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Modeling Transport of Nanoparticles: Pilot Study

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Charles A Weiss Jr., and Alan J. Kennedy

April 2018



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Modeling Transport of Nanoparticles: Pilot Study

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Abstract

Determination of transport of engineered nanomaterials within the aquatic environment is an important area of study due to knowledge and capabilities gaps, leading to uncertainty. The lack of research in this area greatly encumbers accurate and timely risk assessment, regulatory decisions, and thus, technology advancement. The objective of this investigation is to demonstrate the capability of the Particle Tracking Model (PTM), currently parameterized for aquatic transport of sediment particulates, to predict the transport pathways of nanoparticles introduced into complex hydrodynamic flowfields. A hypothetical scenario was developed in which nano-TiO₂ was introduced into the flowfield within an area near Cleveland Harbor as an instantaneous point source due to a weather event. Results show transport pathways are highly dependent on flow conditions as well as the amount of material introduced into the system. It is understood that this is the first stage of more accurate predictions of nanoparticle fate. Future efforts will focus on utilizing previously developed data and relationship to account for nanoparticle specific transport processes.

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Preface

This Technical Report was developed under the Engineer Research Development Center Environmental Quality and Installation (ERDC-EQ/I) Research Program under Project P2 461894 “*Advanced and Additive Materials: Sustainability in Army Acquisitions.*” This research was funded by the U.S. Army Environmental Quality Research Program, Dr. Elizabeth Ferguson, Technical Director. Funding for Stephen Diamond’s participation of this work was supported in part by the U.S. Army Research Office Grant No. W911NF-14-2-0090 to NanoSafe, Inc.

The work was coordinated by the Coastal Processes Branch of the Coastal and Hydraulics Laboratory (CPB-CHL) and the Environmental Processes and Risk Branch (EPR) of the Environmental Processes Division (EP) at the ERDC-Environmental Laboratory (ERDC-EL). Dr. William Nelson was the Branch Chief, CEERD-EPR, Warren Lorentz was the Division Chief, CEERD, and Dr. Elizabeth Ferguson was the Technical Director for Military Environmental Engineering and Sciences. The Deputy Director of ERDC-EL was Dr. Jack Davis and the Director was Dr. Ilker Adiguzel.

Special acknowledgement goes to Mr. Raymond Chapman and Mr. David Mark who developed the original hydrodynamic model that was used to support this work. Mr. Nathan Mays IV was also instrumental in the Particle Tracking Model (PTM) effort.

COL Bryan S. Green was the Commander of ERDC and Dr. David W. Pittman was the Director.

Unit Conversion Factors

Multiply	By	To Obtain
acres	4,046.873	square meters
acre-feet	1,233.5	cubic meters
feet	0.3048	meters
inches	0.0254	meters
miles (nautical)	1,852	meters
miles (U.S. statute)	1,609.347	meters
miles per hour	0.44704	meters per second
square feet	0.09290304	square meters
square inches	6.4516 E-04	square meters
square miles	2.589998 E+06	square meters
square yards	0.8361274	square meters
yards	0.9144	meters

Acronyms and Abbreviations

ADCIRC	Advanced Circulation
CDF	Confined Disposal Facility
CHL	Coastal and Hydraulics Laboratory
CMEDS	Canadian Marine Environment Data Service
CPB	Coastal Processes Branch
DoD	Department of Defense
DOQQ	Digital Orthographic Quarter-Quadrilateral
EHS	Environmental Health and Safety
EL	Environmental Laboratory
ENMs	Engineered Nanomaterials
EP	Environmental Processes
EPRB	Environmental Processes and Risk
EQT	Environmental Quality and Technology
ERDC	Engineer Research Development Center
GLCFS	Great Lakes Coastal Forecasting System
GLERL	Great Lakes Environmental Research Laboratory
NOAA	National Oceanic and Atmospheric Administration
NOS	National Ocean Service
N-PTM	Nano-Particle Tracking Model
OMB	Office of Management and Budget
PTM	Particle Tracking Model
SF	Standard Form
SMS	Surface Water Modeling System
USACE	U.S. Army Corps of Engineers
USGS	United States Geological Survey
UV	Ultra-Violet
2-D	Two-Dimensional
3-D	Three-Dimensional

1 Introduction

1.1 Problem statement

The predominant focus of environmental health and safety research (EHS) on engineered nanomaterials (ENMs) research has been on hazard determination. Environmental risk assessment for ENMs and the manufacturing and use of nano-enabled products requires both basic toxicological information (hazard) and exposure assessment (Dale et al. 2015). However, until recently much less research focus has been given to estimating the release of ENMs to the aquatic environment, organism exposure, and prediction of environmental concentrations (Brame et al. 2015; Collier et al. 2015). This greatly encumbers accurate and timely risk assessment and regulatory decisions, and thus, technology advancement. While various organizations have published ENM-specific fate modeling considerations (Mueller and Nowack 2008; Gottschalk et al. 2009; Gottschalk et al. 2013; Praetorius et al. 2012; Johannes et al. 2014; Dale et al. 2015), existing models available for particle transport should also be considered; provided that extrinsic system factors (e.g., flow rates) are critical to consider for determining ENM transport than intrinsic particle properties (Dale et al. 2015). The Particle Tracking Model (PTM) is an Engineer Research and Development Center (ERDC) developed model used to determine the fate of sediments in complex hydrodynamic systems (coastal, lakes, estuaries, rivers, etc.). The PTM is designed to facilitate integration of system specific attributes. Currently, it is not parameterized for the unique homo- and hetero-agglomeration and settling behaviors of ENMs. Thus, a demonstration of current dynamic model capability is useful, followed by research to improve the PTM's ability to accurately predict ENM distribution and concentration in the aquatic environment.

1.2 Background

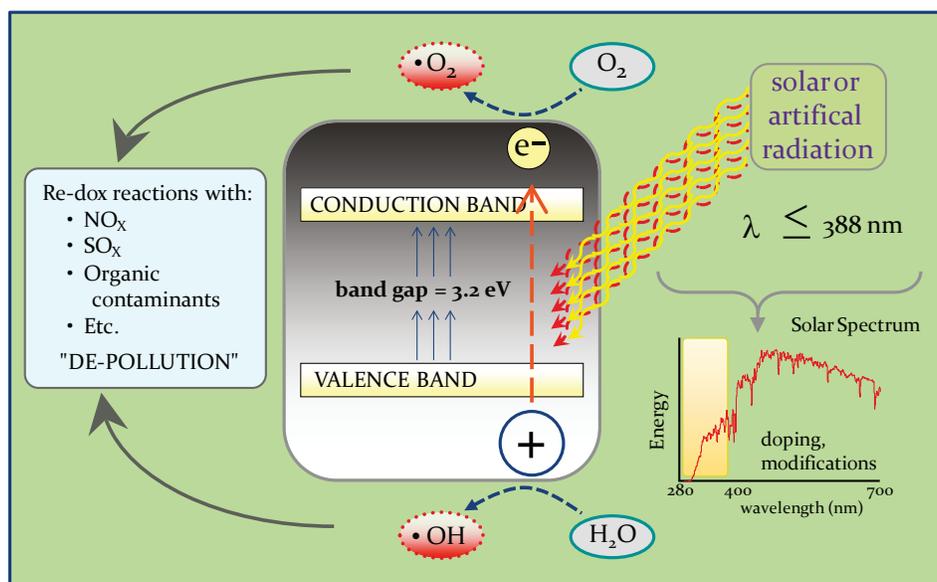
ENMs are purported to enhance material science applications due to their unique properties, such as improved strength, conductivity, and reactivity. The higher relative surface area to volume of ENMs is one factor enhancing reactivity relative to bulk material. An example of a surface area mediated property enhancement is the photocatalytic capacity of nano-TiO₂ particles when exposed to ultraviolet (UV) light, including natural sunlight. TiO₂ is one of the highest volume nanomaterials in production.

