Impact of Titanium Dioxide Nanoparticles on Nutrient and Contaminant Reduction in Wastewater Treatment Wetlands

Madeline J. Hubbard
Portland State University

Follow this and additional works at: https://pdxscholar.library.pdx.edu/cengin_gradprojects

Let us know how access to this document benefits you.

Recommended Citation
Hubbard, Madeline J., "Impact of Titanium Dioxide Nanoparticles on Nutrient and Contaminant Reduction in Wastewater Treatment Wetlands" (2019). Civil and Environmental Engineering Master's Project Reports. 50.
https://pdxscholar.library.pdx.edu/cengin_gradprojects/50
10.15760/CCEMP.49

This Project is brought to you for free and open access. It has been accepted for inclusion in Civil and Environmental Engineering Master's Project Reports by an authorized administrator of PDXScholar. For more information, please contact pdxscholar@pdx.edu.
IMPACT OF TITANIUM DIOXIDE NANOPARTICLES ON NUTRIENT AND CONTAMINANT REDUCTION IN WASTEWATER TREATMENT WETLANDS

by

MADELINE HUBBARD

A project report submitted in partial fulfillment of the requirements for the degree of

MASTERS OF SCIENCE in

CIVIL AND ENVIRONMENTAL ENGINEERING

Advisor: Dr. Gwynn Johnson

Portland State University

2019
EXECUTIVE SUMMARY

Metallic nanoparticles are found in a variety of commercial products and industrial processes, and have become more common in the last few decades. As nanoparticles are toxic to biota and have the potential to spread other types of contamination, their increased use has become a concern. Research into the transport of nanoparticles in subsurface and surface waters shows a wide range in mobility, but that they are most likely to collect in systems with low linear velocities and high organic content. As a result, wetlands are the most vulnerable to nanoparticle contamination. Wetlands receiving and treating wastewater effluent have an even higher risk, both due to the increased loading of nanoparticles from wastewater, as well as the increased organic matter entering the system. A simple numerical model was designed to quantify the impact of nanoparticles on nutrient and contaminant reduction in wastewater treatment wetlands, with titanium dioxide (TiO₂) nanoparticles and cadmium as the nanoparticle and contaminant of interest. Concentrations of nitrogen, phosphorus, BOD, NBOD, total suspended solids, phytoplankton, dissolved oxygen, cadmium and nanoparticles were modeled at a series of nodes along the length of the wetland across a span of 1000 days. Introduction of titanium dioxide nanoparticles at concentrations observed in wastewater effluent resulted in slower rates of nitrification, but otherwise had negligible impacts. Higher levels of nanoparticles saw slight variations in nitrogen, phytoplankton and dissolved oxygen dynamics with no change to steady state concentrations. Increasing nanoparticles also significantly enhanced the removal of dissolved and total cadmium. Nanoparticles could be incorporated into wastewater treatment to target cadmium and other contaminants, should the other impacts on the system and toxicity of the effluent due to remaining nanoparticles be low enough. While nanoparticles at low
concentrations can likely be ignored in water quality models, higher concentrations warrant inclusion to give more accurate predictions.
TABLE OF CONTENTS

