sediments of the Guanting Reservoir suggested the input of treated sewage from upstream regions, which were consistent with the existence of many wastewater treatment plants in upstream cities, such as Zhangjiakou and Xuanhua.

3.2. Spatial Distribution of Sterols. According to Table 1, concentrations of coprostanol and epicoprostanol in the Guishui River reservoir area were generally higher than those in the Yongding River reservoir area. The average concentrations of coprostanol and epicoprostanol in the Yongding River reservoir area were 0.41 μg g^{-1} and 0.34 μg g^{-1}, respectively. The average concentrations of coprostanol and epicoprostanol in the Guishui River reservoir area were 0.72 μg g^{-1} and 0.70 μg g^{-1}, respectively. Higher coprostanol concentrations in the Guishui River reservoir area indicated that the area was more affected by sewage input from the Guishui River as well as reservoir bank areas. In sediments that are not contaminated with feces, the content of coprostanol is approximately 1% to 2% of the total sterol content [13]. The proportions of coprostanol in the total sterol were higher than 1% throughout the Guanting Reservoir (Figure 2). Except for G2 and G17, the contents of coprostanol at other sampling points were higher than 2%, indicating that most of the Guanting Reservoir was affected with animal waste. The research data showed that the contents of coprostanol in the Yongding River mouth area were relatively higher than that of the downstream sections, reaching 9% (G6). Similar to coprostanol, the concentrations of epicoprostanol in the Guishui River reservoir area were much higher than those in the Yongding River reservoir area.

Phytosterols were the dominant types of sterols in sediments at the most of the sampling points in the Guanting Reservoir. Ratios of phytosterols to animal sterols ranged from 0.26 (G15) to 6.92 (G6) as seen in Figure 3. Except at 6 sampling points G11–G15, and G18, ratios of phytosterols to animal sterols were larger than 1 at other sampling points. Among the plant sterols, the proportion of campesterol was minor, and the concentration variation was not significant in the entire Guanting Reservoir. It has been proposed that phytosterols can be derived from municipal pollution besides their terrestrial source [40]. Hence, high proportions of phytosterols in the total sterols in the Guanting Reservoir may be partially due to sewage input.

Cluster analysis of the sterols in the sediment of Guanting Reservoir showed that the entire sediment sampling points can be divided into three groups (see Figure 4 and Table 4). Group 1, including sampling points G6 and G17, were characterized with the highest average values of the total sterol content, sitosterol content, and stigmasterol content, which were 38.00 μg g^{-1}, 23.99 μg g^{-1}, and 8.55 μg g^{-1}, respectively. Spatially, sampling points in Group 1 were located close to the south bank of the reservoir. Group 2 included sampling points G2, G5, and G16 which were located close to the north bank of the reservoir. Group 2 generally had medium average contents of sterols except cholesterol content which was the highest among three groups. Group 3 covered the majority of the points with the lowest average content of total sterol content and individual sterols among the three groups of sampling points. Based on analysis of variance (ANOVA), three groups were significantly different in terms of the contents of the total sterol, sitosterol, and stigmasterol. Compared with Group 3, Group 1 and Group 2 had higher sterol concentrations, which suggested the enhanced input of organic matter with both naturally terrestrial source and sewage source from adjacent reservoir banks. This could be related with fish farming and small leisure resorts or restaurants along the reservoir bank, which may discharge sewage and impose important impacts on water quality of the reservoir.

3.3. Pollution Evaluation Using Sterol Ratios. Besides individual sterol contents, sterol ratio parameters are widely used to more robustly evaluate the sewage contamination [30, 40, 42]. In this study, five sterol ratio parameters were used, including coprostanol/cholestanol,

