

Spectroscopic Characterization of TiO₂ Polymorphs in Wastewater Treatment and Sediment Samples

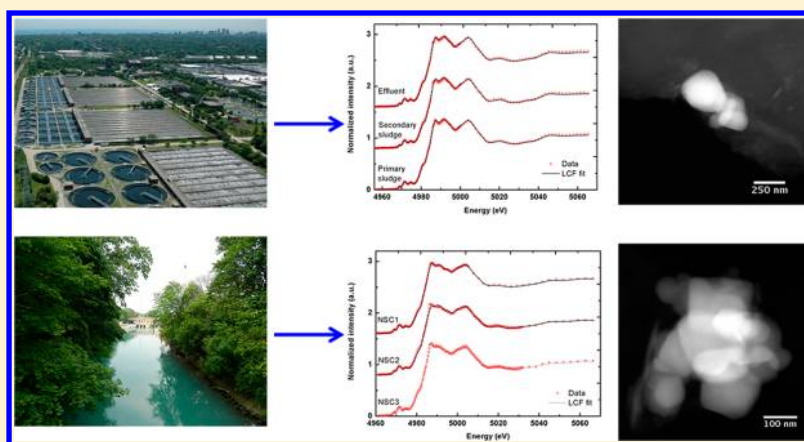
Tiezheng Tong,[†] Andrea N. Hill,[†] Marco A. Alsina,[†] Jinsong Wu,[‡] Karis Y. Shang,[†] John J. Kelly,[§] Kimberly A. Gray,^{*,†} and Jean-François Gaillard^{*,†}

[†]Department of Civil and Environmental Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

[‡]Department of Materials Science and Engineering, NUANCE Center, Northwestern University, Evanston, Illinois 60208, United States

[§]Department of Biology, Loyola University Chicago, 1032 West Sheridan Road, Chicago, Illinois 60660, United States

S Supporting Information



ABSTRACT: The reactivity and toxicity of nano-TiO₂ are controlled to a large extent by its phase composition. Although numerous studies have focused on the environmental impacts of nano-TiO₂, the phase composition of TiO₂ in environmental samples remains unknown. Using Ti K-edge X-ray absorption near-edge structure (XANES) spectroscopy, we reveal the average phase composition of TiO₂ present at various stages of a full-scale wastewater treatment plant (WWTP) and in sediments collected both upstream and downstream of the WWTP discharge point. The XANES spectra provide direct evidence of the presence of TiO₂ in these samples, in particular the coexistence of both anatase and rutile phases. Spectral decomposition using least-squares linear combination fitting shows that Ti in the WWTP samples contained ~30% anatase, 60% rutile, and 10% ilmenite. This composition was stable over a two-month sampling period (nine sampling events) and did not change among primary sludge, activated sludge, and the final effluent. In contrast, sediments located upstream and downstream of the WWTP discharge exhibited distinct XANES spectra reflecting a different TiO₂ phase composition with a reversed relative abundance of anatase to rutile. Electron microscopy imaging of Ti-rich clusters in these various samples shows the presence of aggregates composed of nanoparticles (having a dimension of <100 nm) and larger particles with sizes of up to ~300 nm. This is the first report of the average TiO₂ phase composition in environmental samples based on a methodology that improves the assessment of the environmental risks of TiO₂ under ambient conditions.

INTRODUCTION

Titanium dioxide (TiO₂) is a commodity chemical that is used in numerous consumer and industrial applications, including coatings and pigments.¹ During the recent decade, the TiO₂ industry has been shifting to nanostructured TiO₂ (nano-TiO₂) dominance,² with applications ranging from sunscreens³ and cosmetics⁴ to food additives⁵ and photocatalysts.^{6,7} The rapidly expanding use of nano-TiO₂ is cause for growing concern about its environmental, ecological, and health consequences.

TiO₂ can exist in amorphous or polymorph crystalline phases, including anatase, rutile, and brookite. Although rutile is more stable thermodynamically than anatase and brookite, these three TiO₂ phases are all present in natural minerals,⁸ and transformation from one phase to another requires a high temperature (>400 °C).^{9–12} Anatase is generally more

Received: October 14, 2014

Accepted: December 17, 2014

photoactive than rutile,¹³ and thus, it is potentially more phototoxic to living organisms.^{14–18} For example, our previous study demonstrated that the mineral phase of spherical nano-TiO₂ is a primary factor in determining its acute phototoxicity to bacteria.¹⁶ In addition, rutile has been shown to have less adsorption capability for metal contaminants (e.g., uranium) than predominantly anatase materials.¹⁹ Despite the importance of phase composition in determining the environmental impacts of nano-TiO₂, current environmental risk assessments, based on modeling predictions^{20,21} or life-cycle analysis,^{22,23} consider TiO₂ as a single material type and ignore the effects of TiO₂ phase composition. This is partially due to the lack of detailed information about TiO₂ present in environmental samples.

According to a recent report by the National Research Council (NRC) of the National Academies,²⁴ measurement and characterization of engineered nanomaterials (ENMs) in the environment is a high priority to understand ENM fate and potential for deleterious human and ecological exposure. As compared to numerous studies addressing the toxicity of nano-TiO₂ in laboratory experiments,^{14,16,25–28} however, only a few studies have focused on the occurrence of TiO₂ in the environment. The presence of nano-TiO₂ has been reported in paints from building façades,²⁹ surface waters,³⁰ and wastewater treatment plants.^{31,32} These pioneering studies, solely relying on total Ti measurements and electron microscopy observations, provide limited information about the phase composition and potential reactivity of TiO₂. Recent work by Kim et al. in which transmission electron microscopy and electron diffraction were employed to identify rutile TiO₂ particles in sewage sludge went further toward providing this missing information.³³ Their results, however, correspond to the analysis of a few single particles, and thus neither exclude the possible presence of anatase in their samples nor provide compositional proportions of the crystalline phases.

