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Temporal variability in TiO_2 engineered particle concentrations in rural Edisto River

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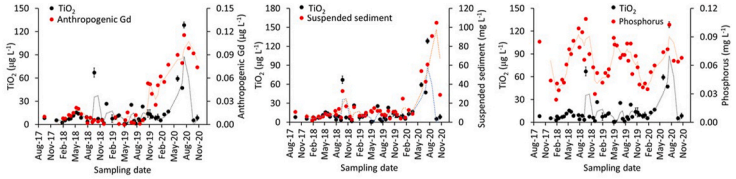
HIGHLIGHTS

- Multiyear precipitation patterns can affect TiO_2 concentrations in the Edisto River.
- Anomalously high TiO_2 concentrations in 2020 followed the 2019 drought.
- TiO_2 concentrations increased with increases in sewage and agriculture contaminants.

GRAPHICAL ABSTRACT



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ABSTRACT

Titanium dioxide (TiO_2) is widely used in engineered particles including engineered nanomaterial (ENM) and pigments, yet its occurrence, concentrations, temporal variability, and fate in natural environmental systems are poorly understood. For three years, we monitored TiO_2 concentrations in a rural river basin (Edisto River, < 1% urban land cover) in South Carolina, United States. The total concentrations of Ti, Nb, Al, Fe, Ce, and La in the Edisto River trended higher during spring/summer compared to autumn/winter. Upward trending Ti/Nb ratio in the spring/summer compared to near-background autumn/winter ratios of 255.7 ± 8.9 indicated agricultural preparation and growing-season-related increases in TiO_2 engineered particles. In contrast, downward trending of the Ti/Al and Ti/Fe ratios in the spring and summer compared to the near-background autumn/winter ratios of 0.05 indicated greater mobilization of Fe and Al, relative to Ti during spring/summer. Surface-water concentrations of TiO_2 engineered particles varied between 0 and 128.7 ± 3.9 µg TiO_2 L^{-1}. Increases in TiO_2 concentrations over the spring/summer were associated with increases in phosphorus, orthophosphate, nitrate, ammonia, anthropogenic gadolinium, water temperature, suspended sediments, organic carbon, and alkalinity, and with decreases in dissolved oxygen. The association between these contaminants together with the timing of the increases in their concentrations is consistent with diffuse wastewater sources, such as reuse application overspray, biosolids fertilization, leaking sewers, or septic tanks, as the driver of instream concentrations; however, other diffuse sources cannot be ruled out. The findings of this study indicate spatially-distributed (non-point source) releases can result in high concentrations of TiO_2 engineered particles, which may pose higher risks to rural stream aquatic ecosystems during the agricultural season. The results illustrate the importance of monitoring seasonal variations in engineered particles concentrations in surface waters for a more representative assessment of ecosystem risk.

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1. Introduction

Titanium dioxide (TiO_2) is widely used as engineered particles, including engineered nanomaterial (ENM) and pigments, yet its occurrence, measured concentrations, and fate in natural environmental systems are poorly understood (Piccinno et al., 2012). The global consumption of TiO_2 as engineered particles, including engineered nanomaterials (1–100 nm particles) and pigments (100–300 nm particles), is projected to reach 8.8 million metric tons by 2025 (Piccinno et al., 2012). The major applications of TiO_2 are architectural and industrial paints and coatings (60%), plastic (28%), paper (5%), and other applications (7%), such as photocatalysts, food additives, cosmetics, and sunblocks (Linak and Inoguchi, 2005). These applications result in environmental releases of TiO_2 engineered particles from diverse sources (Gondikas et al., 2014; Kaegi et al., 2008, 2017; Loosli et al., 2019; Nabi et al., 2021b; Rand et al., 2020; Slomberg et al., 2020; Wang et al., 2020). Consequently, TiO_2 engineered particles are widely distributed in the environment (Baalousha et al., 2020; Gondikas et al., 2014; Loosli et al., 2019; Rand et al., 2020; Slomberg et al., 2020). Many studies have investigated the presence and concentrations of ENMs in various technical and environmental compartments such as wastewater treatment plants (Kiser et al., 2009; Nabi et al., 2021b; Westerhoff et al., 2011), construction and demolition landfills (Kaegi et al., 2017), urban runoff (Wang et al., 2020), and biosolids (Baalousha et al., 2020). Additionally, other studies have investigated the release of ENMs from localized point sources such as manufacturing facilities (Slomberg et al., 2020), painted surfaces (Kaegi et al., 2008), (Reed et al., 2017), municipal wastewater treatment plants (Kiser et al., 2009; Nabi et al., 2021b; Phalyvong et al., 2020), sewage spills (Loosli et al., 2019), and sunscreens (Gondikas et al., 2014; Rand et al., 2020; Reed et al., 2017) to surface waters. However, studies on the potential contribution of more spatially-distributed (non-point) wastewater sources, such as agriculture-applied biosolids and septic tank discharges, to the fluxes of ENMs in river surface waters are scarce, despite the demonstrated presence of ENMs in raw sewage, sewage sludge, and biosolids-amended soils (Kiser et al., 2010, 2012; Westerhoff et al., 2011).

In the United States, approximately 7 million dry tons of biosolids are produced annually, and 55% of the produced biosolids (based on 2004 data) are used for agriculture, silviculture, land restoration, and other land applications (NEBRA, 2007; U.S. EPA, 1999). Seventy-four percent of land-applied biosolids are used for crop agriculture. Biosolids (sewage sludges) are widely recognized as important vectors of chemicals, including heavy metals (Tou et al., 2017), nutrients (Zhang et al., 2006), and ENMs (Kiser et al., 2010; Westerhoff et al., 2011, 2013) to amended agricultural soils and nearby surface waters (Clarke et al., 2016b; Smith et al., 2007; Yang et al., 2014). Titanium oxides, iron oxides, silver and zinc sulfides, and other metal-containing particles have been reported in sewage sludge and sludge-amended soils (Gottschalk et al., 2009; Kim et al., 2010, 2014; Tou et al., 2017). Yang et al. (2014) estimated an average TiO_2 concentration in biosolid amended soils in Texas, USA of 2382 ± 422 mg kg^{-1} (Yang et al., 2014). Additionally, more than 21 million households in the United States, most commonly in rural areas, use septic systems – not a public sewer – to trap and filter toilet/-houshold waste (U.S.CensusBureau, 1990). Septic tanks also are widely recognized as an important source of chemicals to ground and surface waters (Arnade, 1999; Paul et al., 2000). Although it is well recognized that septic tanks and agricultural discharges contribute to the loading of contaminants, including TiO_2 (Boxall et al., 2007; Clarke et al., 2016a; Gottschalk et al., 2009), there are currently no field data on TiO_2 occurrence and concentrations in surface water receiving agricultural discharges.