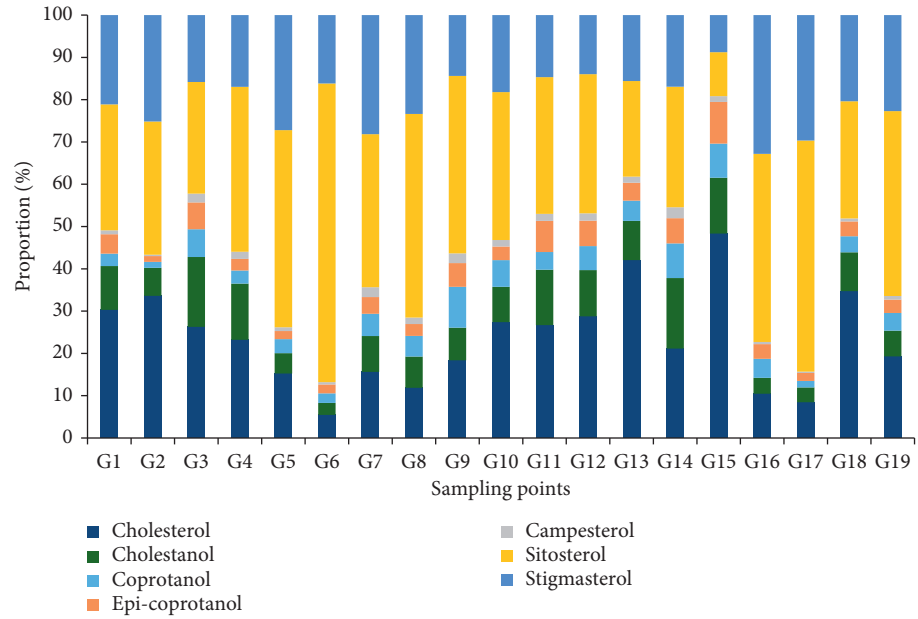

Figure 2: Proportions of seven sterols in total sterols in sediments of the Guanting Reservoir.

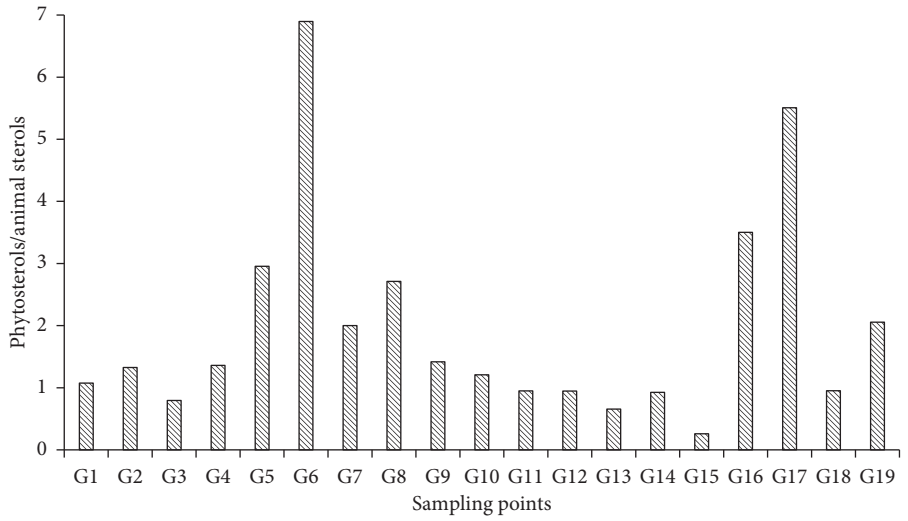

Figure 3: Ratios of phytosterols to animal sterols in sediments of the Guanting Reservoir.

coprostanol/(cholesterol + cholestanol), epicoprostanol/coprostanol, coprostanol/(coprostanol + cholestanol), and coprostanol/cholesterol. The distribution of the five sterol ratios is shown in Table 5.

Coprostanol/(coprostanol + cholestanol) is one of the most used indicators to determine the presence of sewage contamination. Ratio values higher than 0.7 have been commonly considered to indicate sewage contamination, while values less than 0.3 indicate no sewage contamination [19]. Except G5, coprostanol/(coprostanol + cholestanol) ratios at the sections close to dam, S1 and S2, were less than 0.3, which indicated little sewage contamination in the area far away downstream river mouths. The ratios in other areas in the reservoir were generally between 0.3 and 0.7. The ratios of G9 and G16 were relatively high indicating more serious pollution by the animal waste. Similar studies have shown that the ratios of the majority of analyzed sediment samples were between 0.3 and 0.7, which suggested the combined input of sewage and natural sources [43, 44]. Some researchers preferred to use a lower threshold value of coprostanol/(coprostanol + cholestanol) for sewage contamination, such as 0.5 [18, 37]. In our study, sampling points G9 and G16 had ratios larger than 0.5, which suggest more serious sewage pollution in these regions. These two sampling points were also with concentrations of coprostanol larger than 0.7 $\mu g\ g^{-1}$ having an indication of sewage pollution as discussion earlier.