In this study, Ti K-edge X-ray absorption near-edge structure (XANES) spectroscopy was applied to determine and quantify the Ti speciation in samples taken from multiple stages of a full-scale wastewater treatment plant (WWTP) during a two-month sampling period. Primary sludge, activated sludge, and the final effluent of the WWTP were analyzed because they are the potential sources of release of TiO₂ into the environment, through biosolids use, landfill disposal, and discharge of effluent into surface waters.³¹ Sediment samples collected both upstream and downstream of the WWTP effluent outfall were also analyzed for comparison. Our study represents the first report of the average TiO₂ phase composition in such environmental samples, providing new insights for assessing the potential environmental risks of TiO₂ under ambient conditions.

MATERIALS AND METHODS

The North Side Water Reclamation Plant (NSWRP) in Skokie, IL, receives domestic wastewater from a portion of the city of Chicago and northern Cook County suburbs, serving more than 1.3 million people.³⁴ Primary sludge, activated sludge, and the final effluent of the NSWRP were collected on a weekly basis during a two-month sampling period (June 25 to August 20, 2014, total of nine sampling events). In addition, sediments from the North Shore Channel (NSC) were collected approximately 2 km upstream (NSC1, 42.04063°N/87.70974°W), 300 m downstream (NSC2, 42.01934°N/87.71023°W), and 5 km downstream (NSC3, 41.97567°N/

87.70472°W) of the NSWRP outfall. Three replicates of sediments were collected at each sampling site. A graph showing the relative positions of the sampling sites is included in Figure S1 of the Supporting Information.

The primary sludge and activated sludge of the NSWRP were both centrifuged at 11900g (8000 rpm) for 20 min (Avanti J-26 XP, Beckman Coulter). The obtained solid sludge was dried overnight at 75 °C, conditions that do not alter phase composition (Figure S2 of the Supporting Information).^{9–12} The dried sludge was mounted on Kapton tape (DuPont) for XANES spectroscopy analysis. Final effluent samples from the NSWRP were centrifuged at 11900g (8000 rpm) for 30 min. After the supernatant had been discarded, the concentrate from 2.4 L of the final effluent was filtered through 0.2 μm pore-size membranes (polycarbonate, Millipore), after which the membranes were mounted on Kapton tape for XANES analysis. The NSC sediment samples were dried overnight at 75 °C and passed through a 250 μm sieve to remove large particles and reach sample uniformity. The sediments were further ground using an agate pestle mortar and mounted on Kapton tape for XANES analysis. The Ti contents in the NSWRP samples and the NSC sediments were analyzed using muffle furnace-induced alkaline hydrolysis followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Vista MPX ICP Spectrometer, Varian), according to the methods by Silva et al.³⁵ To estimate the amount of TiO₂ entering the NSWRP, four influent samples were collected and analyzed during the two-month sampling period. The Ti recoveries were 88 ± 3 and 90 ± 3% for anatase and rutile, respectively, when 0.1 g of TiO₂ was spiked into 0.25 g of NSC sediments. The Ti contents of all the tested samples are summarized in Figure S3 and Table S1 of the Supporting Information.

Ti K-edge XANES spectra were acquired at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) beamline located at Sector 5 of the Advanced Photon Source, Argonne National Laboratory (Argonne, IL). Anatase (catalog no. 232033), rutile (catalog no. 204757), and brookite (catalog no. 791326) TiO₂ were purchased from Sigma-Aldrich, while amorphous TiO₂ was synthesized in the laboratory according to the procedure described by Vijayan et al.⁹ Ilmenite (FeTiO₃), one of the most common naturally occurring Ti-containing minerals, was purchased from VWR (catalog no. 470025-648). The phase and chemical composition of all the Ti reference compounds were confirmed by X-ray diffraction (Figure S4 of the Supporting Information). The detailed procedure of the XANES experiment is described in our previous work²⁸ and the Supporting Information. Normalization and analysis of XANES spectra were performed with Athena (version 0.9.18),³⁶ while the analysis of the pre-edge region was performed with Larch (version 0.9.23).³⁷ Selection of the set of reference compounds for performing spectral decomposition followed previously published principles.^{38,39} Least-squares linear combination fitting (LCF) was performed from –30 to 80 eV relative to the absorption edge (4966.4 eV) to quantify Ti speciation. Because of time constraints, primary sludge collected on five sampling dates, activated sludge on nine sampling dates, and final effluent on six sampling dates were selected randomly to be analyzed by XANES analysis (Tables S2 and S3 of the Supporting Information).