Available studies have documented the presence of TiO_2 engineered particles in biosolids, biosolids-amended agricultural soils, and other environmental compartments based on elemental analysis of total Ti combined with electron microscopic identification of TiO_2 particles, without estimating the relative fractions of engineered and natural Ti particles (Kiser et al., 2010; Rand et al., 2020; Westerhoff et al., 2011, 2013; Yang et al., 2014). Ti, the 9th most abundant element in the Earth's crust, is mainly found in natural rutile, ilmenite minerals, and/or opaque heavy minerals such as titanomagnetite and magnetite (Barksdale, 1950), with trace concentrations of other elements always present (Craigie, 2018). More than 90 to 95 percent of the whole rock content of Ti, Nb, Ta, Sb, and W has been attributed to rutile and ilmenite minerals, along with 5–45 percent of the whole rock content of V, Cr, Mo, and Sn (Zack et al., 2002). Natural Ti-containing particles derived from weathering have similar elemental ratios, associations, and compositions as the parent rocks. Elemental impurities inherent in natural Ti minerals; such as Al, Si, Fe, Mn, Ce, La, Zr, Nb, Pb, Ba, Th, Ta, W, and U (Gondikas et al., 2018; Loosli et al., 2019); are removed by dissolution and reprecipitation during manufacturing of TiO_2 engineered particles. Elevated ratios of Ti to trace elements in Ti-containing minerals have been used to estimate concentrations of TiO_2 engineered particles in sewage spills (Loosli et al., 2019), urban runoff (Wang et al., 2020), and surface waters (Nabi et al., 2021a); however, there are currently no data on the occurrence and seasonal variability of TiO_2 engineered particles in streams receiving discharges from predominantly agricultural watersheds with biosolid applications.

The aims of this study are to investigate the seasonal variability in TiO_2 engineered particle concentrations and to explore the relationship between TiO_2 and other contaminant concentrations in a rural river basin (Edisto River, South Carolina) with limited urban development (<1%). The concentration of TiO_2 ENM was monitored biweekly/monthly over a period of three years in the Edistor River at the USGS 02175000 Edisto River sampling site.

2. Materials and methods

2.1. Edisto River watershed

The Edisto River basin is situated entirely within the state of South Carolina and is one of the longest free-flowing (un-impounded) black water rivers in the United States (Figure S1) (Bradley et al., 2010; Feaster et al., 2014; U.S.GeologicalSurvey, 2014). The Edisto River basin originates in the sandhill region of west central South Carolina, encompasses over 8030 km^2, flows through the upper and lower coastal plain regions, runs into the coastal zone region, and discharges into the Atlantic Ocean. The river meanders approximately 250 miles through the coastal plains of South Carolina (SCDHEC, 2012.). The Edisto River basin encompasses more than 8000 km of streams, 44.5 km^2 of lakes and ponds, and 81 km^2 of estuary. The basin is primarily rural, with 45% forested land, 29% agricultural land, 15% forested wetland, 5% barren, 3% water, 2% nonforested wetland (saturated marshland), and 1% urban land (SCDHEC, 2012.). The urban land percentage is comprised chiefly of the City of Orangeburg and a portion of the City of Aiken. The city of Orangeburg is 21.5 km^2, with a population of 14,000, according to the 2010 United States census (U.S.CensusBureau, 2021). The city of Orangeburg is located on the North Fork of the Edisto River, 68 km upstream of the sampling site. The city of Aiken is 53.9 km^2, with a population of 29,650 according to the 2010 United State census. The city of Aiken is located on the South Fork of the Edisto River, 140 km upstream of the sampling site. There are 13 permitted wastewater treatment plants (WWTP) along the Edisto River (Figure S1b), and 24 landfill facilities and 52 mining facilities (mainly sand, clay and limestone) in the river basin (SCDHEC, 2012.). Approximately, 40% of homes in South Carolina rely on septic tanks for wastewater treatment, and this number is expected to be even higher in the Edisto River basin given the rural nature of the area (Sowah et al., 2014; U.S. EPA, 2021; U.S.CensusBureau, 1990). The discharge data and stream samples were collected from USGS station 02175000 (33°01′40″N 80°23′30″W), and the rainfall data were from the NOAA station 'Charleston International Airport' (32°53′59″N 80°02′25″W), approximately 36 km from the sampling location.

2.2. Sample collection and analysis

Water samples from the Edisto River were collected at the USGS 02175000 Edisto River sampling site, which is located near Givhans Ferry State Park, SC (Latitude: 33° 01′ 40″, Longitude: 80° 23′ 30″), approximately 3.9 km downstream of the confluence of Edisto River and Four Hole Swamp. Edisto River water samples were collected approximately monthly between September 14, 2017 and October 20, 2020. Composite depth-integrated samples were collected from about 10 different locations from the middle of the river channel immediately upstream (*e.g.,* 1–2 m) of the bridge located on Highway 61 with average annual daily traffic density of 4300. Water samples were collected in 1 L high-density polyethylene bottles (HPDE, Thermo Scientific, USA) according to USGS guidelines for water sample collection (Wilde and Radtke, 1998). The bottles were acid washed prior to sample collection by soaking in 10% nitric acid (Acros Organics, Czech Republic) for at least 24 h, and were then soaked in ultrapure water (UPW, PURELAB Option-Q, ELGA, UK) for 24 h, air dried, and then double-bagged. Before filling with the water samples in the field, the bottles were rinsed three times with river water. The individual samples were double bagged and brought back on ice to the laboratory on the same day, where they were stored at 4 °C in the dark until further analysis. The samples were digested in HF:HNO_3 (3:1) acid mixture (ACS grade acids distilled in the laboratory). The total elemental concentration of the digested samples was analyzed using a PerkinElmer NexION 350D ICP-MS (Waltham, Massachusetts, USA) according to the protocols described in detail in the supplementary information section (section S1, S2 and S3, Table S2) (Loosli et al., 2019). A selected subset of water samples was analyzed using single particle-inductively coupled plasma-time of flight-mass spectrometer (SP-ICP-TOF-MS, Table S3) to determine the elemental ratios of Ti/Nb in natural Ti-containing particles, as described in detail in the supplementary information section (section S4) and elsewhere (Nabi et al., 2021a).