Its use in a self-cleaning concrete provides a relevant, in-use release scenario to the environment due to potential discharges during construction and wear and weathering during use. A partial list of construction applications include:

- Church “Dives in Misericordia,” Rome, Italy
- Music and Arts City Hall, Chambéry, France
- Police Central Station, Bordeaux, France
- Air France Building, Roissy-Charles de Gaulle Airport, France
- Saint John's Court, Montecarlo, Monaco
- Rue Jean Bleuzen, Paris, France
- Umberto I Tunnel, Rome, Italy
- Louisiana State University, Baton Rouge, Louisiana, USA
- I-35 bridge memorial, Minneapolis, Minnesota, USA
- Governor Mifflin School, Shillington, Pennsylvania, USA
- School of Business, University at Albany, Albany, New York, USA.

The known UV-photoreactivity of TiO_2 is purported to *depollute* urban areas by oxidizing NO_x and SO_x as well as photocatalyzing soot and other organic compounds that stain concrete. TiO_2 may enter the environment during production, transport, use, and weathering of TiO_2 -containing concrete. While the aquatic toxicity of nano- TiO_2 is low relative to other metal nanomaterials, formation of reactive oxygen species in presence of UV light dramatically increases toxicity (Ma, Brennan, and Diamond 2012) (Figure 1).

Figure 1. Nano TiO_2 - functions and hazard potential.



1.3 Study objectives

The objective of this investigation was to demonstrate the capability of the U.S. Army Corps of Engineers (USACE) PTM, currently parameterized for aquatic transport of sediment particulates, to model the distribution and concentration of ENMs. This objective was executed by the following tasks:

1. *Task 1. Selection of a Model System.* An area within the Cleveland Harbor was selected for convenience based on system data already entered into the model software.
2. *Task 2. Selection of a Model ENM and Nano-Enabled Product.* The model ENM selected was nano-TiO₂ incorporated as the active ingredient in a photocatalytic, self-cleaning cement.
3. *Task 3. Model Demonstration in a Hypothetical Scenario.* The USACE PTM was used to model transport of TiO₂ in the harbor from point sources (e.g., manufacturing discharges, weathering and release) and non-point discharges (e.g., spills, run-off). The hypothetical scenario was resurfacing of a marina adjacent to the harbor using the photocatalytic cement during a rain event without use of effective erosion and run-off controls.
4. *Task 4. Identification of Parameters to Research.* Based on the model result and knowledge of ENM fate behaviors, specific model inputs were selected to research and re-parameterize the model for ENM behavior.

2 Case Study

2.1 Description of study area

The selected study area is adjacent to Cleveland Harbor (41°28'55.30" N; 81°39'32.99" W). Cleveland Harbor is a deep draft commercial harbor (approximately 4.5 miles²) with an authorized depth of 8.5 m in the outer harbor. The harbor has over 5.5 miles of breakwater structure and contains numerous marinas. The focus area of this study is currently occupied by a marina complex and adjacent park area (Figure 2). The marina is approximately 525,00 m² with an average water depth of 9 m.

The hypothetical redevelopment scenario conceptualized for the model demonstration included a complete rebuild of the marina, park facilities, and infrastructure with photocatalytic cement to be used throughout. Nano-TiO₂ is the active ingredient in the cement enabling photocatalytic properties. The area to be hypothetically paved with photocatalytic cement included main docks, finger docks, walkways around the circumference of the marina (including an extended walkway on top of the seawall), and the seawall. Parking and work areas for the marina, a parking area for the park, and a walkway around the circumference of the park were also designed to be paved with photocatalytic cement.

Figure 2. Map of model marina/park development. Walkways are indicated by white lines and paved parking and marina work areas are roughly outlined in red. All docks are to be rebuilt using the current layout. Walkways, paved areas, and docks are to be constructed using photocatalytic cement. Source: "Cleveland Harbor." 41° 28' 55.30" N 81° 39' 32.99" W. Google Earth. April 18, 2016.



2.2 Description of scenario

The total surface area to be paved was estimated from surface projections in Google Earth. The thickness of photocatalytic cement overlays was set at 0.5 ft for docks and walkways and 1.25 ft for parking and work areas. These area and thickness estimates were then used to calculate a total volume of photocatalytic cement required, equaling 10,000 yd³. The total mass of cement used would be 4,000 lbs/yd³, and assuming the TiO₂ content of the cement was 1.8% w/w, a total of 720,000 lbs of TiO₂ would be used at the construction site.

The hypothetical release scenario was developed for the model demonstration. It was assumed that the release occurred near the end of construction when 100% of waste material from the construction site had accumulated in waste basins. It was further assumed that a severe rain event caused the failure of the waste basins, and that 100% of the waste material was discharged directly into the harbor. Under this scenario, 5% of the total TiO₂ (36,000 lbs) used in construction was released.

3 Hydrodynamic Modeling

The circulation modeling conducted for Lake Erie, including Cleveland Harbor, was performed using the Advanced Circulation (ADCIRC) long-wave hydrodynamic model. The ADCIRC numerical model, a large-domain, two-dimensional (2-D) depth-integrated finite-element hydrodynamic circulation model, was applied in this study to provide water level and depth-averaged current (circulation) information for Cleveland Harbor, Ohio. ADCIRC was run from July 30 at 0:00, 2002 to September 24 at 24:00 with the solution being saved every half-hour. Hydrodynamic conditions were run for a six-month design storm.