Scanning transmission electron microscopy (STEM) was conducted on an ultra-high-resolution field emission scanning transmission electron microscope (Hitachi HD-2300A) to

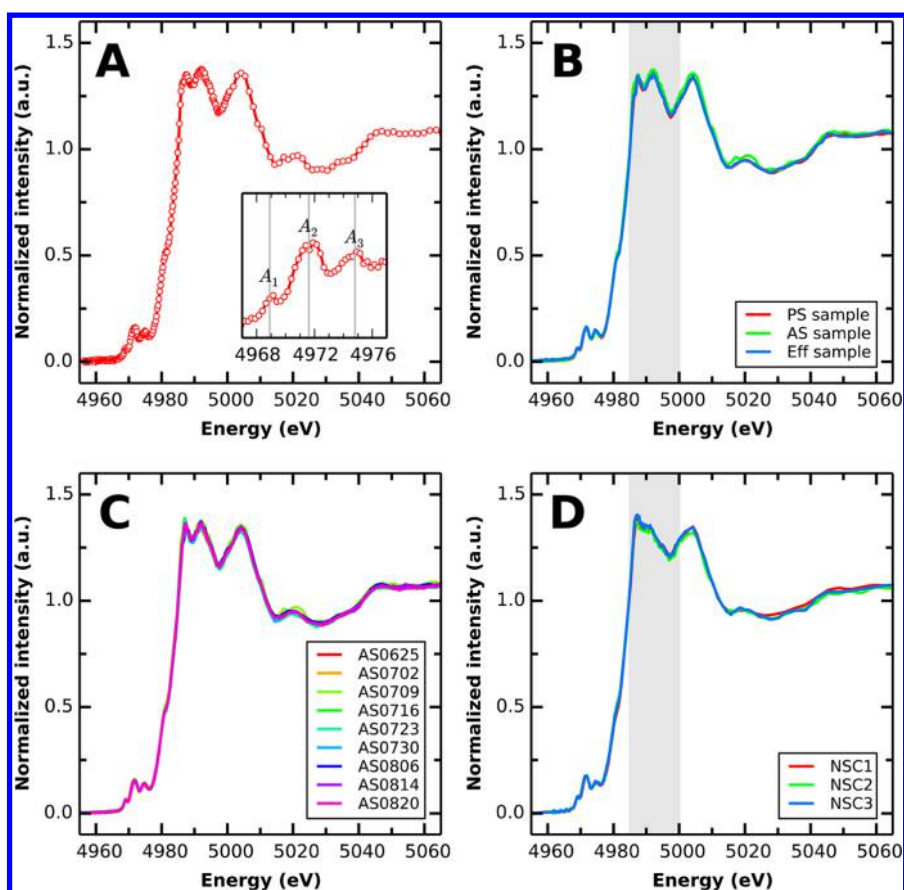


Figure 1. Normalized Ti K-edge XANES spectra of (A) a representative activated sludge sample (collected on June 25, 2014) from the NSWRP; (B) primary sludge (PS), activated sludge (AS), and final effluent (Eff) collected on July 9, 2014, from the NSWRP; (C) activated sludge collected during the two-month sampling period (e.g., AS0625 indicates the June 25 sample); and (D) representative NSC sediments collected upstream (NSC1) and downstream (NSC2 and NSC3) of the NSWRP (replicate 1). The inset of panel A shows the three characteristic pre-edge peaks for TiO_2 . The gray rectangular areas in panels B and D highlight the major differences between the XANES spectra of the NSWRP samples and the NSC sediments.

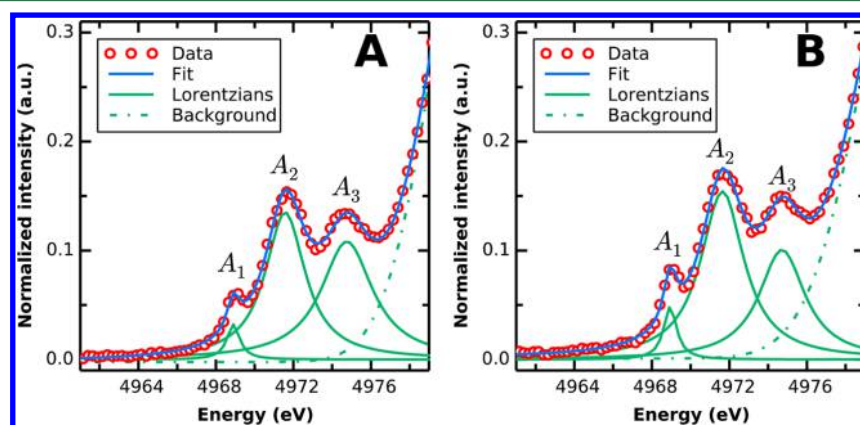


Figure 2. Fitting results of the normalized Ti K-edge XANES pre-edge spectra for a representative activated sludge sample (collected on June 25, 2014) from the NSWRP (A) and a NSC sediment collected upstream of the NSWRP (B).

observe Ti-containing particles and/or aggregates present in both NSC sediments and activated sludge from the NSWRP. Elemental maps of each sample were obtained using the dual energy dispersive spectroscopy (EDS) units (Thermo Scientific, with a Be window on the detector) attached to the Hitachi HD-2300A scanning transmission electron microscope. While the imaging resolution of STEM can reach ~ 0.3 nm, the spatial

resolution for EDS mapping is ~ 1 nm when there is a sufficient signal-to-noise ratio.