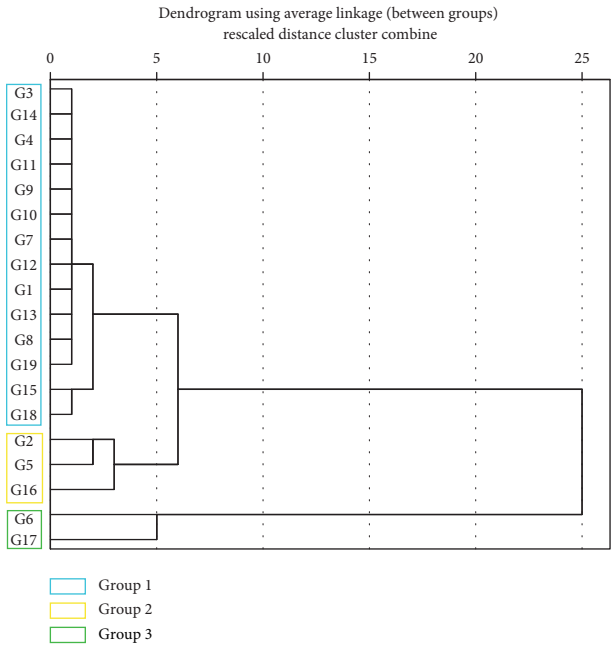

Figure 4: Cluster analysis results of sediment sampling points in the Guanting Reservoir.

Table 4: Average values of sterols of three groups of sampling points in the Guanting Reservoir based on the cluster analysis ($\mu g\ g^{-1}$).

Sterols	Group 1	Group 2	Group 3	ANOVA analysis		
				df	F	p value
Cholesterol	2.61	4.64	2.28	18	1.527	0.247
Cholestanol	1.20	1.178	0.79	18	1.573	0.238
Coprostanol	0.72	0.72	0.43	18	1.637	0.226
Epicoprostanol	0.76	0.54	0.40	18	1.185	0.331
Campesterol	0.16	0.13	0.11	18	1.02	0.383
Sitosterol	23.99	9.40	2.49	18	86.86	<0.001*
Stigmasterol	8.55	6.68	1.44	18	38.66	<0.001*
The total sterol	38.00	23.29	7.95	18	51.49	<0.001*

*The significance level p value is less than 0.05; ANOVA: analysis of variance.

Similar contamination pattern was identified using the ratio of coprostanol/(cholesterol + cholestanol). When the ratio is >0.20, it indicates domestic sewage input, and when the ratio is <0.15, it indicates no domestic sewage input [18, 39]. The ratios of samples at G6, G7, G8, G9, G14, and G16 were higher than 0.2, which indicated significant influence of human domestic sewage near river mouths. The ratio of other points was less than 0.15, and there was no obvious indication of domestic sewage input.

Coprostanol/cholestanol is also one of the important indicators for indicating the pollution of human sewage [13]. When the ratio is >0.50, it indicates human sewage source. When the ratio is <0.30, it indicates no human sewage input. Except sampling points G1–G4, G11, G14, G17, and G18, the ratios of coprostanol/cholestanol all exceeded 0.50, indicating obvious influences from human domestic sewage. The ratio values of sampling points G9 and G16 in the river mouths were especially higher. At the most downstream section S1 close to the dam, the ratios were less than 0.30, indicating no influence by human domestic sewage. Coprostanol/cholesterol can be used to characterize different sources of pollutants with a criterion of >0.5 for human fecal inputs [45]. In the Guanting Reservoir, the ratio of G9 was greater than 0.50, indicating human fecal contamination from the Yongding River Basin.

Epicoprostanol/coprostanol can be used as an important indicator of untreated domestic sewage pollution. For sediments contaminated by raw, untreated sewage, the ratio is less than 0.20, while for sediments with no contamination or affected by treated sewage, this value increases to 0.80 [46, 47]. The ratios of most points in the reservoir were higher than 0.80, indicating that the entire reservoir area was not affected by severe untreated sewage, but the ratios of G5, G7, G8, G9, G10, G14, and G16 were between 0.20 and 0.80, indicating that in these regions near river mouths or near banks, sediments were partly affected with untreated sewage. Although there were many sewage treatment plants in the upstream regions of the Guanting Reservoir Basin, such as in cities of Zhangjiakou and Xuanhua in Heibei Province, untreated sewage discharge input from upstream river input or adjacent bank regions still existed in the Guanting Reservoir.