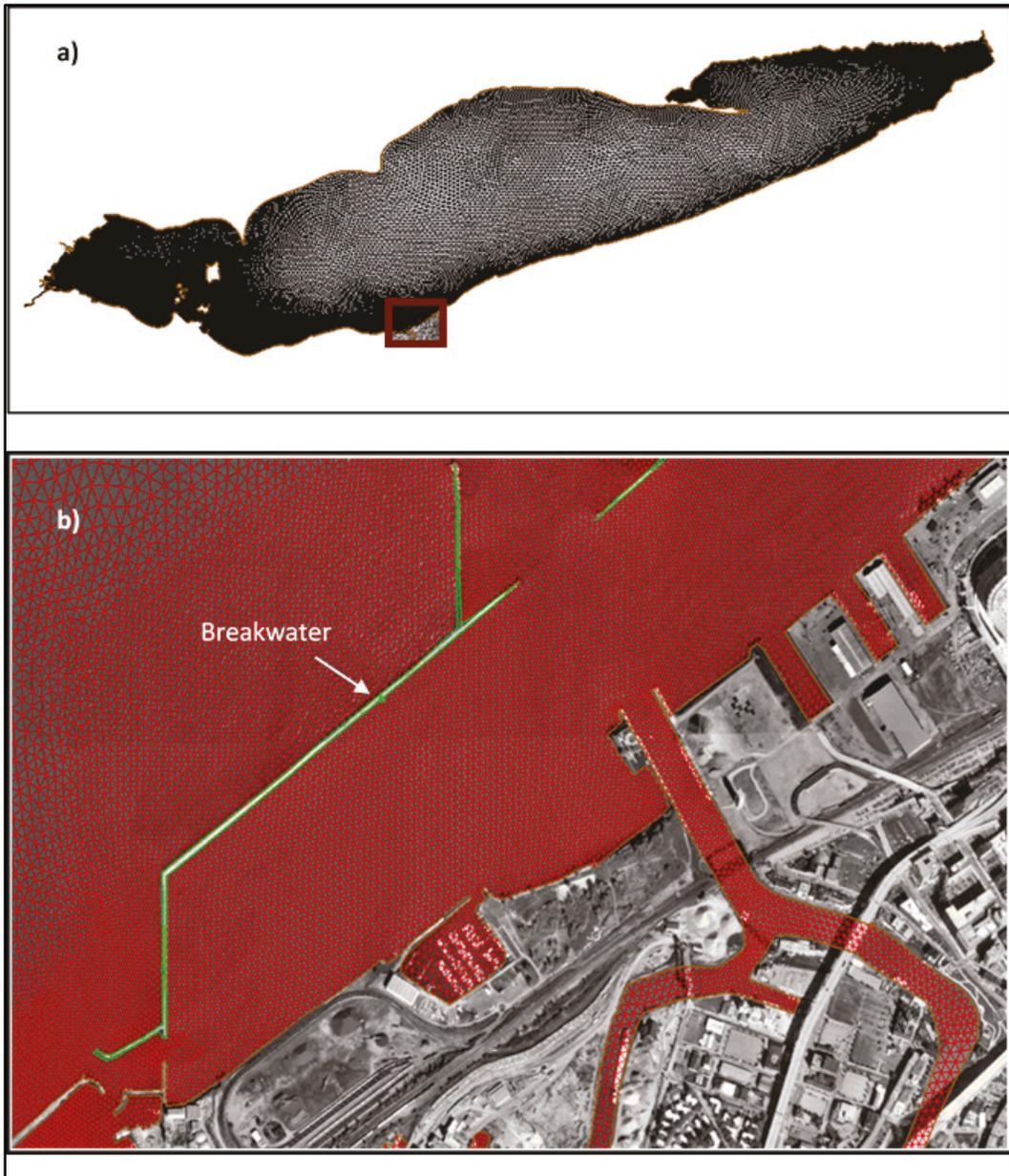
3.1 Bathymetry and mesh

Figure 3a displays the grid developed for this study. As shown, the model domain encompasses the entire Lake, and includes the lower reaches of the Cuyahoga, Maumee, Detroit, and Niagara Rivers. Figure 3b displays the grid in the vicinity of Cleveland Harbor projected onto a map of the area.

The grid highly resolves the entire Harbor and its main, western, and eastern entrances, together with the lower reaches of the Cuyahoga River. This existing-configuration, or base grid, consists of 95,255 nodes and 183,034 elements, of which 30,628 nodes and 62,038 elements re-solve the Harbor. The largest elements reside in the central Lake basin, having nodal spacing of about 24 km, whereas the smallest elements re-solve the western Harbor entrance, where their widths are approximately 15 m. For most of the Harbor, including the area of the proposed confined disposal facility (CDF), nodal spacings are approximately 20 m. Included in the grid are the power plant's outfall and intake structures.

The grid boundary along the Canadian shoreline was aligned with the shoreline shown on satellite imagery published by NaturalVue, these were digitally enhanced images taken by the Landsat satellite. These imagery have a 15 m resolution. For areas within the United States, shore-line positions are based on satellite imagery published by the U.S. National Geo-spatial Intelligence Agency (formerly the Defense Mapping Agency), and have a resolution of 5 m. In the vicinity of Cleveland Harbor, U.S. Geological Survey Digital Orthographic Quarter-Quadrilateral (DOQQ) imagery was used in aligning the grid shoreline and its coastal structures. The DOQQs have a resolution of about 1 m.

Figure 3. a) Lake Erie ADCIRC grid and b) Lake Erie ADCIRC grid in project area.



3.2 Boundary conditions and forcing

Wind data were obtained from the National Oceanic and Atmospheric Administration's (NOAA) Great Lakes Environmental Research Laboratory (GLERL), and were generated as part of their Great Lakes Coastal Forecasting System (GLCFS). One component of the GLCFS is the generation of wind fields, subsequently used in circulation and water level now-cast simulations. Hourly wind speeds and directions were extracted

from GLCFS archives. These data are provided at 5 km intervals encompassing the entire lake.

Water level data for model calibration and validation consist of 12 gauges, and were obtained from the U.S. National Ocean Service (NOS) and the Environment Canada-Canadian Marine Environment Data Service (CMEDS). River inflow data measured in the Detroit River were obtained from the U.S. Army District, Detroit, whereas flow rate data specified for the Cuyahoga, Niagara, and Maumee Rivers were obtained from the United States Geological Survey (USGS) streamflow web site (<https://waterdata.usgs.gov/nwis/rt>).

4 Methods: Transport of Nanoparticles

4.1 The particle tracking model (PTM)

The PTM is an ERDC-developed model designed specifically to track the fate of point-source constituents (sediment, chemicals, debris, etc.) released from local sources (outfalls, dredges, etc.) in complex hydrodynamic and wave environments (McDonald et al. 2006; Gailani et al. 2016). Each local source is defined independently and may have multiple constituents. Therefore, model results include the fate of each constituent from each local source. The PTM simulates transport using pre-calculated hydrodynamic model output. The hydrodynamic model is not coupled to the sediment transport model and therefore, can be run once for multiple PTM simulations. The PTM utilizes periodically saved hydrodynamic (and wave) model output. Each particle in PTM represents a specific mass (or number of particulates) of one constituent. Hydrodynamic and wave in-put are used to transport the particles. Total mass is conserved because particles are conserved. Hydrodynamic output does not need to be conservative, so the user can specify hydrodynamic model output for PTM without concern for conservation of water mass. A random walk method is used to represent particle diffusion. PTM simulations can be either three-dimensional (3-D) or 2-D. For this application, 3-D mode is used.

In addition to the hydrodynamic input (i.e., water surface elevation and velocities) that is used as a forcing for particle dynamics, PTM requires mesh and bathymetry information, and sediment characterization of the native or bed sediment. Although PTM does not model native sediment bed transport, it does model interactions between native bed sediments and deposited particles (hiding, burial, etc.). Therefore, bed sediment characteristics must be described by the user. PTM also requires detailed constituent or source information. The user specifies particle characteristics and processes, including settling, critical stresses, and erosion rates. If processes data are not available, these values may be calculated within the model based on theoretical relationships. The specific equations for those processes are discussed in detail by McDonald et al. (2006).

Model output includes time dependent parcel positions throughout the domain. Various other attributes such as mass, density, and suspension

status are also assigned to each of the output parcels. Elevation in the water column is calculated and stored. The PTM setup and execution are done within the ERDC-sponsored Surface Water Modeling System (SMS) interface. The SMS includes multiple tools for post-processing PTM output to assess distribution of concentration, deposition, and other results at any time during the simulation. These results are processed for each constituent from each source, or for combined constituents or sources.

4.2 Modeling assumptions for nanoparticle transport

In this hypothetical simulation, PTM is used to transport nanoparticles. A severe rain event occurs resulting in a catastrophic failure of the wash-out enclosure. TiO₂ particles are washed into the harbor and then tracked using PTM from the initial source location. The following assumptions and estimates were used to derive the mass of TiO₂ to be used in the project:

- Concrete mass of 4,000 lb/ yd³ (estimate for model demonstration purposes).¹
- TiO₂ mass % in photocatalytic cement = 1.8.
- The total TiO₂ used at the construction site= 720,000 lbs.
- Waste cement at 5% (typical waste allocation used by concrete estimators¹= 36,000 lbs.
- All waste material is captured and stored on-site in temporary wash-out basins. This is a common practice in many construction projects¹.
- The PTM source term is described as an instant mass source due to the pulse release of the entire wash-out basin contents directly to the harbor.
- The particles are initially evenly distributed vertically within the entire water column and horizontally within a meter radius (multiple horizontal distances were tested, with very little change in ultimate transport).
- The total model scenario release of TiO₂ into the harbor = 36,000 lbs.