RESULTS AND DISCUSSION

The normalized Ti K-edge XANES spectrum of a representative activated sludge sample from NSWRP is shown in Figure 1A and clearly exhibits the three pre-edge absorption features characteristic of TiO_2 polymorphs.⁴⁰ The XANES spectra of

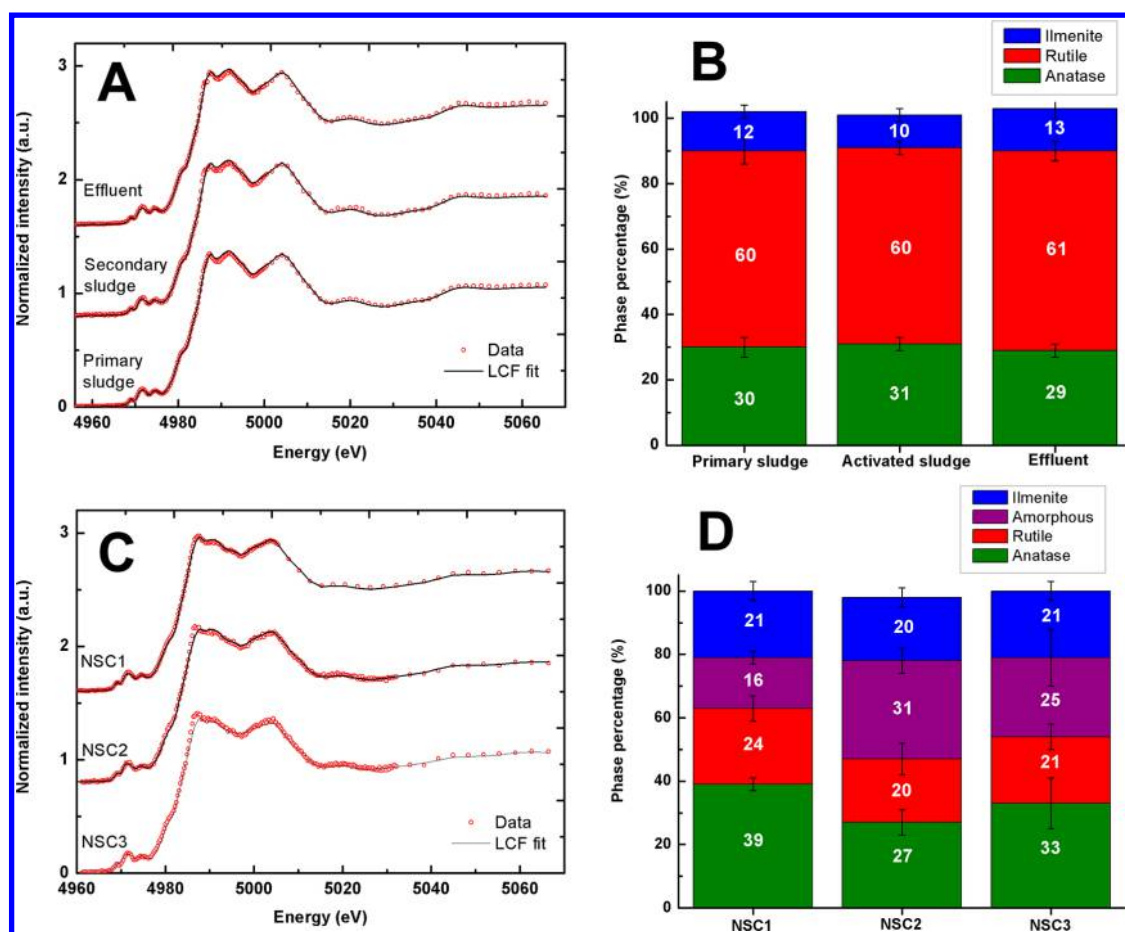


Figure 3. Results of the linear combination fits on the Ti K-edge XANES spectra of representative NSWRP samples (collected on July 9, 2014, as examples) (A) and NSC sediments (replicate 1 as examples) (C). The average Ti phase compositions in the NSWRP samples and NSC sediments are shown in panels B and D, respectively.

samples collected in different compartments of the NSWRP (i.e., primary sludge, activated sludge, and final effluent) were almost identical across the two-month sampling period, as shown in panels B and C of Figure 1. In contrast, the XANES spectra of the NSC sediments differed from those of the NSWRP samples (Figure 1D and Figure S5 of the Supporting Information), revealing the distinct TiO_2 phase composition contained in these two groups of samples. The NSC sediments collected both upstream and downstream of the NSWRP showed similar spectra.

The three pre-edge peaks of the samples were fit with the Lorentzian functions, to derive their location and relative intensity (details of the fitting procedure are described in the Supporting Information). Figure 2 shows the fitting results of spectra representative for both the NSWRP samples and the NSC sediments, while the results for all the samples are summarized in Table S2 of the Supporting Information. According to Table S2, the first, second, and third pre-edge peaks (A1–A3, respectively) of the XANES spectra occur at approximately 4968.9, 4971.6, and 4974.8 eV, respectively. These peak positions, along with the relative peak intensity, closely resemble those reported for TiO_2 ,⁴⁰ in which Ti(IV) has a six-fold octahedral coordination structure. The origin of these three pre-edge peaks has been explained and summarized in the literature by Farges et al.⁴⁰ and Chen et al.⁴¹

XANES spectral decomposition by means of LCF was performed to determine the relative proportion of each Ti

phase present in the samples. The XANES spectra of the Ti reference compounds, on which the LCF was based, are shown in Figure S6 of the Supporting Information. The data and the results of the curve fitting are presented in Figure 3 and summarized in Table S3 of the Supporting Information. For the NSWRP samples (Figure 3A,B), only three Ti reference spectra were required to adequately decompose the XANES spectra: those of anatase, rutile, and ilmenite (the addition of a fourth Ti species did not improve the fit). For the final effluent of NSWRP, for example, the best LCF fits yielded $29 \pm 2\%$ anatase, $61 \pm 4\%$ rutile, and $13 \pm 3\%$ ilmenite on average. The goodness of fit (reported by the *R*-factor in Table S3 of the Supporting Information), along with the three characteristic pre-edge absorption features as discussed above, provides substantial evidence of the presence of TiO_2 in the NSWRP samples. Consistent with the almost identical XANES spectra shown in Figure 1, the Ti phase composition was similar among different compartments of the NSWRP and remained stable during the two-month sampling period. On average, the Ti phases present in all the NSWRP samples correspond to $31 \pm 2\%$ anatase, $60 \pm 3\%$ rutile, and $11 \pm 3\%$ ilmenite (Table S3 of the Supporting Information).