EXECUTIVE SUMMARY ........................................................................................................... 2
LIST OF TABLES .......................................................................................................................... 6
LIST OF FIGURES ....................................................................................................................... 7
LIST OF VARIABLES .................................................................................................................. 8
1.0 INTRODUCTION .................................................................................................................... 12
2.0 RISKS OF NANOPARTICLES .............................................................................................. 14
3.0 BACKGROUND .................................................................................................................... 22
   3.1 COLLOID ATTACHMENT THEORY ...................................................................................... 22
   3.2 TRANSPORT AND FATE OF NANOPARTICLES IN THE ENVIRONMENT ......................... 24
      3.2.1 SUBSURFACE TRANSPORT AND FATE ........................................................................ 24
      3.2.2 SURFACE TRANSPORT AND FATE ............................................................................ 28
4.0 MODEL DESIGN .................................................................................................................. 31
   4.1 MODEL DESCRIPTION ....................................................................................................... 31
   4.2 GENERAL GOVERNING EQUATIONS ................................................................................. 33
   4.3 GENERAL FINITE DIFFERENCE APPROXIMATIONS .......................................................... 33
   4.4 CONSTITUENT GENERAL EQUATIONS AND FINITE DIFFERENCE
      APPROXIMATIONS ................................................................................................................ 34
      4.4.1 NITROGEN .................................................................................................................. 34
      4.4.2 PHOSPHORUS ............................................................................................................. 37
      4.4.3 BIOCHEMICAL OXYGEN DEMAND .......................................................................... 38
      4.4.4 NITROGENOUS BIOCHEMICAL OXYGEN DEMAND .................................................... 40
      4.4.5 TOTAL SUSPENDED SOLIDS ..................................................................................... 40
      4.4.6 PHYTOPLANKTON ...................................................................................................... 42
      4.4.7 DISSOLVED OXYGEN ................................................................................................. 44
      4.4.8 NANOPARTICLES ..................................................................................................... 47
      4.4.9 CADMIUM ................................................................................................................... 48
   4.5 MODEL RUN INPUTS .......................................................................................................... 51
5.0 RESULTS AND DISCUSSION ............................................................................................. 52
   5.1 IMPACT OF BACKGROUND NANOPARTICLE CONCENTRATIONS ................................. 52
   5.2 NANOPARTICLE CONCENTRATION SENSITIVITY ANALYSIS ......................................... 54
      5.2.1 NITROGEN, DISSOLVED OXYGEN AND PHYTOPLANKTON .................................. 54
      5.2.2 CADMIUM .................................................................................................................. 55
6.0 CONCLUDING REMARKS ................................................................................................... 74
7.0 REFERENCES

APPENDIX A1: WETLAND MODEL WITHOUT NANOPARTICLES

APPENDIX A2: WETLAND MODEL WITH NANOPARTICLES AND A POSITIVE CORRELATION TO PHYTOPLANKTON GROWTH RATE

APPENDIX A3: WETLAND MODEL WITH NANOPARTICLES AND A NEGATIVE CORRELATION TO PHYTOPLANKTON GROWTH RATE
LIST OF TABLES

Table 1: List of variables.................................................................8
Table 2: Summary of selected papers on the effects of MENPs on microbial communities......12
Table 3: Summary of selected papers on the effects of MENPs on plants...............................15
Table 4: Summary of selected papers on the uptake of contaminants by MENPs..................18
Table 5: Summary of selected papers on transport of MENPs in the subsurface.....................24
Table 6: Model influent and initial conditions.................................................................31
Table 7: Effluent concentrations of constituents of interest at 1000 days.............................53
Table 8: Cadmium concentrations in final wetland effluent.............................................55
LIST OF FIGURES

Figure 1: Size reference for nanoparticles .......................................................... 11
Figure 2: Interaction energy profile ................................................................. 21
Figure 3: Subsurface nanoparticle transport ..................................................... 23
Figure 4: Surface nanoparticle transport ........................................................ 28
Figure 5: Schematic showing physical parameters of modeled wetland .......... 31
Figure 6: Division of wetland into series of nodes .......................................... 33
Figure 7: Phytoplankton concentration profile at 1000 days and effluent concentration ........ 57
Figure 8: Dissolved oxygen concentration profile at 1000 days and effluent concentration .......... 58
Figure 9: Phosphorus concentration profile at 1000 days and effluent concentration ........ 59
Figure 10: Total suspended solids concentration profile at 1000 days and effluent concentration .......................................................... 60
Figure 11: BOD concentration profile at 1000 days and effluent concentration ........ 61
Figure 12: Cadmium concentration profile at 1000 days and effluent concentration .......... 62
Figure 13: NBOD concentration profile at 1000 days and effluent concentration .......... 63
Figure 14: Organic nitrogen, ammonia, nitrite and nitrate concentration profiles at 1000 days .... 64
Figure 15: Organic nitrogen, ammonia, nitrite and nitrate wetland effluent concentrations .... 65
Figure 16: Nanoparticle sensitivity analysis wetland effluent concentrations ........... 66
Figure 17: Ammonia sensitivity analysis wetland effluent concentrations ............ 67
Figure 18: Nitrite sensitivity analysis wetland effluent concentrations ............... 68
Figure 19: Nitrate sensitivity analysis wetland effluent concentrations ............... 69
Figure 20: NBOD sensitivity analysis wetland effluent concentrations ............... 70
Figure 21: Dissolved oxygen sensitivity analysis wetland effluent concentrations ....... 71
Figure 22: Phytoplankton sensitivity analysis wetland effluent concentrations ......... 72
Figure 23: Cadmium sensitivity analysis wetland effluent concentrations ............ 73
# LIST OF VARIABLES