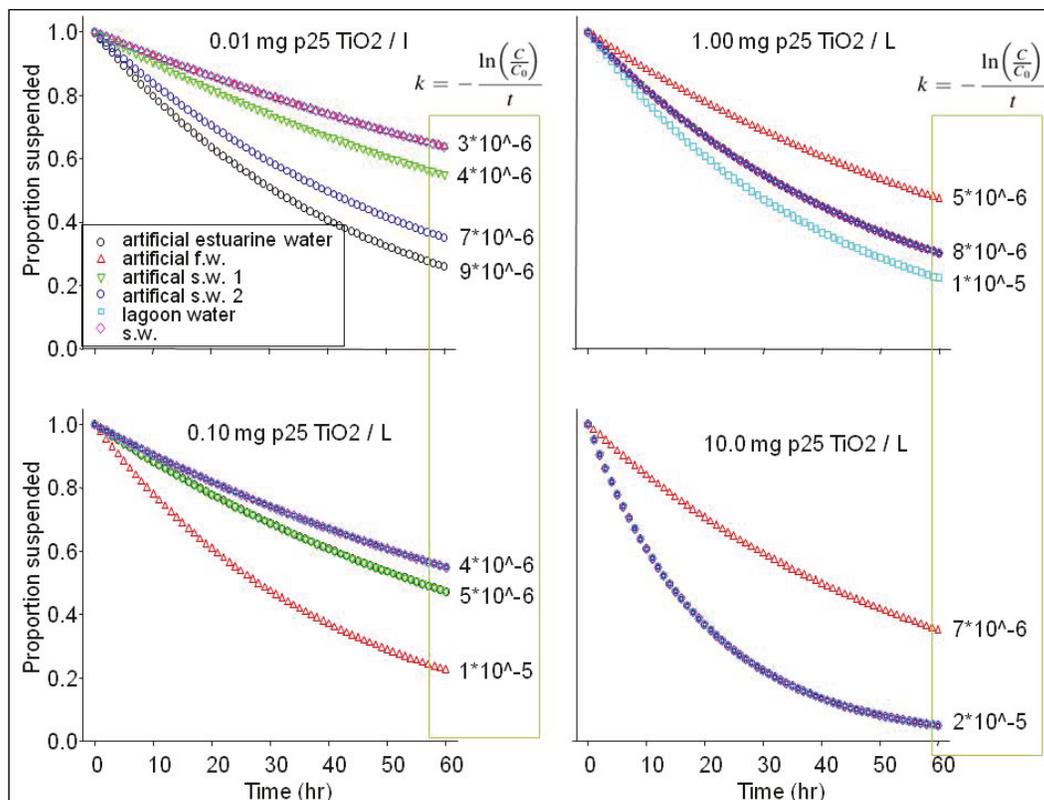
4.3 Settling rates

Brunelli et al. (2013) provides settling rate information for nano-TiO₂, where setting rate constants were derived by testing nano-TiO₂ in a variety of synthetic and natural waters (Figure 4). A limitation of these constants

¹ Susan Gollon, Aristeo Construction, Livonia, Michigan, USA, personal communication, April 10, 2016.

is that they were derived in relatively simple systems that did not address the complexities of a TiO_2 mixture containing several concrete constituents.

Figure 4. Settling rates (K) for four nano- TiO_2 concentrations in four synthetic and two natural waters. Curves are generated using rate constants from Brunelli et al. (2013).



A range of settling rate parameters K were chosen for this work based on settling constants derived by Brunelli et al. (2013) for Aeroxide P25 (Evonik Degussa, Essen, Germany, <http://www.tandfonline.com/doi/abs/10.1080/17435390.2017.1317863>) TiO_2 titanium dioxide suspended in a variety of artificial and natural waters.

The K value can be converted to meters per second based on Brunelli et al. (2013):

$$w = kh$$

In this equation, w is the settling rate in m/s , and h is the control volume height used to determine k . In this case h is 16.5 mm, this obtains the values listed in Table 1.

Table 1. Settling rate parameters (K) and settling velocities used for the test case.

Settling Rate Parameter (K)	Settling Velocity (m/s)
3.00E-06	4.95E-08
1.20E-05	1.98E-07
2.00E-05	3.3E-07

4.4 Simulation details

The PTM model was used to simulate a three-week period of transport starting 22 August 2002. The three-week period was designed to allow particles to be transported away from the initial release location and the region inside the breakwater. Six different simulations were run, varying the parameters of the fall velocity and mass of TiO₂ released. Table 2 shows the parameters for each simulation.

Table 2. Simulation matrix.

Scenario #	Fall Velocity(m/s)	Pulse Release TiO ₂ (lbs)
1	4.95E-08	36000
2	1.98E-07	36000
3	3.30E-07	36000
4	4.95E-08	7200
5	1.98E-07	7200
6	3.30E-07	7200

Approximately 16,000 particles were used for scenarios 1–3, and 3,200 particles were used for scenarios 4–6.

4.5 Analysis methods

Analysis was performed in two ways: particle position and concentration. The particle positions give a qualitative description of particle pathways and transport direction. The concentration gives a quantitative description of mass transport. Concentration analysis is performed by placing an analysis grid within the simulated area and calculating the mass of particles in each grid cell. This value is divided by the volume of water within the cell. The volume of water varies temporally based on the water surface elevation, and so, requires a time accurate hydrodynamic solution to calculate. Figure 5 shows the computational grid used for concentration calculations. Each grid cell is approximately 90m x 125m.

Figure 5. Computational grid for concentration calculations.