2.3. Calculation of TiO_2 engineered particle concentration

The concentration of TiO_2 engineered particles in the Edisto River surface water was calculated based on mass balance according to Eq. 1

$$[TiO_2]_{engineered\ particles} = \frac{TiO_{2\ MM}}{Ti_{\ MM}}\left[Ti_{sample} - Nb_{sample}\cdot\left(\frac{Ti}{Nb}\right)_{background}\right] \quad (1)$$

where, $[TiO_2]_{engineered\ particles}$ is the concentration of TiO_2 engineered particles, $Ti_{\ MM}$ and $TiO_{2\ MM}$ are the molar masses of Ti and TiO_2, Ti_{sample} and Nb_{sample} are the concentrations of Ti and Nb in a given sample, $Ti/Nb_{background}$ is the natural background elemental concentration ratio of Ti/Nb. The background Ti/Nb ratio (255.7 ± 8.9) was estimated as that observed during the drought low-flow period of the summer of 2019 (May 23, 2019 no rainfall or surface runoff). We hypothesize that under such conditions the contribution of anthropogenic Ti to the suspended sediments in the Edisto River is neglible.

There are three assumptions for Eq (1): 1) all Ti was in particulate form, 2) anthropogenic Ti occurred only as pure TiO_2 engineered particles, and 3) the natural background elemental ratio of Ti/Nb was constant through the sampling period. These assumptions are supported by the following. TiO_2 has very low solubility and, consequently, Ti is expected to occur only in particulate form in the Edisto River surface water (Antignano and Manning, 2008). Mined Ti bearing ores (approx. 95%) are treated to yield nearly pure TiO_2 for use in numerous industrial applications (Zhang et al., 2011). The concentration of Nb in commercially available TiO_2 engineered particles is below the ICP-MS detection limit (*e.g.,* < 7 ng L^{-1}) for TiO_2 concentrations up to 1000 μg L^{-1} (Wang et al., 2020). On the other hand, natural TiO_2 minerals are the dominant carriers (*e.g.,* > 90–95% of the whole rock content) of Ti and Nb (Gaspar and Wyllie, 1983). The elemental ratios of Ti/Nb, Ti/Fe, and Ti/Al in naturally occurring particles in the Edisto River waters were constant throughout the sampling campaigns (*see results and discussion section 3.3*).

2.4. Base flow and runoff separation

"WHAT: Web-based Hydrograph Analysis Tool" (WHAT), an online based web tool, was used to separate the discharge into base flow and direct runoff (Lim et al., 2005). WHAT is linked to the USGS National Water Information System (NWIS (U.S.GeologicalSurvey, 2016)) database. Discharge data at the USGS station number 02175000 was analyzed for separation of base flow and direct runoff (both overland flow and shallow groundwater discharge) using WHAT, and the following method and conditions: Method: Recursive digital filter; aquifer type: perennial streams with porous aquifer; filter parameter: 0.98; BFImax: 0.80; date range: April 16, 1957 to October 20, 2020.

3. Results and discussion

3.1. Precipitation and discharge

Precipitation was recorded on 362 days during the sampling period from September 14, 2017 to October 20, 2020, with the highest rainfall (124 mm) observed on May 19, 2018 within 35.9 km of the Givhans gage (Figure S2). River discharge varied markedly during the sampling period. The maximum discharge was 320.0 m^{-3} s^{-1} on February 27, 2020, and the minimum discharge was 9.6 m^{-3} s^{-1} on October 01, 2019. The discharge was split into base flow and direct runoff using WHAT (Lim et al., 2005). The maximum base flow was 210.7 m^{-3} s^{-1} on March 13, 2020, and the minimum base flow was 8.2 m^{-3} s^{-1} on October 13, 2019. The maximum direct runoff was 157.5 m^{-3} s^{-1} on February 12, 2020, and the minimum direct runoff was 0 m^{-3} s^{-1} on several dates. Most of the collected samples had a runoff contribution, except those collected on May 08, 2018, June 12, 2018, August 20, 2018, March 20, 2019, April 29, 2019, May 23, 2019, March 19, 2020, and May 05, 2020. South Carolina experienced a drought between March 19, 2019 and December 10, 2019, resulting in lower discharge in the Edisto River during summer and fall 2019 (9.6–70.8 m^3 s^{-1}) compared to the same period in 2018 (13.2–184.3 m^3 s^{-1}) and 2020 (21.1–194.2 m^3 s^{-1}) (Figure S2) (NIDIS, 2021).

3.2. Water chemistry

The physicochemical conditions of the Edisto River water exhibited seasonal variations throughout the sampling period (Figure S3). Air and water temperature, nitrate and ammonia, phosphorus, organic carbon, alkalinity, and suspended sediments followed the same trend with higher values during the spring and summer (April to October) and lower values during the fall and winter (November to March, Figure S3a-f). The air and water temperature varied from 6.4 to 32.5 and 7.3 to 29.3 °C, respectively (Figure S3a). Nitrate and ammonia ranged from 0 to 0.83 mg L^{-1} and 0–0.04 mg L^{-1}, respectively (Figure S3b). Phosphorus and orthophosphate varied from 0.02 to 0.11 mg L^{-1} and 0.02–0.14 mg L^{-1}, respectively (Figure S3c). Organic carbon ranged from 3.0 to 20.4 mg L^{-1} (Figure S3d). Alkalinity ranged from 9.3 to 25.9 mg L^{-1} $CaCO_3$ (Figure S3e). Suspended sediment concentrations ranged from 2.0 to 105 mg L^{-1} (Figure S3f).