For the NSC sediment samples (Figure 3C,D), four Ti reference spectra were required in the LCF analysis: those of anatase, rutile, amorphous TiO_2 , and ilmenite. For the NSC sediment collected upstream of the NSWRP, the best LCF fits yielded $39 \pm 2\%$ anatase, $24 \pm 4\%$ rutile, $16 \pm 2\%$ amorphous

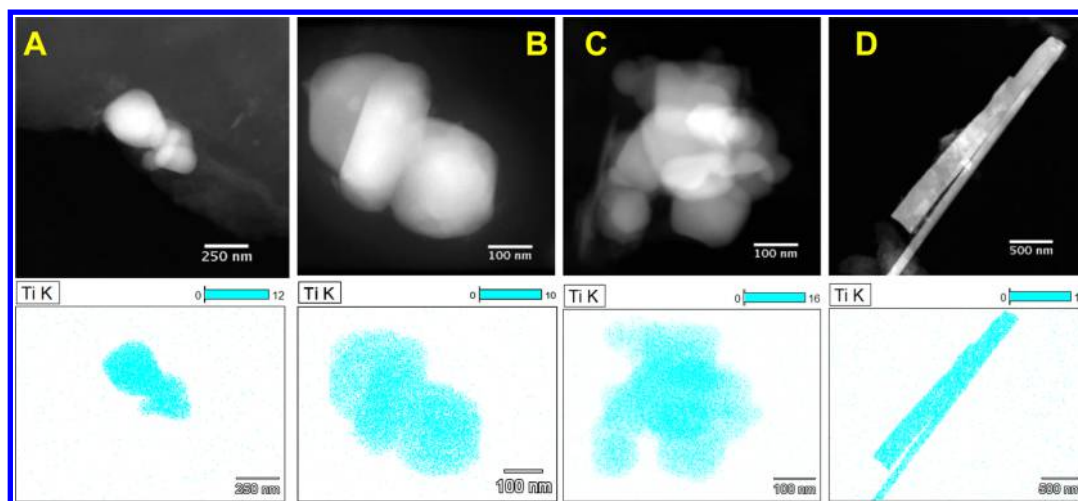


Figure 4. Large-angle annular dark-field images of Ti-containing aggregates in activated sludge collected from the NSWRP (A and B) and NSC sediments (C and D). The Ti elemental maps obtained by STEM–EDS mapping are shown below the corresponding STEM micrographs.

TiO₂, and 21 ± 3% ilmenite. The spectra of sediments collected downstream of the NSWRP show similar Ti phase compositions. Therefore, we found that the NSWRP samples have a distinct TiO₂ phase compositional fingerprint compared to that of the NSC sediments. In particular, the relative abundance of anatase to rutile is essentially reversed between the two groups of samples. This difference is likely a result of the different sources of TiO₂ contained in those samples, with TiO₂ in the NSWRP likely influenced predominantly by anthropogenic activities. The higher abundance of rutile versus that of anatase in the NSWRP samples may be related to the high level of domestic usage of rutile in pigments and personal care products such as cosmetics and sunscreen,^{3,42} in which the high photoactivity of anatase is undesired. In contrast, the NSC sediment samples likely reflect a greater variety of anthropogenic (e.g., stormwater runoff, combined sewer overflow, and treated wastewater effluent) and geological sources.⁸

The Ti concentrations in the NSWRP samples and NSC sediments are shown in Figure S3 of the Supporting Information, which have also been converted to the equivalent TiO₂ concentrations (Table S1 of the Supporting Information). The average TiO₂ concentrations were ~128.9 µg/L for the WWTP influent, 2.4 mg/g of dry sludge in the primary sludge, 2.4 mg/g of dry sludge in the activated sludge, and 12.1 µg/L for the effluent of the NSWRP during our sampling period, values consistent with those reported in the literature.^{31,32} The average TiO₂ concentrations in the sediments were ~2.5 mg/g of dry sediment upstream and 1.0 mg/g of dry sediment downstream of the NSWRP. According to the Metropolitan Water Reclamation District of Greater Chicago,⁴³ the NSWRP had an annual average treated flow of 7.7×10^5 m³/day (204 MGD) and produced 33880 tons of dry solids in 2013, which correspond to ~3.4 tons (1.1 ton of anatase and 2.3 tons of rutile) and 81.3 tons (27.7 tons of anatase and 53.6 tons of rutile) of TiO₂ released from the NSWRP via final effluent and sludge per year, respectively. Therefore, our results indicate that most of the TiO₂ particles entering the NSWRP are discharged with the sludge and a smaller quantity is released in the final effluent, which was also observed by Kiser, Westerhoff, and co-workers.³¹

In our study, the NSWRP effluent does not appear to control the TiO₂ phase composition of the NSC sediments. This is due, in part, to the significant removal of TiO₂ by the wastewater

treatment process. In addition, Battin et al.⁴⁴ reported that TiO₂ nanoparticles with primary sizes of 10–20 nm and aggregate sizes of up to ~1 µm can travel more than 10 km before 99% of the initial mass concentration is removed from the water. It is possible, then, that a proportion of effluent-derived TiO₂ particles did not settle down into the sediments until they were beyond our farthest sampling site (i.e., 5 km downstream of the NSWRP outfall) and thus made little contribution to the phase composition of TiO₂ revealed in our study. Additionally, it should be noted that our study represents only a two-month snapshot of the release of TiO₂ from the NSWRP, a continuous and long-term process. Although a mass-balance study of TiO₂ to the NSC system is beyond the scope of this work, we should not ignore the possibility that the TiO₂ released from the NSWRP effluent may significantly alter the phase composition of TiO₂ in the downstream sediments in the future, especially considering the exponential growth of nano-TiO₂ production and usage.² This work provides a baseline against which to monitor the ongoing effects of the environmental release and fate of TiO₂.