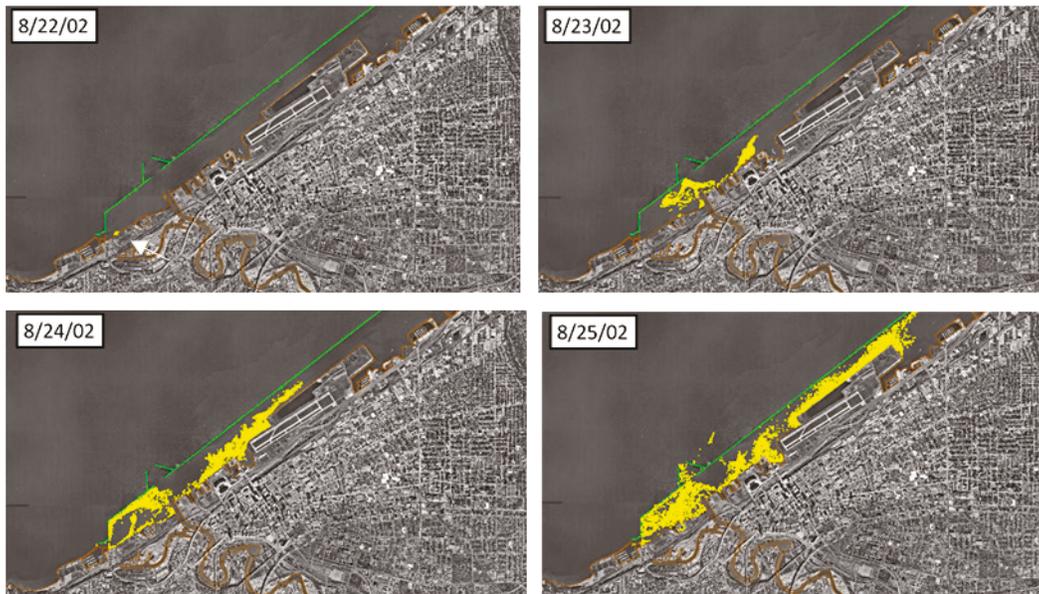


5 Modeling Results

5.1 Particle pathways

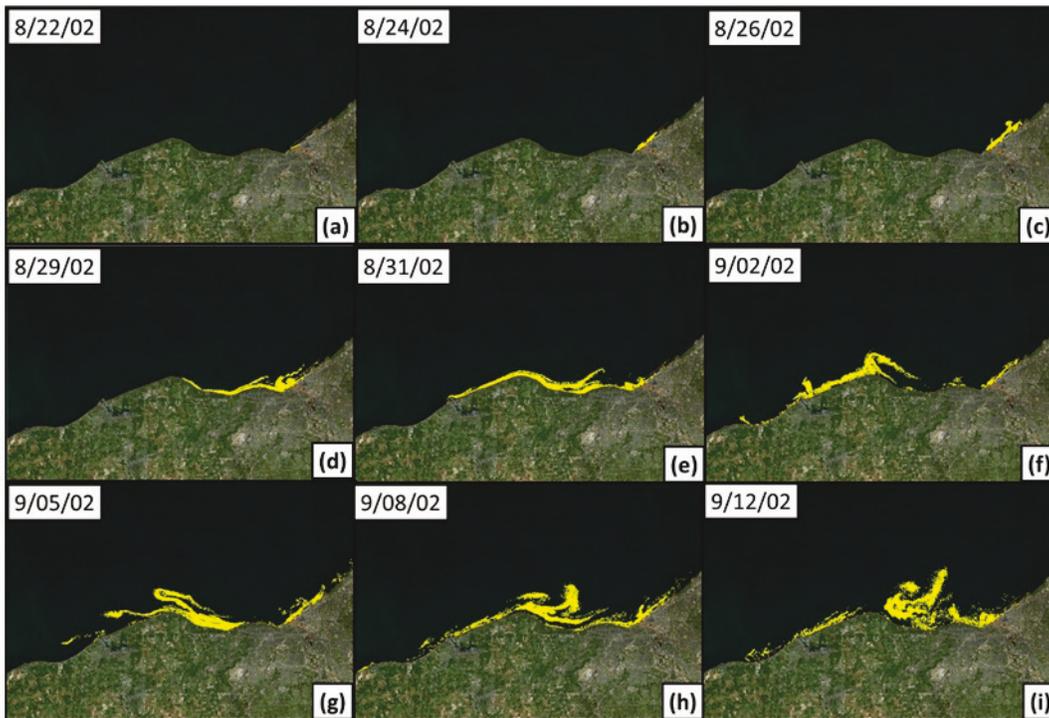
Snap shots in time of particle positions for Scenario 1 (Fall Velocity is $4.95\text{E-}08\text{ m/s}$, Mass is 36,000 lb) are shown in Figure 6 during the first four simulated days. During this phase, results are focused on the area within the breakwater (shown in green in Figure 6). During the initial release, the particles are introduced into the system adjacent to the marina. Within day one, the particles remain close to the marina in a tightly packed configuration. The movement of the particles is dominated by the flow and the complex mixing patterns become visible. After two days, the particle paths begin to extend to the eastern portion of the breakwater. Finally, after three days, some particles begin to escape the confinement of the breakwater and into the outer region of Lake Erie.

Figure 6. Scenario 1 Particle positions for the first four days. Fall Velocity = $4.95\text{E-}08\text{m/s}$, Mass = 36000 lb.



A slightly more expansive view of the simulation is displayed in Figure 7. After four days, the TiO_2 is transported beyond the breakwater. Initially, transport is towards the east, but after a week, the main transport direction moves in a westward direction and material is transported along the shoreline. The particles continue to disperse along the shoreline for the remaining two weeks for 50,000 meters. The particle mixing patterns are indicative of the circulation.

Figure 7. Particle positions snapshots over the entire simulation time period. Fall Velocity = $4.95E-08\text{m/s}$, Mass = 36000 lb.



Because the settling rate is relatively slow in comparison to the flow velocities, the flow seems to dominant transport. The settling rate also has minimum effect to the particle pathway results.

5.2 Concentration

The concentration of TiO_2 for each scenario was calculated and is described in this section. Shown in Figure 8 to Figure 10 are results for Scenarios 1, 2, 3, and 4. Figure 8 shows concentration snap shots for Scenario 1 for the first four days. Maximum concentration is approximately 1.0 mg/L. Initially, the maximum concentration level can be seen close to the marina where the TiO_2 enters the system. As the transport begins to disperse, the TiO_2 , a complex concentration pattern develops. Particle trajectories move the TiO_2 further eastward. By Day four, some of the material escapes the region inside the breakwater and low concentrations are visible.

Figure 8. Concentration 1 (Fall Velocity= $4.95E-08$ m/s, Mass =36,000 lb).

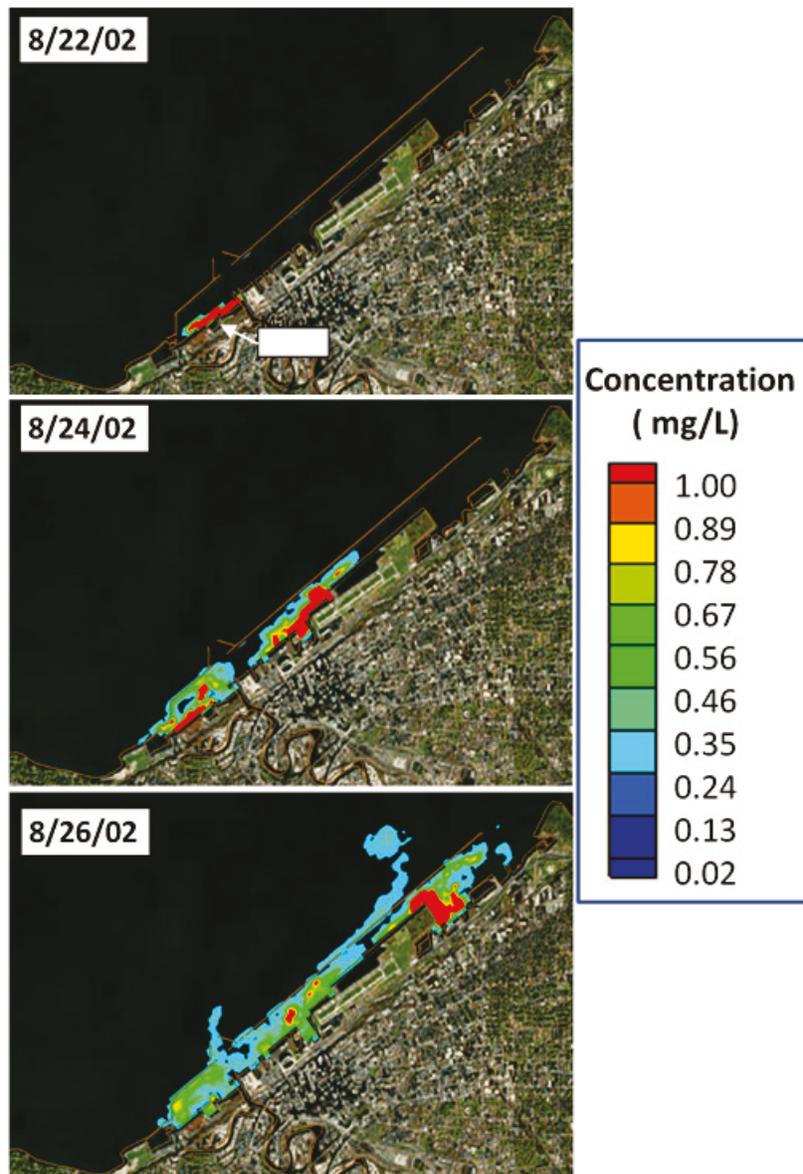
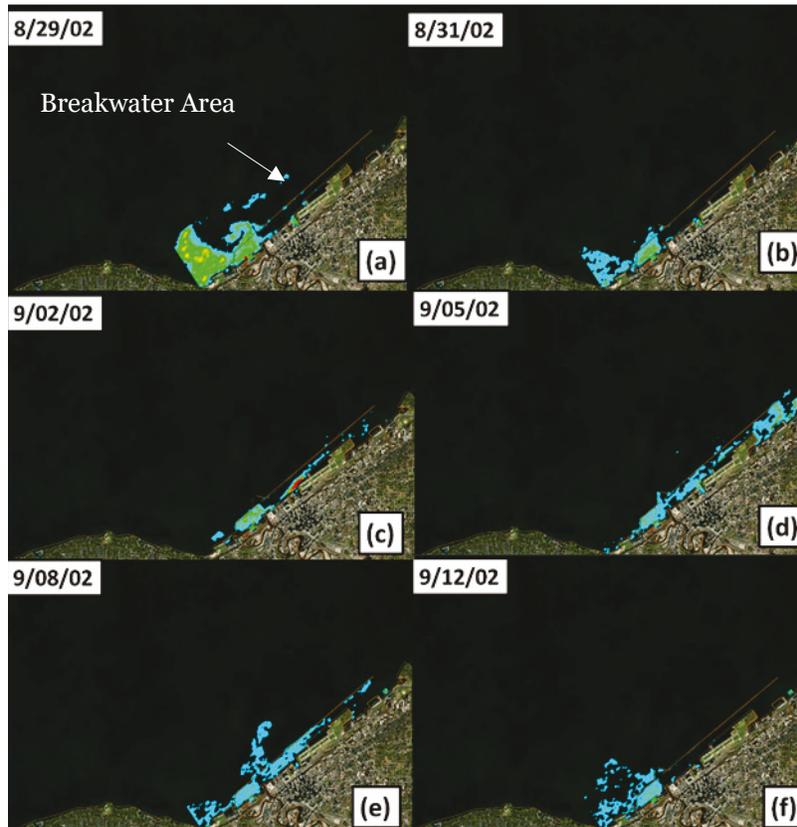