## Table 1 – List of variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Concentration of a constituent in water</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>u</td>
<td>Velocity in the x-direction</td>
</tr>
<tr>
<td>rxn</td>
<td>Reactions associated with a constituent</td>
</tr>
<tr>
<td>C&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Concentration of a constituent in compartment a</td>
</tr>
<tr>
<td>C&lt;sub&gt;b&lt;/sub&gt;</td>
<td>Concentration of a constituent in compartment b</td>
</tr>
<tr>
<td>C&lt;sub&gt;i&lt;/sub&gt;&lt;sup&gt;n&lt;/sup&gt;</td>
<td>Concentration of a constituent in water at timestep n and node i</td>
</tr>
<tr>
<td>Δt</td>
<td>Change in time</td>
</tr>
<tr>
<td>Δx</td>
<td>Distance between two nodes</td>
</tr>
<tr>
<td>No</td>
<td>Concentration of organic nitrogen in water as nitrogen</td>
</tr>
<tr>
<td>k&lt;sub&gt;oa&lt;/sub&gt;</td>
<td>Reaction constant describing the transformation of organic nitrogen to ammonia</td>
</tr>
<tr>
<td>f&lt;sub&gt;nitr&lt;/sub&gt;</td>
<td>Nitrification factor describing the slowing of nitrogen transformation with the decrease of dissolved oxygen in the system</td>
</tr>
<tr>
<td>Na</td>
<td>Concentration of ammonia in water as nitrogen</td>
</tr>
<tr>
<td>a&lt;sub&gt;na&lt;/sub&gt;</td>
<td>Mass ratio between nitrogen and chlorophyll-a found in phytoplankton</td>
</tr>
<tr>
<td>k&lt;sub&gt;death&lt;/sub&gt;</td>
<td>Rate constant describing phytoplankton death</td>
</tr>
<tr>
<td>A</td>
<td>Concentration of phytoplankton in water, represented by mass of chlorophyll-a in water</td>
</tr>
<tr>
<td>k&lt;sub&gt;ai&lt;/sub&gt;</td>
<td>Reaction constant describing the transformation of ammonia to nitrite</td>
</tr>
<tr>
<td>Ni</td>
<td>Concentration of nitrite in water as nitrogen</td>
</tr>
<tr>
<td>k&lt;sub&gt;in&lt;/sub&gt;</td>
<td>Reaction constant describing the transformation of nitrite to nitrate</td>
</tr>
<tr>
<td>k&lt;sub&gt;growth&lt;/sub&gt;</td>
<td>Rate constant describing maximum phytoplankton growth</td>
</tr>
<tr>
<td>k&lt;sub&gt;sn&lt;/sub&gt;</td>
<td>Half-saturation constant for nitrogen limitation of phytoplankton growth</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$k_{nitr}$</td>
<td>First-order nitrification inhibition coefficient</td>
</tr>
<tr>
<td>DO</td>
<td>Concentration of dissolved oxygen in water</td>
</tr>
<tr>
<td>P</td>
<td>Concentration of phosphorus dissolved in water</td>
</tr>
<tr>
<td>$a_{pa}$</td>
<td>Mass ratio between phosphorus and chlorophyll-a found in phytoplankton</td>
</tr>
<tr>
<td>$k_{sp}$</td>
<td>Half-saturation constant for phosphorus limitation of phytoplankton growth</td>
</tr>
<tr>
<td>L</td>
<td>Concentration of biochemical oxygen demand (BOD) in water</td>
</tr>
<tr>
<td>$k_d$</td>
<td>Rate constant describing BOD decay</td>
</tr>
<tr>
<td>$a_{oa}$</td>
<td>Mass ratio between oxygen consumed by decomposing phytoplankton and chlorophyll-a found in phytoplankton</td>
</tr>
<tr>
<td>$DO_{sat}$</td>
<td>Dissolved oxygen water saturation concentration</td>
</tr>
<tr>
<td>$k_a$</td>
<td>Rate constant describing oxygen diffusion into water</td>
</tr>
<tr>
<td>$P_{net}$</td>
<td>Net addition of dissolved oxygen by phytoplankton via photosynthesis and respiration</td>
</tr>
<tr>
<td>$r_{on}$</td>
<td>Mass ratio between oxygen consumed and organic nitrogen oxidized into nitrate</td>