Figure 4 shows typical Ti-containing particles or aggregates found in the NSWRP activated sludge and the NSC sediments as imaged by STEM, with the Ti elemental maps delineating clear outlines of the particles consistent with the dark-field images. Although it is difficult to obtain direct size information about the individual particles composing these aggregates, it is clear from the difference in electron density that some of these particles have at least one dimension of <100 nm, which classify them as nanosized (Figure 4A,B). These observations were in agreement with those of TiO₂ particles found in studies by Kim et al.³³ and Kiser et al.³¹ On the basis of the elemental maps (Figures S7 and S8 of the Supporting Information) and the XANES results, the observed particles are likely TiO₂ that are of nanosized or nearly nanosized (sizes of 100–300 nm). However, besides similar aggregates composed of Ti-containing nanoparticles (Figure 4C), large Ti-containing particles (~3 µm in the longer dimension) with an irregular morphology were also observed in the NSC sediment samples (Figure 4D). The micrographs of the NSC sediment samples show the more complex nature of Ti in this environment, as corroborated by the presence of additional phases revealed by the LCF analysis of the XANES spectra.

Overall, TiO₂ phase compositional fingerprints in samples collected from the NSWRP and nearby sediments can be established by Ti K-edge XANES analysis. In contrast to previous studies based on total Ti measurement and electron microscopy, the XANES spectra provide direct evidence of the presence of TiO₂ in these samples, as well as the coexistence of anatase and rutile. As compared to rutile, anatase exhibits higher phototoxicity to aquatic organisms (such as bacteria^{14,16} and algae¹⁷) and produces greater oxidative DNA damage.⁴⁵ Therefore, a quantitative measurement of the percentages of anatase and rutile present in environmental samples is valuable to both regulatory agencies and toxicologists for assessing potential environmental risks accurately. According to our results, Ti released from the NSWRP through sludge and final effluent is composed of approximately 30% anatase and 60% rutile (the remaining 10% is ilmenite) and contains a significant fraction of TiO₂ that is nanosized or nearly nanosized. Therefore, an assumption that TiO₂ released from WWTP is either only anatase or only rutile could overstate or underestimate the potential environmental risk. Furthermore, the differences in TiO₂ phase composition between the NSWRP samples and the NSC sediments indicate varied sources of TiO₂ for these two types of samples. It should be noted that in this work we performed XANES analysis on bulk environmental samples, which reflects the average TiO₂ phase composition but is not specific to TiO₂ at the nanoscale. Therefore, future work will focus, if possible, on targeting XANES spectroscopy to the nanofraction of the samples.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional tables, figures, and text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: k-gray@northwestern.edu. Phone: (847) 467-4252. Fax: (847) 491-4011.

*E-mail: jf-gaillard@northwestern.edu. Phone: (847) 467-1376. Fax: (847) 491-4011.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (Grant CBET-1067751 to K.A.G. and J.-F.G. and Grant CBET-1067439 to J.J.K.). We thank Dr. Qing Ma for his technical assistance with XANES analysis, Kevin Schwartzberg for synthesizing amorphous TiO₂, Aruch Poonsapaya and Sandra Matual from the North Side Water Reclamation Plant for collecting the NSWRP samples, Dr. Joseph Kozak from the Metropolitan Water Reclamation District of Greater Chicago for his help with the sampling logistics, and Dr. Tim Hoellein for collecting sediment samples. Portions of this work were performed at the DND-CAT Synchrotron Research Center located at Sector 5 of the APS. DND-CAT is supported by the E. I. DuPont de Nemours & Co., The Dow Chemical Co., the U.S. National Science Foundation through Grant DMR-9304725, and the State of Illinois through the Department of Commerce and the Board of Higher Education Grant IBHE HECA NWU 96. STEM observation was performed in the NUANCE Center at Northwestern University.