Dissolved oxygen varied between 5.0 and 12.1 mg L^{-1} (63–105% saturation) and followed the opposite trend, with lower values during the spring and summer and higher values during the fall and winter (Figure S3g). The oxygen concentration of 12.1 mg L^{-1} (105% saturation) occurred at a water temperature of 9.5 °C. The higher than 100% oxygen saturation concentration can be due to the production of pure oxygen by photosynthetically-active organisms or non-equilibrium between the water and the air above it (YSI, 2003). This seasonal variation in O_2 may be attributed to both natural and anthropogenic factors (Bellos and Sawidis, 2005). Key natural factors that might influence DO

concentrations include stream discharge, flow velocity, temperature, channel gradient, channel bottom substrate, and degree of channel confinement (Ice and Sugden, 2003). Anthropogenic factors that influence instream DO include organic and nutrient discharges (*e.g.,* from wastewater agricultural activities) (Joyce et al., 1985; Santhi et al., 2002). Specific conductivity varied between 49 and 113 μs cm^{-1} (Figure S3h), and the pH varied between 5.5 and 6.9 (Figure S3i). Conductivity and pH did not exhibit a consistent temporal trend.

The crustal normalized rare earth element (REE) pattern indicated the presence of a Gd anomaly (Gd/Gd*) in the Edisto River water (Figure S4a). The size of the Gd anomaly varied between 0.95 and 1.8 (Figure S4b) with a peak in 2018 and a higher peak in 2020 and no increases in 2019. The geogenic ratio of Gd/Gd* should be close to one, and any values exceeding at least 1.3 represent anthropogenic Gd input (Knappe et al., 2005; Moeller et al., 2002). Despite the small size of the Gd anomaly (*e.g.,* 0.95 and 1.8) relative to those reported in urban rivers (*e.g.,* 2.1 to 30, Table S4), the manifestation of these anomalies in 2018 and 2020 and their absence during the drought period of 2019 are strong indications that these anomalies are true Gd contamination signatures. REE distribution patterns of surface water and groundwater from industrialized and highly populated areas show anthropogenic Gd anomalies as a result of the use of Gd compounds as a contrast agent in magnetic resonance imaging (Knappe et al., 2005). The Gd compounds enter the surface water mostly via wastewater sources such as wastewater treated effluent discharge directly as permitted point sources or indirectly through reuse application overspray, sewage spills, leaking sewage pipes, and leaking or improperly designed septic tanks (Knappe et al., 2005; Oppenheimer et al., 2012). These results indicate a possible contribution of wastewater sources to the discharge in the Edisto River in the spring/summer of 2018 and 2020. The notably higher concentrations of suspended sediment, anthropogenic Gd, and Ti during 2020 may be due in part to the precedent 2019 dry conditions, with limited runoff and associated increased land accumulation of these constituents between March 19, 2019 and December 10, 2019 and subsequent elevated runoff during 2020.

The spring/summer timing of the increases in P, N, OC, Alkalinity, suspended sediment, and Gd anomaly (*e.g.,* spring and summer) and the concurrent decreases in DO coincide with the agriculture season and with the application of biosolids on agricultural fields (Table S5) (Lu et al., 2012). This pattern is consistent with agriculture-linked spatially-distributed wastewater sources (*e.g.,* land application of biosolids/wastewater effluent reuse overspray) as drivers of these contaminants in the Edisto River as discussed in more detail in section 3.5.