</tr>
<tr>
<td>TSS</td>
<td>Concentration of total suspended solids in water</td>
</tr>
<tr>
<td>$v_{s,TSS}$</td>
<td>Settling velocity of total suspended solids</td>
</tr>
<tr>
<td>$A_s$</td>
<td>Bottom area of control volume onto which particles are settling (size width by Δx)</td>
</tr>
<tr>
<td>V</td>
<td>Volume of control volume surrounding node (size width by depth by Δx)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Form factor of a particle</td>
</tr>
<tr>
<td>g</td>
<td>Gravitational constant</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Particle density</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>Water density</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity of water</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Particle diameter</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$k_{ga}$</td>
<td>Rate constant describing the growth of phytoplankton with nutrient limitation</td>
</tr>
<tr>
<td>AN</td>
<td>Concentration of nitrogen available to phytoplankton in water</td>
</tr>
<tr>
<td>AP</td>
<td>Concentration of phosphorus available to phytoplankton in water</td>
</tr>
<tr>
<td>$k_{growth}$</td>
<td>Rate constant describing the maximum growth of phytoplankton with the addition of nanoparticles</td>
</tr>
<tr>
<td>$r_{oa}$</td>
<td>Mass ratio between ammonia consumed and oxygen consumed by conversion of ammonia to nitrite</td>
</tr>
<tr>
<td>$r_{oi}$</td>
<td>Mass ratio between nitrite consumed and oxygen consumed by conversion of nitrite to nitrate</td>
</tr>
<tr>
<td>q</td>
<td>Average linear velocity</td>
</tr>
<tr>
<td>d</td>
<td>Water depth</td>
</tr>
<tr>
<td>$r_{o}$</td>
<td>Mass ratio between oxygen generated by phytoplankton and mass of chlorophyll-a in phytoplankton</td>
</tr>
<tr>
<td>P</td>
<td>Daily average phytoplankton photosynthesis rate</td>
</tr>
<tr>
<td>$G_{max}$</td>
<td>Rate constant describing maximum phytoplankton growth for optimal light conditions and excess nutrients</td>
</tr>
<tr>
<td>T</td>
<td>Water temperature</td>
</tr>
<tr>
<td>$\varphi_l$</td>
<td>Attenuation of phytoplankton growth due to light</td>
</tr>
<tr>
<td>$k_{ra}$</td>
<td>Rate constant describing the respiration of phytoplankton</td>
</tr>
<tr>
<td>NP$_w$, NP</td>
<td>Concentration of titanium dioxide nanoparticles suspended in water</td>
</tr>
<tr>
<td>NP$_{TSS}$</td>
<td>Concentration of titanium dioxide nanoparticles sorbed to suspended solids</td>
</tr>
<tr>
<td>$v_{s,NP}$</td>
<td>Settling velocity of titanium dioxide nanoparticles</td>
</tr>
<tr>
<td>$k_{NP-TSS}$</td>
<td>Sorption constant for titanium dioxide nanoparticles onto suspended solids</td>
</tr>
<tr>
<td>Cd$_w$, Cd</td>
<td>Concentration of cadmium dissolved in water</td>
</tr>
<tr>
<td>Cd$_{TSS}$</td>
<td>Concentration of cadmium sorbed to suspended solids</td>
</tr>
<tr>
<td>Cd$_{NP}$</td>
<td>Concentration of cadmium sorbed to titanium dioxide nanoparticles</td>
</tr>
<tr>
<td>$k_{Cd-TSS}$</td>
<td>Sorption constant for cadmium onto suspended solids</td>
</tr>
<tr>
<td>$k_{\text{Cd-NP}}$</td>
<td>Sorption constant for cadmium onto titanium dioxide nanoparticles</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>$f_{\text{NP-TSS}}$</td>
<td>Fraction of nanoparticles sorbed to suspended solids</td>
</tr>
</tbody>
</table>
1.0 INTRODUCTION