■ REFERENCES

- (1) *Nanomaterial Case Studies: Nanoscale Titanium Dioxide in Water Treatment and in Topical Sunscreen*; U.S. Environmental Protection Agency: Research Triangle Park, NC, 2010.
- (2) Robichaud, C. O.; Uyar, A. E.; Darby, M. R.; Zucker, L. G.; Wiesner, M. R. Estimates of upper bounds and trends in nano-TiO₂ production as a basis for exposure assessment. *Environ. Sci. Technol.* **2009**, *43* (12), 4227–4233.
- (3) Nohynek, G. J.; Lademann, J.; Ribaud, C.; Roberts, M. S. Grey goo on the skin? Nanotechnology, cosmetic and sunscreen safety. *Crit. Rev. Toxicol.* **2007**, *37* (3), 251–277.
- (4) Auffan, M.; Pedetour, M.; Rose, J.; Masion, A.; Ziarelli, F.; Borschneck, D.; Chaneac, C.; Botta, C.; Chaurand, P.; Labille, J.; Bottero, J. Y. Structural degradation at the surface of a TiO₂-based nanomaterial used in cosmetics. *Environ. Sci. Technol.* **2010**, *44* (7), 2689–2694.
- (5) Weir, A.; Westerhoff, P.; Fabricius, L.; Hristovski, K.; von Goetz, N. Titanium dioxide nanoparticles in food and personal care products. *Environ. Sci. Technol.* **2012**, *46* (4), 2242–2250.
- (6) Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **1995**, *95* (1), 69–96.
- (7) Li, G. H.; Ciston, S.; Saponjic, Z. V.; Chen, L.; Dimitrijevic, N. M.; Rajh, T.; Gray, K. A. Synthesizing mixed-phase TiO₂ nanocomposites using a hydrothermal method for photo-oxidation and photoreduction applications. *J. Catal.* **2008**, *253* (1), 105–110.
- (8) Force, E. R. *Geology of Titanium-mineral Deposits*; The Geological Society of America: Boulder, CO, 1991; Issue 259.
- (9) Vijayan, B.; Dimitrijevic, N. M.; Rajh, T.; Gray, K. Effect of calcination temperature on the photocatalytic reduction and oxidation processes of hydrothermally synthesized titania nanotubes. *J. Phys. Chem. C* **2010**, *114* (30), 12994–13002.
- (10) Hanaor, D. A. H.; Sorrell, C. C. Review of the anatase to rutile phase transformation. *J. Mater. Sci.* **2011**, *46* (4), 855–874.
- (11) Zhang, H. Z.; Banfield, J. F. Phase transformation of nanocrystalline anatase-to-rutile via combined interface and surface nucleation. *J. Mater. Res.* **2000**, *15* (2), 437–448.
- (12) Gouma, P. I.; Mills, M. J. Anatase-to-rutile transformation in titania powders. *J. Am. Ceram. Soc.* **2001**, *84* (3), 619–622.
- (13) Luttrell, T.; Halpegamage, S.; Tao, J. G.; Kramer, A.; Sutter, E.; Batzill, M. Why is anatase a better photocatalyst than rutile? Model studies on epitaxial TiO₂ films. *Sci. Rep.* **2014**, *4*, 4043.
- (14) Binh, C. T. T.; Tong, T. Z.; Gaillard, J. F.; Gray, K. A.; Kelly, J. J. Common freshwater bacteria vary in their responses to short-term exposure to nano-TiO₂. *Environ. Toxicol. Chem.* **2014**, *33* (2), 317–327.
- (15) Sayes, C. M.; Wahi, R.; Kurian, P. A.; Liu, Y. P.; West, J. L.; Ausman, K. D.; Warheit, D. B.; Colvin, V. L. Correlating nanoscale titania structure with toxicity: A cytotoxicity and inflammatory response study with human dermal fibroblasts and human lung epithelial cells. *Toxicol. Sci.* **2006**, *92* (1), 174–185.
- (16) Tong, T. Z.; Binh, C. T. T.; Kelly, J. J.; Gaillard, J. F.; Gray, K. A. Cytotoxicity of commercial nano-TiO₂ to *Escherichia coli* assessed by high-throughput screening: Effects of environmental factors. *Water Res.* **2013**, *47* (7), 2352–2362.
- (17) Ji, J.; Long, Z. F.; Lin, D. H. Toxicity of oxide nanoparticles to the green algae *Chlorella* sp. *Chem. Eng. J.* **2011**, *170* (2–3), 525–530.
- (18) Binh, C. T. T.; Tong, T. Z.; Gaillard, J. F.; Gray, K. A.; Kelly, J. J. Acute effects of TiO₂ nanomaterials on the viability and taxonomic composition of aquatic bacterial communities assessed via high-throughput screening and next generation sequencing. *PLoS One* **2014**, *9* (8), e106280.
- (19) Comarmond, M. J.; Payne, T. E.; Harrison, J. J.; Thiruvoth, S.; Wong, H. K.; Aughterson, R. D.; Lumpkin, G. R.; Muller, K.; Foerstendorf, H. Uranium sorption on various forms of titanium dioxide: Influence of surface area, surface charge, and impurities. *Environ. Sci. Technol.* **2011**, *45* (13), 5536–5542.
- (20) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Modeled environmental concentrations of engineered nanomaterials

(TiO₂, ZnO, Ag, CNT, Fullerenes) for different regions. *Environ. Sci. Technol.* **2009**, *43* (24), 9216–9222.

(21) Mueller, N. C.; Nowack, B. Exposure modeling of engineered nanoparticles in the environment. *Environ. Sci. Technol.* **2008**, *42* (12), 4447–4453.

(22) Keller, A. A.; Lazareva, A. Predicted releases of engineered nanomaterials: From global to regional to local. *Environ. Sci. Technol. Lett.* **2014**, *1*, 65–70.

(23) Keller, A. A.; McFerran, S.; Lazareva, A.; Suh, S. Global life cycle releases of engineered nanomaterials. *J. Nanopart. Res.* **2013**, *15* (6), DOI: 10.1007/s11051-013-1692-4.

(24) A Research Strategy for Environmental, Health, and Safety Aspects of Engineered Nanomaterials; National Research Council of the National Academies: Washington, DC, 2012.

(25) Adams, L. K.; Lyon, D. Y.; Alvarez, P. J. J. Comparative ecotoxicity of nanoscale TiO₂, SiO₂, and ZnO water suspensions. *Water Res.* **2006**, *40* (19), 3527–3532.