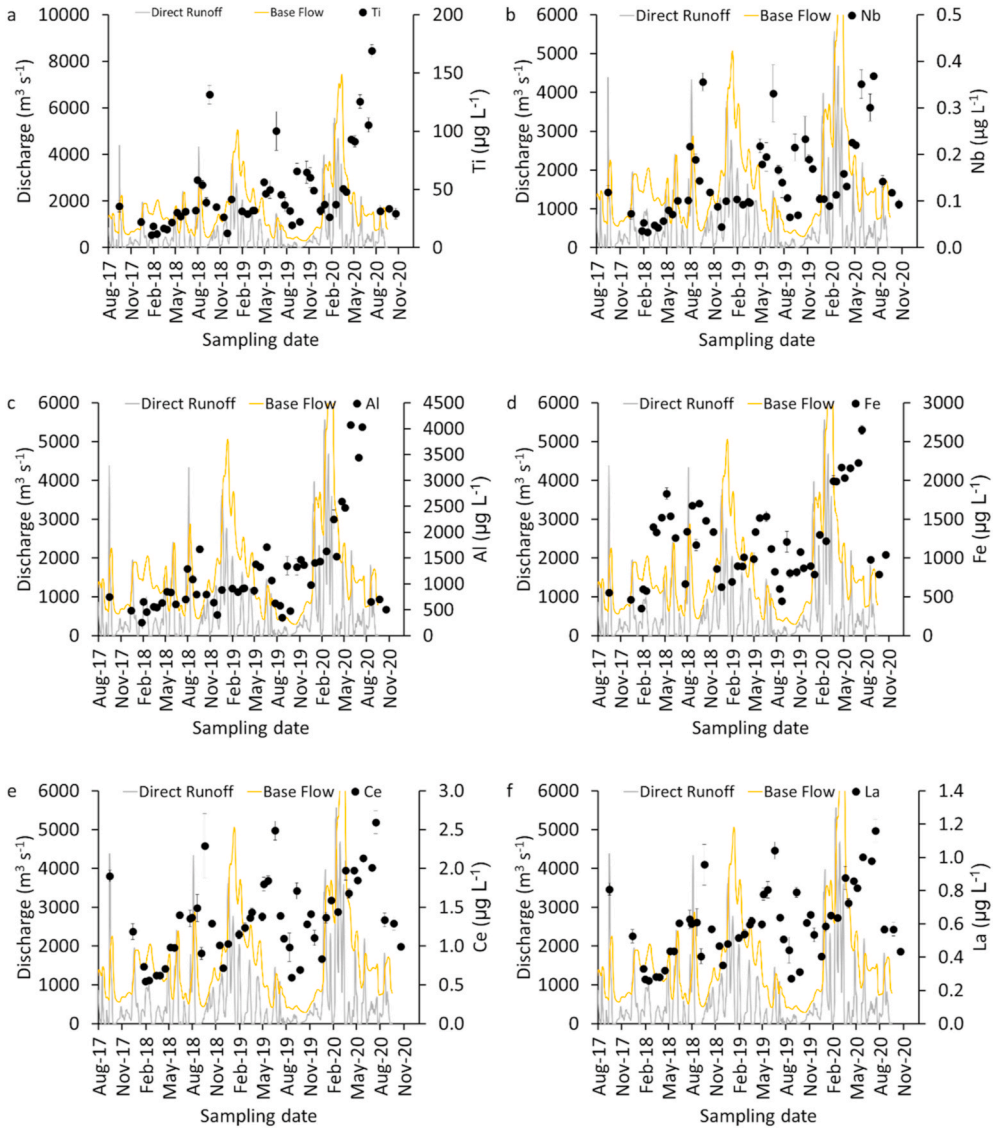

Fig. 1. Temporal variation in (a) Ti, (b) Nb, (c) Al, (d) Fe, (e) Ce, and (f) La concentration in the Edisto River water at the sampling site.

3.3. Elemental concentrations and ratios

The concentrations of Ti, Nb, Al, Fe, Ce and La followed the same seasonal pattern of increases during the spring and summer compared to fall and winter (Fig. 1), suggesting a common environmental driver. Elemental ratios (*e.g.,* Ti/Nb, Ti/Al, Ti/Fe, and Ce/La), however, exhibited different patterns (Fig. 2a–d). Except during the 2019 spring/summer drought, Ti/Nb trended higher between February and August, with lower values between September and January (Fig. 2a). The lowest Ti/Nb ratio (255.7 ± 8.9) was observed during the drought period of summer 2019 in the absence of precipitation-driven surface runoff (Fig. 2a). This value was consistent with a natural background ratio of Ti/Nb (266.4 ± 8.9) in our previous study in the tributaries of the Congaree River (Loosli et al., 2019). Thus, 255.7 was used herein as the natural background Ti/Nb ratio to estimate natural and anthropogenic Ti concentrations. The Ti/Al and Ti/Fe ratios followed the opposite trend compared to that of Ti/Nb (Fig. 2b and c). This might be due to the co-release of Al and Fe with Ti from the same source such as sewage spills, biosolids, or urban runoff (Loosli et al., 2019; Nabi et al., 2021a, 2021b; Wang et al., 2020). The Ce/La ratio exhibited limited variability (*e.g.,* 2.0 ± 0.01 to 2.4 ± 0.02), with an average observed value (2.2 ± 0.1) consistent with the average crustal Ce/La (2.13) and the average background water Ce/La (2.15 ± 0.01) (Loosli et al., 2019). This pattern indicates little anthropogenic Ce or La contamination (Fig. 2d). The near constant Ce/La ratio and the high concentration of Ce and La in the Edisto River water during high discharge indicates a significant introduction of natural particles during runoff events in the Edisto River.

Given the significant contribution of natural particles, as indicated by the high Ce and La concentrations, and the presence of Nb in natural titanium minerals (Gaspar and Wyllie, 1983; Nakashima and Imaoka, 1998), observed differences in Ti/Nb elemental ratios in Edisto River bulk water samples plausibly may result from **1)** variability in the elemental ratios within naturally-occurring Ti-containing particles, or **2)** variability in the introduction of anthropogenic Ti-containing particles that do not contain Nb (Wang et al., 2020). Strong associations between Ti and Nb in titanium minerals and no apparent explanation for seasonal changes in Ti and Nb contents of natural mineral sources suggest that these variations are due to anthropogenic Ti contamination. To further test this hypothesis, the elemental associations and variability in Ti/tracer ratios in multi-element Ti-bearing particles in a select set of Edisto River water sample with low and high bulk Ti/Nb ratios was investigated using SP-ICP-TOF-MS (Table S6). Despite the significant differences in bulk water Ti/Nb ratios (varied between 243 ± 29 to 417 ± 4) in the selected Edisto River samples, the elemental ratios of Ti/Nb in multi-element Ti-bearing particles did not vary substantially (varied between 212 ± 185 and 263 ± 183). Thus, the observed variability in Edisto River bulk sample Ti/Nb ratios is attributed to seasonal differences in the supply of anthropogenic, Nb-free, Ti-particles to the stream.

3.4. Concentration and co-occurrence of TiO_2 and other contaminants

The estimated TiO_2 engineered particle concentrations based on shifts in Ti/Nb elemental ratios varied between 0 μg L^{-1} and 128.5 ± 3.9 μg L^{-1} (Fig. 3a). These TiO_2 concentrations are similar to those measured in other surface waters in South Carolina receiving sewage spills, such as Gills Creek and Stoops Creek (1–100 μg L^{-1}) (Loosli et al., 2019), and receiving urban runoff such as the Broad River (20–150 μg L^{-1}) (Nabi et al., 2021a). These TiO_2 concentrations are notably higher, however, than those (*e.g.,* 0.55–6.5 μg L^{-1}) reported in surface water from the Dommel River in the Netherlands and Ribble/Wyre and upper Severn rivers UK. (Donovan et al., 2016; Markus et al., 2018; Neal et al., 2011).