Nanoparticles are a collection of molecules smaller than 100 nm in any direction (see Figure 1). Nanoparticles may form naturally, incidental to other industrial processes, or via engineering. Natural nanoparticles form in the environment without human intervention, and include organic acids, some carbon-based nanoparticles such as fullerenes and carbon nanotubes, metals such as silver and gold, metal oxides such as iron oxide, and clays. Incidental nanoparticles result from human activity but are not deliberately created, such as carbon and metal nanoparticles as byproducts of combustion. Engineered nanoparticles (ENPs) are created in an industrial or lab setting, and include carbon nanoparticles, polymers, metals, metal oxides, salts such as metal-phosphates, and aluminosilicates. ENPs may also have coatings or surface modifications to improve properties such as mobility[1].

ENPs are widely used in industry and manufacturing, and can be found in paints, batteries, fuel additives, catalysts, transistors, lasers, lubricants, medical implants, water purifiers, sunscreens, cosmetics, and food additives[2]. ENPs are released into the environment...
either through waste products or use in soil and groundwater restoration. Metallic ENPs (MENPs) have been of interest in recent research regarding their use as an enhancement of contaminant removal, their mobility in the surface and subsurface, and their toxicity to various organisms.
2.0 RISKS OF NANOPARTICLES

Rising concerns over MENPs have revealed several risks associated with their use and release into the environment. Nanoparticles have been shown to be toxic to some biota. While the exact mechanisms are not fully understood, toxicity seems related to uptake and accumulation in cells. Nanoparticles have been observed damaging DNA and cells to the point of cell mortality\(^3\). Microbial toxicity has been well demonstrated (see Table 2). Chronic exposure to MENPs in microorganisms causes decreased microbial metabolic function, cellular processes and enzyme activity\(^4\), and overall increases microbe mortality\(^4,\,^5,\,^6,\,^7\). As a result of decreased cell counts and function, lower removal rates of chemical oxygen demand and total nitrogen have also been observed\(^4,\,^5,\,^6,\,^7\). Damage to microbial communities could have wide reaching consequences, disrupting biodegradation and nutrient consumption in natural and manmade environments.

Table 2 – Summary of selected papers on the effects of MENPs on microbial communities