Figure 9 shows additional concentration results for scenario 1, for the entire harbor area. Initially, concentration near the breakwater is approximately 0.7 mg/L as the material exits the main area of interest. Concentration levels quickly decrease to approximately 0.35 mg/L and lower after two weeks. Hot spots of approximately 0.3 mg/L develop as particles move out of the system and travel through low velocity or shallow areas, this allows for a buildup of particulates. However, by the end of the simulation most of the TiO_2 has moved away from the region near the breakwater.

Figure 9. Concentration Scenario 1 (Fall Velocity= $4.95\text{E-}08$ m/s, Mass= 36000 lb).



Figures 10 and 11 show results for Scenarios 2 and 3, where the fall velocities of the TiO_2 particles have been reduced to $2.0 \text{ E-}07$ m/s and $3.3 \text{ E-}07$ respectively. The change in fall velocities within these ranges appears to have been little impact on the overall concentration levels. The results are very similar to those seen in Scenario 1.

Figure 10. Concentration Scenario 2 (Fall Velocity = $1.98E-07$ m/s, Total Mass = 36,000 lb).

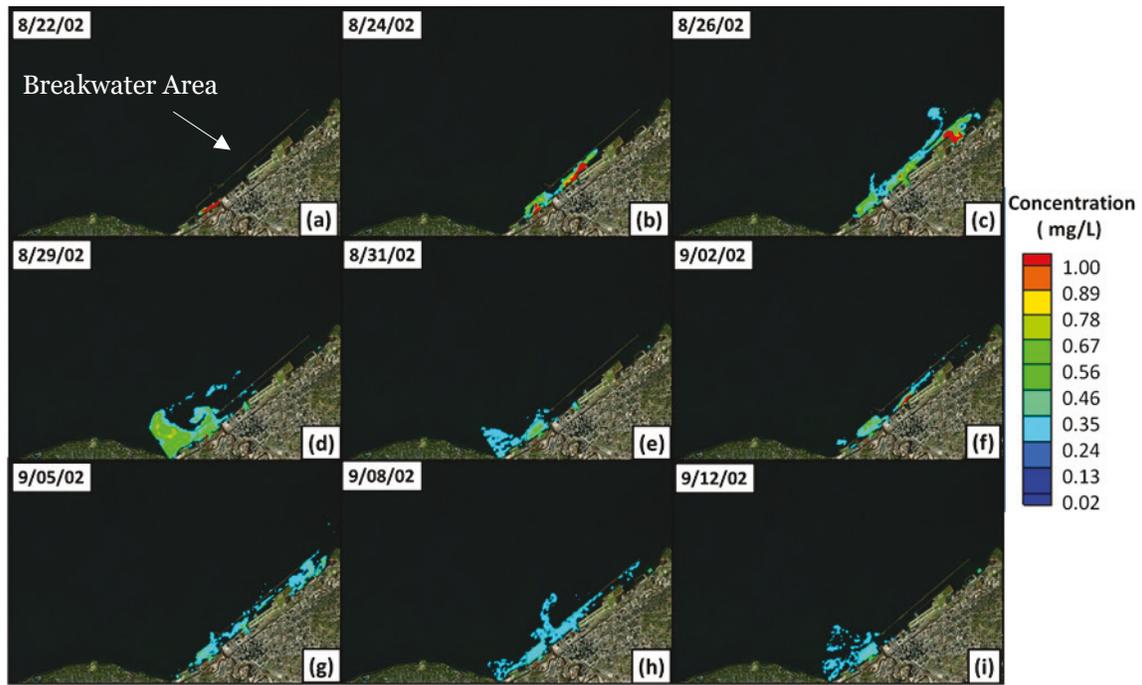
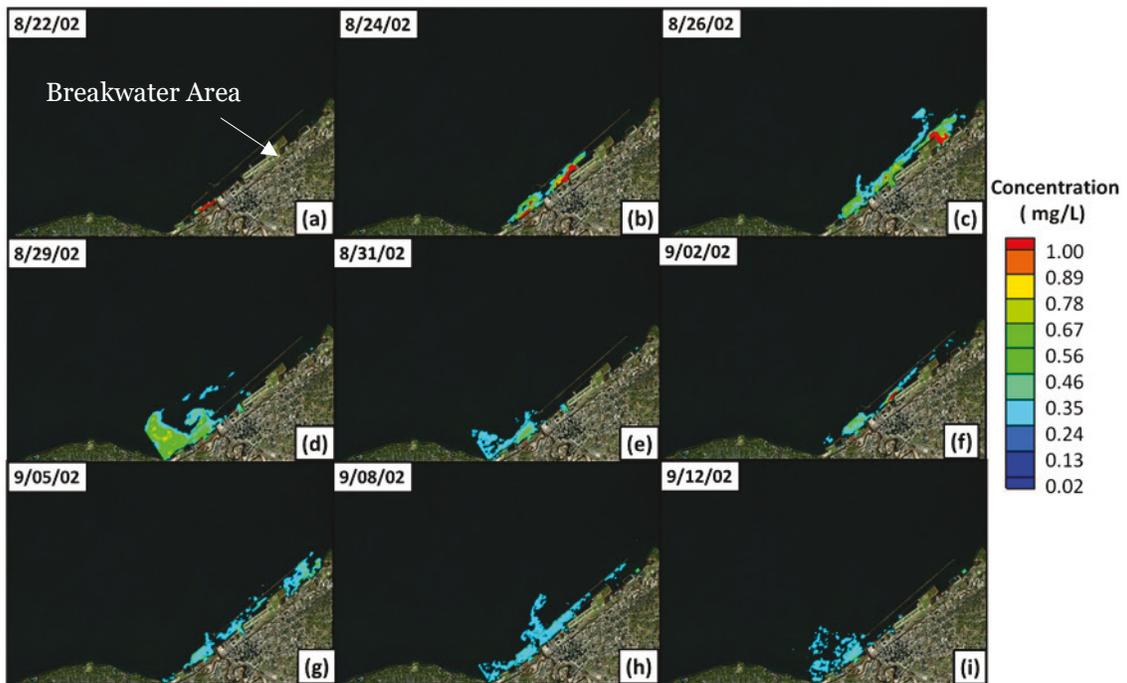
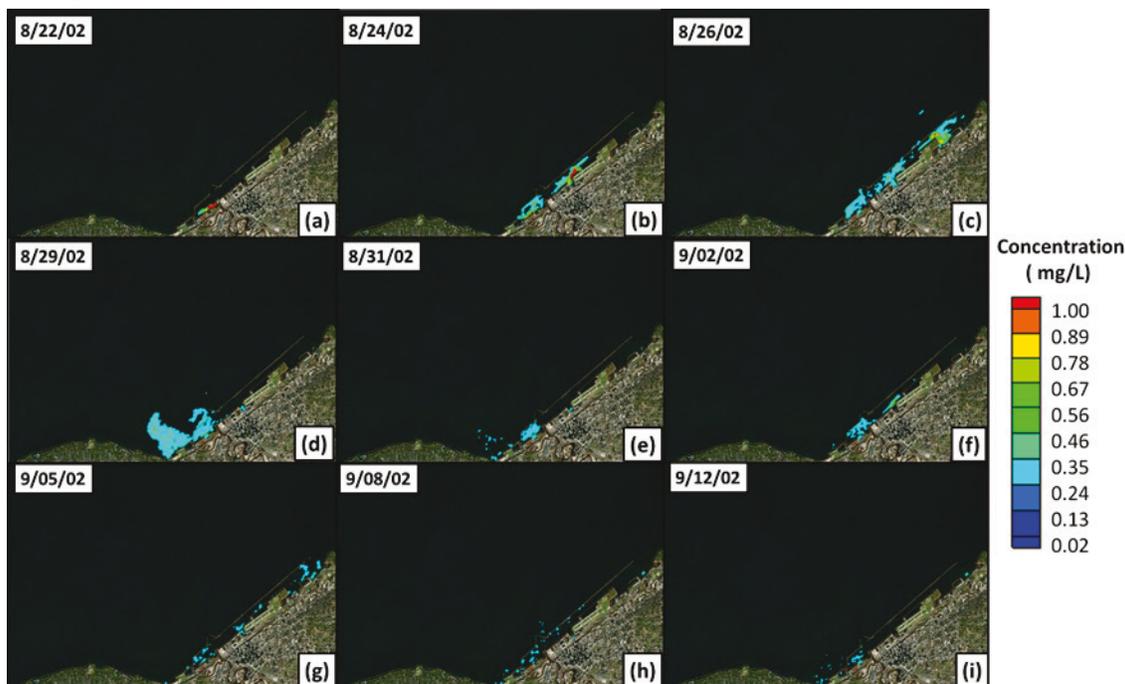