The TiO_2 followed the same trends of rise and fall as those of phosphorus, orthophosphate, nitrate, ammonia, anthropogenic Gd, temperature, and suspended sediment (Fig. 3a–e, Table S7); and the opposite trend as that of organic carbon and DO (Fig. 3f and g, Table S7). The co-occurrence of TiO_2 with phosphorus and nitrogen (Fig. 3a and b), both recognized agriculture-related contaminants, suggests that the release of TiO_2 is possibly associated with agricultural runoff. The concentration of nitrogen in streams draining fields with applied sewage sludge follows the same trend as those shown here (Showers et al., 2006). The co-occurrence of TiO_2 with anthropogenic Gd (Fig. 3c), a recognized

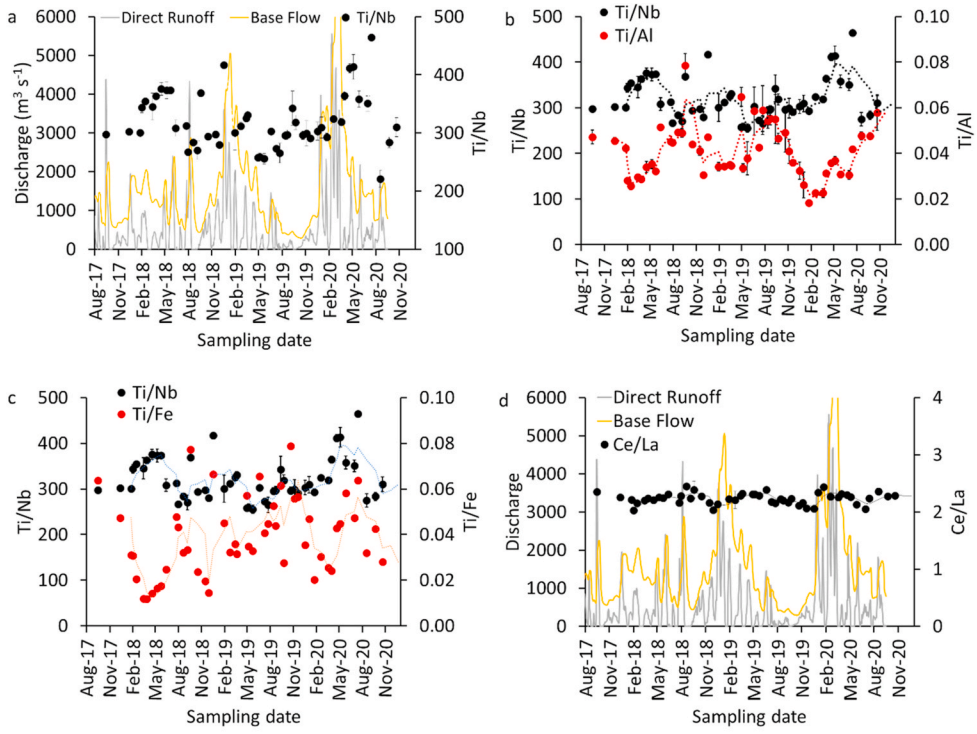

Fig. 2. Temporal variability of elemental ratios of (a) Ti/Nb, (b) Ti/Al, (c) Ti/Fe, and (d) Ce/La in the Edisto River water at the sampling site.