Through comprehensive analysis of the above sterol ratios, it can be found that in the river mouth areas and near bank regions, presences of domestic sewage were indicated. The main source in the river mouths was the upstream input from the Yongding River and the Guishui River. At the same time, because there were many locations for fish farming and small leisure resorts or restaurants along the reservoir bank, untreated domestic sewage from these reservoir bank locations may be an important source of pollution in the reservoir. Section S1 close to the dam was far away from the river mouths, and no presence of sewage contamination was identified there.

3.4. Source Discrimination Using Principal Component Analysis. In order to determine the source of sterols in sediments of the Guanting Reservoir, correlation analysis and principal component analysis were performed. Results of Pearson correlation analysis (see Table 6) showed that the correlation coefficient between cholesterol and cholestanol was 0.92, with the significance level less than 0.01, indicating these two sterols were both from the same source. Cholestanol was also extremely significantly associated with epicoprostanol, indicating these two sterols were from the same source of contamination. Coprostanol was significantly correlated with epicoprostanol, and coprostanol was significantly correlated with epicoprostanol with the correlation coefficient of 0.893. However, coprostanol was also significantly correlated with campesterol, sitosterol, and stigmasterol, with correlation coefficients 0.703, 0.466, and 0.494, respectively. The significant correlation between fecal sterols and plant sterols has also been reported by other studies [39, 48]. One reason for this phenomenon may be because plant sterols,

Table 5: Sterol ratio parameters in the Guanting Reservoir sediment.

Sample point	Coprostanol/ (coprostanol + cholestanol)	Coprostanol/ (cholesterol + cholestanol)	Coprostanol/ cholestanol	Coprostanol/ cholesterol	Epicoprostanol/ coprostanol
G1	0.22	0.07	0.28	0.10	1.56
G2	0.17	0.03	0.21	0.04	0.97
G3	0.28	0.15	0.40	0.25	0.97
G4	0.19	0.08	0.23	0.13	0.90
G5	0.41	0.16	0.68	0.22	0.58
G6	0.44	0.27	0.79	0.41	0.94
G7	0.38	0.22	0.62	0.34	0.75
G8	0.40	0.25	0.66	0.41	0.58
G9	0.55	0.37	1.25	0.53	0.58
G10	0.43	0.18	0.75	0.23	0.52
G11	0.24	0.10	0.32	0.16	1.76
G12	0.34	0.14	0.52	0.20	1.06
G13	0.34	0.09	0.51	0.11	0.89
G14	0.33	0.22	0.49	0.39	0.72
G15	0.38	0.13	0.61	0.17	1.22
G16	0.55	0.32	1.20	0.43	0.78
G17	0.30	0.13	0.43	0.18	1.22
G18	0.29	0.09	0.41	0.11	0.93
G19	0.41	0.16	0.69	0.22	0.76

Table 6: Relevance of sterols in sediments of the Guanting Reservoir.

Sterols	Cholesterol	Cholestanol	Coprostanol	Epicoprostanol	Campesterol	Sitosterol	Stigmasterol
Cholesterol	1						
Cholestanol	**0.919****	1					
Coprostanol	0.417	**0.602****	1				
Epicoprostanol	**0.560***	**0.770****	**0.893****	1			
Campesterol	0.144	0.323	**0.703****	**0.589****	1		
Sitosterol	0.124	0.352	**0.466***	0.413	0.411	1	
Stigmasterol	0.344	**0.491***	**0.494***	0.424	0.212	**0.819****	1

such as sitosterol and stigmasterol, are also derived from municipal sewage besides their terrestrial source [40, 48]. Also, discharge of domestic sewage may lead to phytoplankton growth in the reservoir which could increase the amount of phytosterols, particularly campesterol [48]. Epicoprostanol is also significantly correlated with campesterol but had no significant correlation with the other two plant sterols. For plant sterols, the correlation coefficient between sitosterol and stigmasterol was 0.819, and the significance level was less than 0.01, indicating these two sterols had the same source, mainly from terrestrial plants input. There were no significant correlations between campesterol and other two plant sterols, suggesting that sources of campesterol were very different from sources of sitosterol and stigmasterol.