Figure 11. Concentration Scenario 3 (Fall Velocity = $3.3E-07$ m/s, Total Mass = 36,000 lb).



The total mass introduced in the system is reduced from 36,000 lb to 7,200 lb for Scenarios 4–6. Figure 12 shows the results for Scenario 4. In this case, the concentrations are much lower and within a two-week period, much of the concentration of TiO_2 has been reduced to levels less than 0.1 mg/L. Scenario 5 and 6 results are very similar to scenario 4 results and concentration magnitude and transport pathways.

Figure 12. Concentration Scenario 4 (Fall Velocity = $4.95\text{E-}08$ m/s, Mass = 7200 lb).



Figures 13 and 14 give a broader view to show concentration within a much larger region into Lake Erie. From this perspective it is possible to see how far the TiO_2 travels and visualize the mixing patterns that develop. In Figure 13, Scenario 3 results show transport as far as 45km along shore to the west of the breakwater region. Concentration levels remain less than 0.3 mg/L as the TiO_2 disperses further into the system. These results are of interest because they show that the transported material remains close to the shoreline where water depths remain relatively low (<10m). Scenario 4 results (Figure 14) are similar, except the overall concentration levels are lower and the foot print of significant concentration is smaller, this is consistent with previous observations of the impact of releasing a lower total mass of TiO_2 .

Figure 13. Concentration Scenario 3 (Fall Velocity = $3.3E-07m/s$, Total Mass = 36,000lb).

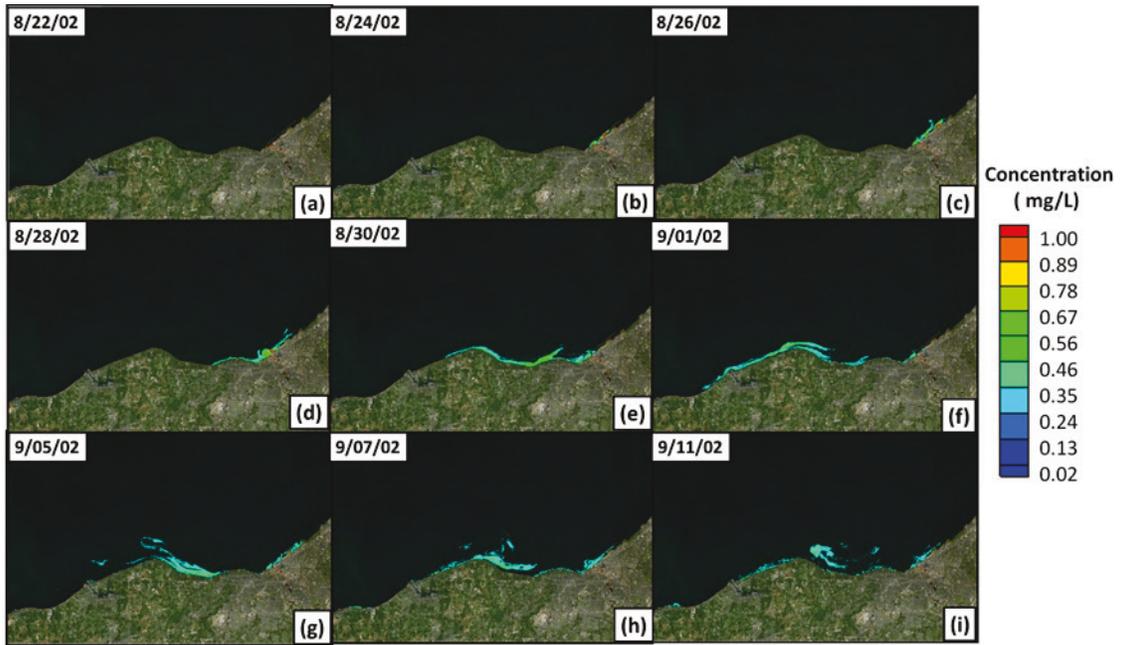
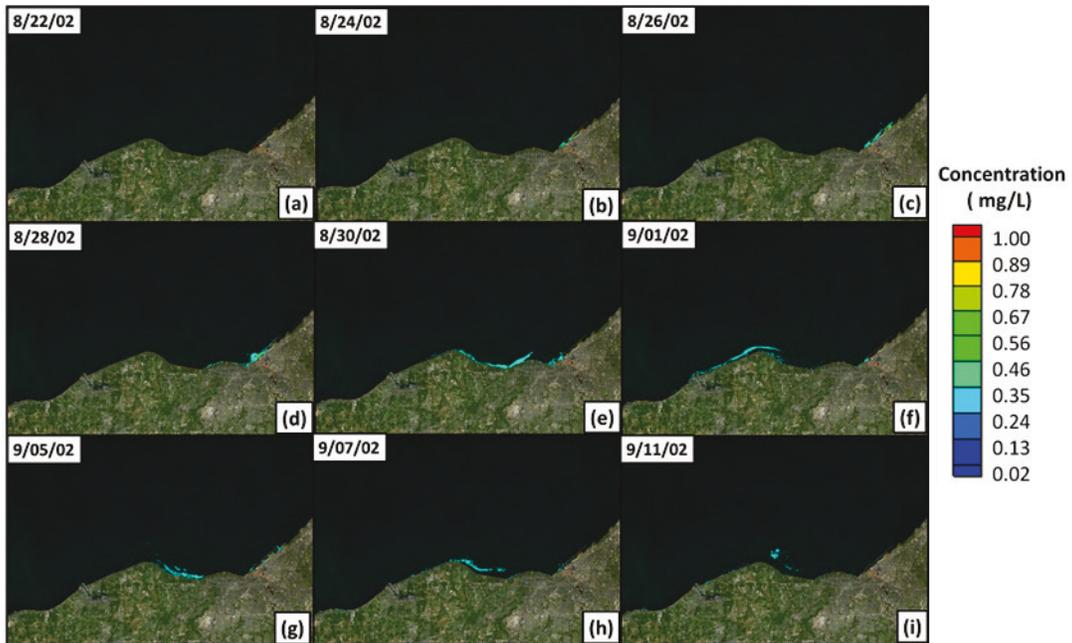