<table>
<thead>
<tr>
<th>Study</th>
<th>Nanoparticle Type</th>
<th>Experimental Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alizadeh et al. (2019)</td>
<td>Silver</td>
<td>1 L moving bed biofilm reactor tests 18 day experiments 1 hour hydraulic retention time pH = 7.4 DO = 6.5 mg/L Total COD = 261 mg/L Nanoparticle concentration = 10.8, 131 or 631 μg/L</td>
<td>No significant membrane damage at low Ag concentration Noticeable increase in cell mortality at medium and high Ag concentrations No change in COD removal efficiency at low Ag concentration 22-25% decrease in COD removal efficiency at medium and high Ag concentrations</td>
</tr>
<tr>
<td>Yang et al. (2018)</td>
<td>n-TiO(_2)</td>
<td>0.3 m x 0.3 m x 0.5 m microcosms 12 L pore volume Gravel substrate planted with _Phragmites australis_ T = 25° C 5- or 60-day experiment Nanoparticle concentration = 0, 1 or 50 mg/L</td>
<td>No significant acute impact on nutrient removal Long-term nutrient removal - COD: 1 mg/L = 93.1% removal; 50 mg/L = 85.6% - TN: 0 mg/L = 78.2%; 1 mg/L = 38%; 50 mg/L = 50.3% - TP = negligible impacts</td>
</tr>
<tr>
<td>Study</td>
<td>Material</td>
<td>Methodology</td>
<td>Results</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Zhao et al. (2018)</td>
<td>ZnO</td>
<td>Anaerobic sludge digestion in 500 mL flask</td>
<td>- NH&lt;sub&gt;4&lt;/sub&gt;: 0 mg/L = 77.5%; 1 mg/L = 38%; 50 mg/L = 1.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Long-term impact on cellular function</td>
<td>- Major metabolic function: 50 mg/L = 58-76.8% decrease</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Cellular processes: 50 mg/L = 75.5-93.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Enzyme activity: 1 mg/L = 69.8-92.4%; 50 mg/L = 43.8-64.8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Decrease in abundance of N removers, major nitrifiers, denitrifiers, P- accumulators</td>
</tr>
<tr>
<td>Liu et al. (2019)</td>
<td>Silver</td>
<td>0.3 x 0.3 x 0.5 m microcosms</td>
<td>Moderate and high ZnO decreased CH&lt;sub&gt;4&lt;/sub&gt; production by 23.2% and 28.6%, respectively</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 L pore volume</td>
<td>ZnO impact on metabolism</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gravel substrate planted with <em>Phragmites australis</em></td>
<td>- 28.5% decrease in protein dehydration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5- or 60-day experiments</td>
<td>- 7.2% decrease in carbohydrate dehydration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Synthetic wastewater:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 200 mg/L COD</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 45 mg/L TN</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 35 mg/L NH&lt;sub&gt;4&lt;/sub&gt;-N</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 10 mg/L TP</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nanoparticle concentration = 0, 1, or 50 mg/L Ag</td>
<td></td>
</tr>
<tr>
<td>Walden &amp; Zhang (2018)</td>
<td>Silver</td>
<td>100 μL cell suspension applied to sterile microtiter 96-well plate</td>
<td>No change in live/dead cell ratio</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-hour experiments</td>
<td>No significant difference in reduction of COD or change in pH, sulfate or ammonia</td>
</tr>
</tbody>
</table>
Microbes = *Camamonas testosterone*, *Acinetobacter calcoaceticus*, *Delftia acidovorans*

Synthetic wastewater:
- 140 mg/L glucose
- 300 mg/L Difco nutrient broth
- 43.9 mg/L KH$_2$PO$_4$
- 25 mg/L NaOH
- 3 mg/L KNO$_3$
- 175 mg/L NaHCO$_3$
- 118 mg/L (NH$_4$)$_2$SO$_4$
- 133 mg/L CaCl$_2$
- 5 mg/L FeCl$_3$.6H$_2$O
- 100 mg/L MgSO$_4$
- 12.8 mg/L MnSO$_4$

Nanoparticle concentration = 1 μg/L

Effects on plants is less well established. Some researchers have found that plants seem to benefit from nanoparticle exposure: Yang et al. (2018)$^{[4]}$ found that plants exposed long term to TiO$_2$ nanoparticles had increased rates of net photosynthesis, transpiration, stomatal conductance and root activity. Other researchers reported negative effects: Bao et al. (2019)$^{[8]}$ saw decreased root and leaf activity and decreased root film biomass in plants exposed to silver nanoparticles. Interactions between plants and MENPs seem to depend significantly on plant species and MENP type (see Table 3)$^{[9]}$.$^{[10]}$.$^{[11]}$. Impact may also be dosage dependent, with benefits at lower doses and toxic effects at higher doses.