The principal component analysis method is a technique for studying the relationships between variables and extracting the main factors. Results of principal component analysis in the sediment of the Guanting Reservoir showed that three principal components were extracted from the seven sterols in this study (see Figure 5). In total, 91.97% of the total variances were explained using the three components. The load variance of PC1 was 58.05%, the load variance of PC2 was 18.60%, and the load variance

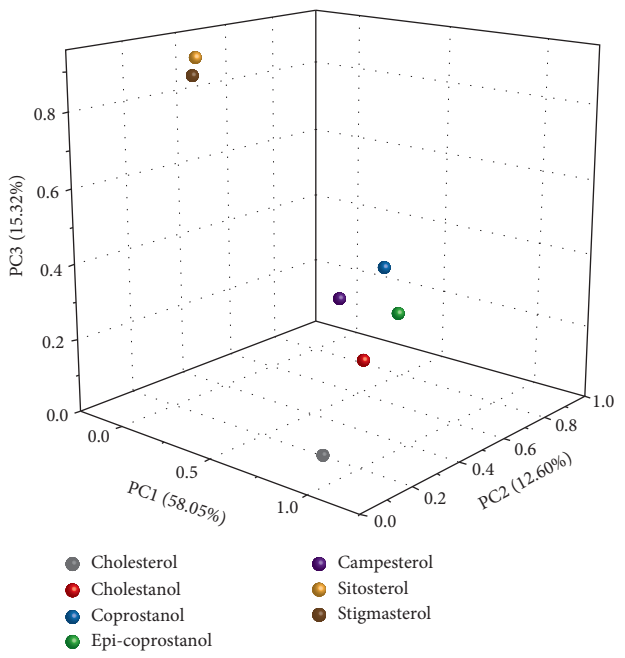

Figure 5: Principal component analysis of sterols in sediments of the Guanting Reservoir.

Table 7: Principal component analysis interpretation variables of sterols in sediments of the Guanting Reservoir.

Component	Initial eigenvalue			Extracting squares sum			Rotating squares sum		
	Sum	Variance %	Accumulation %	Sum	Variance %	Accumulation %	Sum	Variance %	Accumulation %
1	4.064	58.05	58.05	4.064	58.05	58.05	2.312	33.03	33.03
2	1.302	18.60	76.65	1.302	18.60	76.65	2.228	31.83	64.86
3	1.072	15.32	91.97	1.072	15.32	91.97	1.897	27.11	91.97
4	0.323	4.62	96.59						
5	0.160	2.29	98.88						
6	0.060	0.86	99.74						
7	0.020	0.26	100.00						

Table 8: Component factor matrix of principal component analysis of sterols in sediments of the Guanting Reservoir.

Sterol	Principal component		
	1	2	3
Cholesterol	0.968	0.079	0.069
Cholestanol	0.910	0.289	0.241
Coprostanol	0.371	0.821	0.289
Epicoprostanol	0.571	0.721	0.209
Campesterol	−0.004	0.921	0.129
Sitosterol	0.023	0.293	0.919
Stigmasterol	0.286	0.107	0.920

of PC3 was 15.32%. As shown in Table 7, the high load rates indicated that these three components can be used to analyze the overall sterol situation of the Guanting Reservoir sediments. The factor loadings of PCA analysis are shown in Table 8. PC1 had positive factor loadings with other sterols except for the negative correlation with campesterol, and factor loadings with cholesterol, cholestanol, and epicoprostanol were larger than 0.50, representing domestic sewage input. PC2 had positive factor loadings with all sterols, and particularly with campesterol, representing the input of phytoplankton sterols. PC3 had high factor loadings with sitosterol (0.919) and stigmasterol (0.920), representing the input from terrestrial higher plants.

4. Conclusions

In this study, domestic sewage contamination was traced using sterols for sediment samples in the Guanting Reservoir, one important water source reservoir in Beijing, China. Results revealed the spatial distribution of domestic sewage pollution in the reservoir with obvious sewage signals near river mouth regions while diminished downstream, which can provide scientific directions for sediment pollution remediation and river basin management. The use of a combined approach of sterols concentrations and diagnostic ratios of several sterols improves the determination of sterol sources in the Guanting Reservoir, which indicates sterol fingerprinting is an efficient tool for tracking sources of sewage contamination. By tracking sterols and other geochemical markers (such as fluorescent whitening agents and linear alkylbenzenes), it should provide more reliable evidence of the source and severity of sewage pollution as well as integrated river basin management.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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