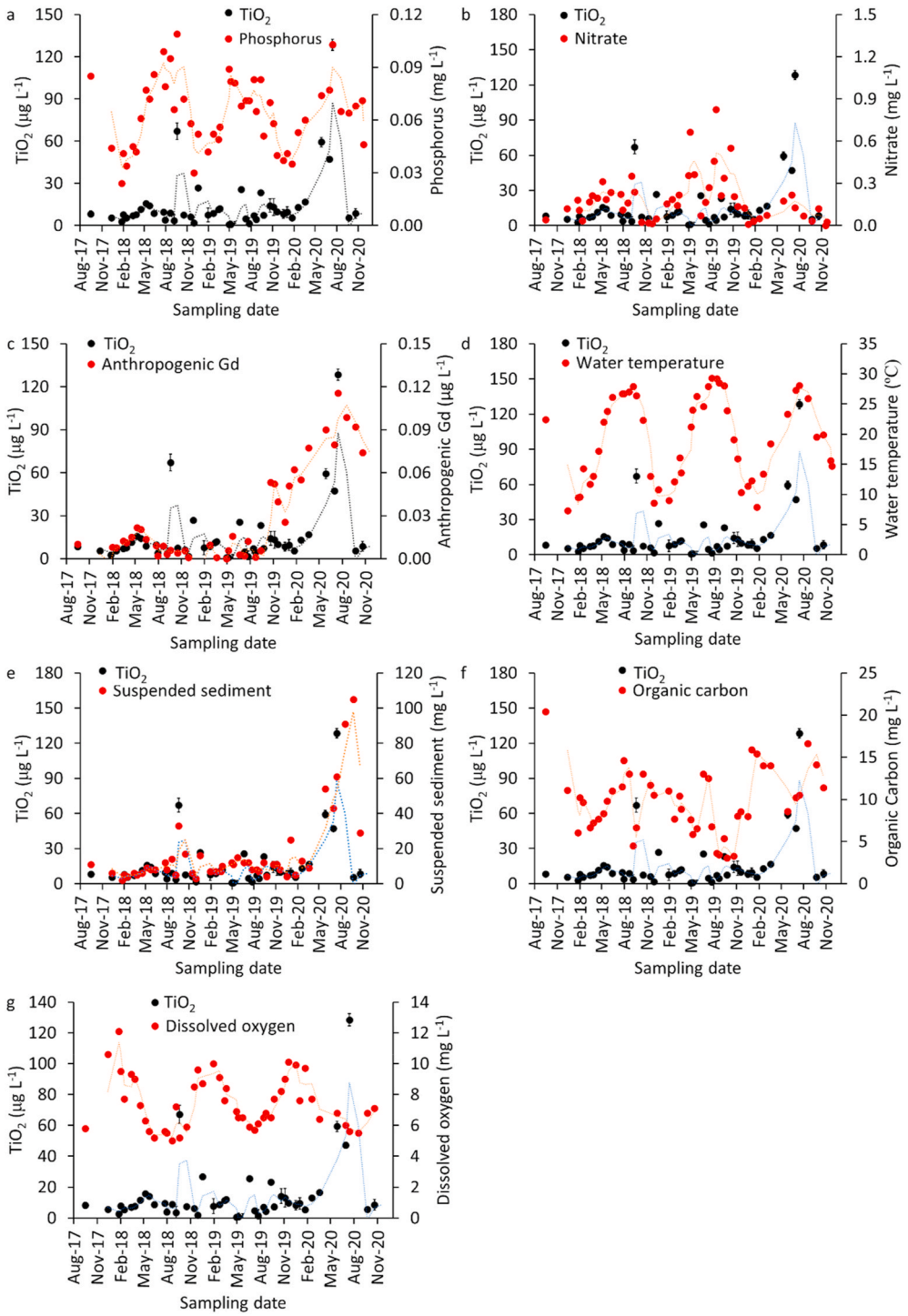

Fig. 3. TiO_2 engineered particle concentrations compared to (a) phosphorus, (b) nitrate, (c) anthropogenic Gd, (d) water temperature, (e) suspended sediment, (f) organic carbon, and (g) dissolved oxygen in the Edisto River water at the sampling site.

wastewater contaminant, suggests that the release of TiO_2 is associated with human waste. Together these co-occurrences suggest that the release of TiO_2 is associated with human waste disposal, such as discharges to the stream and sewage sludge land application on adjacent agricultural fields.

The rise and fall of TiO_2 particles with temperature is likely due to seasonal effect such as agricultural land application and associated release of TiO_2 during the spring and summer seasons. The co-occurrence of TiO_2 with suspended sediment (Fig. 3e) is likely due to the heteroaggregation of TiO_2 particles with the suspended solids. The opposite trends of TiO_2 and DO (Fig. 3g) is also consistent with co-release of TiO_2 with wastewater discharge and/or runoff of biosolids from agricultural fields.

3.5. *Potential source of TiO_2 in the Edisto River*

Releases of TiO_2 into the Edisto River might originate from various sources including 1) treated sewage (Kiser et al., 2009; Westerhoff et al., 2011), 2) sewage spills (Loosli et al., 2019), 3) urban runoff (Nabi et al., 2021a), and/or 4) agricultural runoff from fields amended with

biosolids or irrigated with reuse water. Below we discuss the likely contribution of these sources to TiO_2 concentrations in the Edisto River.

Thirteen WWTP were identified along the Edisto River (Table S8). The effluent volume varies from 0.11 to 18.5 $\times$ 10^6 L day^{-1} (0.0013–0.21 m^3 s^{-1}) with a total effluent volume of all WWTPs of 32.1 $\times$ 10^6 L day^{-1} (0.37 m^3 s^{-1}) (Seiple et al., 2017). The largest WWTP along the Edisto River is Orangeburg WWTP, with an effluent volume of 18.5 $\times$ 10^6 L day^{-1} (0.21 m^3 s^{-1}) and located approximately 75 km upstream the sampling site. The total effluent volume from all WWTPs is negligible (<4%) compared to the lowest discharge of 9.6 m^3 s^{-1} at the sampling site and would result in significant dilution (*e.g.,* > 25 fold in the worst-case scenario) of WWTP effluent. Given the low concentration of TiO_2 engineered particles in WWTP effluents in the USA (*e.g.,* 1–50 μg L^{-1}) (Kiser et al., 2009; Nabi et al., 2021b; Westerhoff et al., 2011), this would result in TiO_2 concentrations of <2.0 μg L^{-1}, much lower than the surface-water TiO_2 concentrations observed in this study. Therefore, WWTP effluent is estimated to be a minor contributor to total concentrations of TiO_2 in the Edisto River.

Fifty-three sewage spills were identified in the Edisto River watershed (SCDHEC, 2020). These occurred mainly in Orangeburg and Aiken Counties, the largest urban areas in the Edisto River watershed and the closest to the sampling location (Table S9). The total volumes of sewage spills were approximately 81,000, 188,000, and 163,000 L in 2018, 2019, and 2020, respectively. The short duration (*e.g.,* 5 min to 14 h) and small volumes (*e.g.,* 1100 to 50,000 L, Table S9) of these sewage spills, and their distance from the sampling site (*e.g.,* 75 and 140 km for Orangeburg and Aiken, respectively) would result in significant dilution of any associated TiO_2 releases to background level concentrations at the sampling site. Therefore, sewage spills occurring in the rural areas of Orangeburg and Aiken cities are also unlikely to be significant contributors to TiO_2 loads observed at the sampling site in the Edisto River.

Urban land use represents only 1% of the Edisto watershed area and is comprised of the City of Orangeburg (21.5 km^2) and a portion of the City of Aiken (total area of Aiken is 53.9 km^2), located at approximately 68 and 140 km, respectively upstream of the sampling site. This is likely to result in significant dilution of any TiO_2 emitted from Aiken and/or Orangeburg to the background level at the sampling site. Paul and Meyer (2001) reported that urban runoff varies between 20 and 55% of total rainfall in the impervious urban corridor depending on percentage of infiltration, evapotranspiration, and imperviousness (Paul and Meyer, 2001). Consequently, the total urban runoff generated from both cities would vary in the range from 23.1 to 63.4 $\times$ 10^6 L day^{-1} (0.27–0.73 m^3 s^{-1}), assuming average annual rainfall of 1194 and 1220 mm in Orangeburg and Aiken cities respectively in the same day (South Carolina State Climatology Office, 2020). The total urban runoff from both cities is negligible compared to the lowest discharge of 9.6 m^3 s^{-1} at the sampling site and would result in significant dilution (*e.g.,* 13- to 35-fold in the worst-case scenario) of urban runoff. The concentration of TiO_2 engineered particles in urban runoff in the USA ranges from 5 to 150 μg L^{-1} (Wang et al., 2020). Therefore, the resulting TiO_2 concentration would be between 4.3 and 11.5 μg L^{-1} in the stream water adjacent to the urban areas, well below the in-stream TiO_2 concentrations observed in this study. Thus, urban sources are unlikely to account for the total TiO_2 load at the sampling site.