(26) Bar-Ilan, O.; Chuang, C. C.; Schwahn, D. J.; Yang, S.; Joshi, S.; Pedersen, J.; Hammers, R. J.; Peterson, R. E.; Heideman, W. TiO₂ nanoparticle exposure and illumination during zebrafish development: Mortality at parts per billion concentrations. *Environ. Sci. Technol.* **2013**, *47*, 4726–4733.

(27) Bar-Ilan, O.; Louis, K. M.; Yang, S. P.; Pedersen, J. A.; Hamers, R. J.; Peterson, R. E.; Heideman, W. Titanium dioxide nanoparticles produce phototoxicity in the developing zebrafish. *Nanotoxicology* **2012**, *6* (6), 670–679.

(28) Tong, T. Z.; Fang, K. Q.; Thomas, S. A.; Kelly, J. J.; Gray, K. A.; Gaillard, J. F. Chemical interactions between nano-ZnO and nano-TiO₂ in a natural aqueous medium. *Environ. Sci. Technol.* **2014**, *48* (14), 7924–7932.

(29) Kaegi, R.; Ulrich, A.; Sinnet, B.; Vonbank, R.; Wichser, A.; Zuleeg, S.; Simmler, H.; Brunner, S.; Vonmont, H.; Burkhardt, M.; Boller, M. Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* **2008**, *156* (2), 233–239.

(30) Gondikas, A. P.; von der Kammer, F.; Reed, R. B.; Wagner, S.; Ranville, J. F.; Hofmann, T. Release of TiO₂ nanoparticles from sunscreens into surface waters: A one-year survey at the Old Danube Recreational Lake. *Environ. Sci. Technol.* **2014**, *48* (10), 5415–5422.

(31) Kiser, M. A.; Westerhoff, P.; Benn, T.; Wang, Y.; Perez-Rivera, J.; Hristovski, K. Titanium nanomaterial removal and release from wastewater treatment plants. *Environ. Sci. Technol.* **2009**, *43* (17), 6757–6763.

(32) Westerhoff, P.; Song, G. X.; Hristovski, K.; Kiser, M. A. Occurrence and removal of titanium at full scale wastewater treatment plants: Implications for TiO₂ nanomaterials. *J. Environ. Monit.* **2011**, *13* (5), 1195–1203.

(33) Kim, B.; Murayama, M.; Colman, B. P.; Hochella, M. F. Characterization and environmental implications of nano- and larger TiO₂ particles in sewage sludge, and soils amended with sewage sludge. *J. Environ. Monit.* **2012**, *14* (4), 1129–1137.

(34) Drury, B.; Rosi-Marshall, E.; Kelly, J. J. Wastewater treatment effluent reduces the abundance and diversity of benthic bacterial communities in urban and suburban rivers. *Appl. Environ. Microbiol.* **2013**, *79* (6), 1897–1905.

(35) Silva, R. G.; Nadagouda, M. N.; Webster, J.; Govindaswamy, S.; Hristovski, K. D.; Ford, R. G.; Patterson, C. L.; Impellitteri, C. A. Examining the efficiency of muffle furnace-induced alkaline hydrolysis in determining the titanium content of environmental samples containing engineered titanium dioxide particles. *Environ. Sci.: Processes Impacts* **2013**, *15* (3), 645–652.

(36) Ravel, B.; Newville, M. Athena, Artemis, Hephaestus: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12*, 537–541.

(37) Newville, M. Larch: An analysis package for XAFS and related spectroscopies. *J. Phys.: Conf. Ser.* **2013**, *430*, 012007.

(38) Da Silva-Cadoux, C.; Zanella, L.; Gaillard, J. F. Selecting reference compounds for determining chemical speciation by X-ray absorption spectroscopy. *J. Anal. At. Spectrom.* **2012**, *27* (6), 957–965.

(39) Gaillard, J. F.; Webb, S. M.; Quintana, J. P. G. Quick X-ray absorption spectroscopy for determining metal speciation in environmental samples. *J. Synchrotron Radiat.* **2001**, *8*, 928–930.

(40) Farges, F.; Brown, G. E.; Rehr, J. J. Ti K-edge XANES studies of Ti coordination and disorder in oxide compounds: Comparison between theory and experiment. *Phys. Rev. B* **1997**, *56* (4), 1809–1819.

(41) Chen, L. X.; Rajh, T.; Wang, Z. Y.; Thurnauer, M. C. XAFS studies of surface structures of TiO₂ nanoparticles and photocatalytic reduction of metal ions. *J. Phys. Chem. B* **1997**, *101* (50), 10688–10697.

(42) *Paint and coating testing manual: Fourteenth edition of the Gardner-Sward handbook*; American Society for Testing and Materials: Philadelphia, 1995.

(43) Annual Biosolids Management Report for 2013; Metropolitan Water Reclamation District of Greater Chicago: Chicago, 2014.

(44) Battin, T. J.; Kammer, F. V. D.; Weilhartner, A.; Ottofuelling, S.; Hofmann, T. Nanostructured TiO₂: Transport behavior and effects on aquatic microbial communities under environmental conditions. *Environ. Sci. Technol.* **2009**, *43* (21), 8098–8104.

(45) Hirakawa, K.; Mori, M.; Yoshida, M.; Oikawa, S.; Kawanishi, S. Photo-irradiated titanium dioxide catalyzes site specific DNA damage via generation of hydrogen peroxide. *Free Radical Res.* **2004**, *38* (5), 439–447.