Figure 14. Concentration Scenario 4 (Fall Velocity = $4.95E-08m/s$, Mass = 7200lb).



6 Conclusions and Recommendations

The objective of this investigation was to demonstrate the capability of the PTM, currently parameterized for aquatic transport of sediment particulates, to predict transport pathways of nanoparticles introduced into complex hydrodynamic flowfields. A hypothetical scenario was developed in which TiO_2 was introduced into the flowfield, within an area near Cleveland Harbor, as an instantaneous point source due to a weather event. A three-week simulation was run to determine the fate of the nano- TiO_2 particles. Computational parameters of settling velocity and the total mass of the source were varied.

Results show that total mass of TiO_2 introduced into the system had a significant influence on concentration results, as expected. However, for the range of settling rates within this simulation, the overall impact to ultimate fate was minimal. It is expected that settling rates will influence results to a larger degree when agglomeration is considered.

In future research efforts, fundamental data leveraged from previous EQT6.1, 6.2 and the current Advanced and Additive Materials: Environmental Sustainability research effort will be used to optimize the model for predicting the (homo- and hetero-) agglomeration, settling environmental fate and ultimately spatially and temporally relevant concentrations of released engineered nanomaterials. The optimized model will be called Nano-Particle Tracking Model (N-PTM).

References

- Brame, J. A., A. R. Poda, A. J. Kennedy, and J. A. Steevens. 2015. "EHS testing of products containing nanomaterials: What is nano?" *Environmental Science and Technology* 49:11245–11246.
- Brunelli, A., G. Pojana, S. Callegaro, and A. Marcomini. 2013. "Agglomeration and sedimentation of titanium dioxide nanoparticles (n-TiO₂) in synthetic and real waters." *Journal of Nanoparticle Research* 15:1–10.
- Collier, Z. A., A. J. Kennedy, A. R. Poda, M. F. Cuddy, R. D. Moser, R. I. MacCuspie, A. Harmon, K. Plourde, C. D. Haines, and J. A. Steevens. 2015. "Tiered guidance for risk-informed environmental health and safety testing of nanotechnologies." *Journal of Nanoparticle Research* 17:155.
- Dale, A. L., G. V Lowry, and E. A. Casman. 2015. "Stream dynamics and chemical transformations control the environmental fate of silver and zinc oxide nanoparticles in a watershed-scale model." *Environmental Science and Technology* 49:7285–7293. Doi: 10.1021/acs.est.5b01205.
- Gailani, J. Z., T. C. Lackey, D. B. King, D. Bryant, S. C. Kim, and D. J. Shafer. 2016. "Predicting dredging effects to coral reefs in Apra Harbor, Guam: Sediment exposure modeling." *Journal of Environmental Management* 168:16–26. <https://doi.org/10.1016/j.jenvman.2015.10.027>.
- Gottschalk, F., T. Sonderer, R. W. Scholz, and B. Nowack. 2009. "Modeled environmental concentrations of engineered nanomaterials (TiO₂, ZnO, Ag, CNT, Fullerenes), for different regions." *Environmental Science and Technology*. Doi: 43:9216–9222. 10.1021/es9015553.
- Gottschalk, F, E. Kost, and B. Nowack. 2013. "Engineered nanomaterials in water and soils: A risk quantification based on probabilistic exposure and effect modeling." *Society of Environmental Toxicology and Chemistry* 32:1278-1287.
- Johannes, A., J. A. Meesters, A. Koelmans, J. T. K. Quik, A. J. Hendricks, and D. Van De Meent. 2014. "Multimedia modeling of engineered nanoparticles with simplebox4nano: Model definition and evaluation." *Environmental Science and Technology* 48:5726–5736. Doi: 10.1021/es500548h.
- Ma, H., A. Brennan, and S. A. Diamond. 2012. "Phototoxicity of TiO₂ nanoparticles under solar radiation to two aquatic species: *Daphnia magna* and *Japanese medaka*." *Environmental Toxicology and Chemistry* 31:16211629. Doi: 10.1002/etc.2177.
- MacDonald, N. J., M. H. Davies, A. K. Zundel, J. C. Howlett, Z. Demirbilek, J. Z. Gailani, T. C. Lackey, and J. Smith. 2006. "PTM: Particle Tracking Model: Model theory, implementation, and example applications." ERDC/CHL TR-06-20. Vicksburg MS: U.S. Army Engineer Research and Development Center.
- Mueller, N. C., and B. Nowack. 2008. "Exposure modeling of engineered nanoparticles in the environment." *Environmental Science and Technology* 42 (12):4447–4453.

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14. ABSTRACT Determination of transport of engineered nanomaterials within the aquatic environment is an important area of study due to knowledge and capabilities gaps, leading to uncertainty. The lack of research in this area greatly encumbers accurate and timely risk assessment, regulatory decisions, and thus, technology advancement. The objective of this investigation is to demonstrate the capability of the Particle Tracking Model (PTM), currently parameterized for aquatic transport of sediment particulates, to predict the transport pathways of nanoparticles introduced into complex hydrodynamic flowfields. A hypothetical scenario was developed in which nano-TiO ₂ was introduced into the flowfield within an area near Cleveland Harbor as an instantaneous point source due to a weather event. Results show transport pathways are highly dependent on flow conditions as well as the amount of material introduced into the system. It is understood that this is the first stage of more accurate predictions of nanoparticle fate. Future efforts will focus on utilizing previously developed data and relationship to account for nanoparticle specific transport processes.					
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