Bridge runoff also could contribute to in-stream TiO_2 concentrations (Wang et al., 2020). One bridge (State Road 18-19) was identified near (3.4 km) and upstream of the sampling site. The average daily traffic in 2019 on this bridge was 250 vehicles per day (SCDOT, 2019). This average daily traffic is much lower (~358 times less) than that reported for bridges in a recent study (Wang et al., 2020) in which TiO_2 engineered particles in bridge runoff was estimated to vary between 5 and 150 μg L^{-1}. Based on that report, the in-stream TiO_2 concentration associated with bridge runoff from State road 18-19 was estimated to be < 0.5 μg L^{-1} (in the worst case scenario) at the bridge and to decrease downstream due to dilution. Thus bridge runoff also is unlikely to contribute substantially to total TiO_2 loads observed at the sampling site.

Approximately 33,929 dry U.S. metric tons of total solids is generated in South Carolina annually, with land application estimated at 12,758 dry U.S. metric tons (*e.g.,* 38% of the total solids) per year (NEBRA, 2007). Therefore, the total solids applied annually on land in South Carolina is estimated to be approximately 5.5 $\times$ 10^6 μg solids m^{-1} of agricultural land. The concentration of TiO_2 in sewage sludge in the United States is estimated at 1.67–10.0 kg TiO_2 ton^{-1} dry weight (Table S10) (Kiser et al., 2009). Thus, the estimated TiO_2 mass applied annually on land in SC is approximately 21–130 tons TiO_2 (or 21 $\times$ 10^{12} to 13 $\times$ 10^{13} μg TiO_2). Accordingly, the estimated TiO_2 mass applied annually on land in the Edisto River watershed is estimated to be approximately 1100 to 6600 μg TiO_2 per square meter of agricultural land, a substantial potential contributor to TiO_2 loads in the Edisto River. Therefore, based on this preliminary source apportionment, the seasonal patterns in in-stream TiO_2 concentrations and elemental ratios and the co-occurrence of TiO_2 and agriculture and sewage related contaminants (*e.g.,* increased phosphorus, nitrogen, and anthropogenic Gd and decreased DO) in the Edisto River are most easily reconciled with seasonally-intensive human-waste biosolid applications or reuse overspray on agricultural land against a non-seasonal background signal from normal operation and episodic bypass effluent discharges from the limited number of upstream WWTP point-sources and numerous spatially-distributed (functionally non-point source) upstream residential on-site septic discharges.

4. Conclusions

This study demonstrated seasonal variability in TiO_2 concentrations in a rural river in South Carolina, United States. This study is the first to characterize and quantify engineered particles in a river reach draining a rural watershed with less than 1% urban land cover and concomitantly few WWTP point-source discharges. In this setting, long-term monitoring of the concentration of TiO_2 engineered particles was required to discern the temporal variability in surface-water TiO_2 engineered particles and to establish the background natural Ti/Nb ratio. Using the elemental ratio approach, the total, natural, and engineered Ti concentrations were quantified in Edisto River water. The elemental ratio of Ti/Nb varied from 255.7 ± 8.9 to 464.5 ± 2.8. The lowest measured Ti/Nb ratios, observed in the absence of runoff and precipitation during the 2019 drought, were in good agreement with average Ti/Nb ratios in sediments upstream in the Edisto River basin and with previously established natural background ratios in tributaries of the Congaree River (*e.g.,* 266.4 ± 8.9) (Loosli et al., 2019). Thus, this Ti/Nb elemental ratio (*e.g.,* 255.7 ± 8.9) was employed as the natural background ratio to calculate natural and anthropogenic Ti concentrations by mass-balance.

The Edisto River TiO_2 engineered particle concentration ranged from 0 to 128.7 ± 3.9 μg L^{-1}. The concentrations of TiO_2 engineered particles increased during the spring and summer seasons and decreased during the fall and winter seasons, which coincided with increases and decreases in phosphorus, nitrogen, ammonia, organic carbon, anthropogenic Gd. While the source(s) of TiO_2 ENM loading to the stream was not specifically identified, seasonal patterns in the instream concentrations and elemental ratios are most easily reconciled with seasonally-intensive biosolid or overspray application on agricultural land against a non-seasonal background signal from normal-operation and episodic bypass effluent discharges from the limited number of upstream WWTP point-sources and numerous spatially-distributed (non-point source) upstream residential on-site septic discharges, because: **1)** WWTP effluent discharge and bypass sewage spills are small contributors (<4%) to the Edisto River discharge at the Givhans gage, **2)** no seasonal pattern in effluent discharge and by-pass events was observed during the study period, **3)** the increase in TiO_2 concentrations during the spring and summer coincided with the onset of the growing season and the timing of agricultural biosolids application, and **4)** TiO_2 was associated with other agriculture-runoff and wastewater signatures such as nutrients and anthropogenic gadolinium, respectively.

The instream engineered TiO_2 concentrations observed in the current study are higher than the predicted no effect concentration for TiO_2 ENMs to freshwater organisms (*e.g.,* 1–18 μg L^{-1}). Further, fluvial transport of TiO_2 engineered particles from the Edisto River as well as other rivers to the ocean could lead to bioaccumulation in estuarine and coastal microflora and induce coral bleaching and coral population declines (Corinaldesi et al., 2018; Jovanović and Guzmán, 2014). Further research is needed on the occurrence and temporal variability of TiO_2 engineered particle concentrations in streambed sediments to better understand the fate, transport, and potential aquatic effects of TiO_2 engineered particles on rural stream ecosystems and estuarine and coastal receptors.

Author contribution statement

Mr. Md Mahmudun Nabi and Dr. Jingjing Wang performed the experimental work, data analysis, and wrote the first draft. Dr. Celeste A Journey and Dr. Paul M Bradley planned the field sampling and collected samples. Dr. Mohammed Baalousha conceptualized the study, supervised Mr. Md Mahmudun Nabi and Dr. Jingjing Wang in performing the experimental work and analyzing the data. All authors contributed to the manuscript writing and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.134091.

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