**Table 3 – Summary of selected papers on the effects of MENPs on plants**

<table>
<thead>
<tr>
<th>Study</th>
<th>Nanoparticle Type</th>
<th>Experimental Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avellan et al. (2017)</td>
<td>Gold</td>
<td><em>Arabidopsis thaliana</em> grown in gel Positively and negatively charged gold Nanoparticle concentration = 10 mg/L</td>
<td>Au nanoparticles found in root cells (+) Au nanoparticles showed more root growth Less (-) Au detected than (+) Au in roots (+) Au formed larger accumulations/aggglomerations (+) Au generally trapped in outer mucilage</td>
</tr>
<tr>
<td>Study</td>
<td>Metal</td>
<td>Plant Species</td>
<td>Procedure</td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------</td>
<td>-------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
| Canivet et al. (2014)    | Metallic iron with oxide and hydroxide layer | *Aphanorrhegma patens* grown on solid BCD medium  
Nanoparticle concentration = 5, 50, 500, 5000, or 50000 ng/plant  
3-, 7-, or 21-day experiments | Agglomerations visible on leaf surfaces at 500 ng applications and above  
Agglomerations found inside plants at 5000 and 50000 ng applications | (-) Au inside roots between cell wells, near cell walls, or in intracellular spaces |
| Glenn & Klaine (2013)    | Gold    | *M. simulans, E. densa, A. caroliniana* cuttings exposed suspended in water  
Cuttings with and without roots tested  
Nanoparticle concentration = 250 μg/L  
Nanoparticle size = 4, 8 or 30 nm  
DOC = 0.1 or 2 mg C/L | E. densa  
- 2.3-21.1 mg Au/kg  
- Presence of roots does not significantly impact uptake  
- Size does not significantly impact uptake  
- Some sizes saw decline in uptake with increasing DOC  
*Myriophyllum simulans*  
- 8.7-33.4 mg Au/kg  
- Presence of roots does not significantly impact uptake  
- Some sizes saw decline in uptake with increasing DOC  
*Azolla caroliniana*  
- 9-145.5 mg Au/kg  
- Presence of roots significantly impacts uptake  
- Strong decline in uptake with increasing DOC for small sizes, weak decline in larger sizes | |
| Haverkamp & Marshall (2009) | Silver | *Brassica juncea* exposed to metals in hydroponics system  
AgNO₃, [Ag(NH₃)₂]NO₃, Na₃[Ag(S₂O₃)₂] used  
Input concentration = 10 g Ag/L when comparing silver solutions;  
2.5 g/L, 4.5 g/L, 10 g/L for AgNO₃  
Nanoparticles formed inside plants  
- AgNO₃ = 4-35 nm particles  
- [Ag(NH₃)₂]NO₃ = 3-7 nm particles  
- Na₃[Ag(S₂O₃)₂] = 2-7 nm particles  
Maximum concentration = 0.35% Ag by dry weight | Silver ions transported into roots independent of concentration  
Nanoparticles formed inside plants  
- AgNO₃ = 4-35 nm particles  
- [Ag(NH₃)₂]NO₃ = 3-7 nm particles  
- Na₃[Ag(S₂O₃)₂] = 2-7 nm particles  
Maximum concentration = 0.35% Ag by dry weight | |
| Li et al. (2016)         | Gold    | *Oryza sativa* L. and *Solanum lycopersicum* grown in nutrient solution  
Input concentration = 500 μg/L | Strong presence of Au in roots (<20 nm tends to pass)  
Uptake:  
- *Solanum lycopersicum*: roots = 125-475 mg/kg; shoots = 4-12 mg/kg  
- *Oryza sativa* L.: roots = 50-150 mg/kg; shoots = 3-7 mg/kg | |
<p>| Lv et al. (2015)         | ZnO     | <em>Zea mays</em> L. exposed in hydroponics system | Increasing Zn caused initial rapid increase in Zn in plant tissues, then plateau at higher | |</p>
<table>
<thead>
<tr>
<th>Study</th>
<th>Type</th>
<th>Plant Species</th>
<th>Description</th>
</tr>
</thead>
</table>
| ZnO nanoparticles and ZnSO₄  | ZnO        | Nutrient solution              | ZnO concentrations for shoots and slow increase in roots  
- Discontinuity occurs at ~2000 mg/kg in shoots, ~7000 mg/kg in roots  
Solubility of Zn increased in presence of plants  
Zn uptake seems largely due to dissolution of ZnO and uptake as metal ions, not uptake of whole ZnO nanoparticles |
| Peng et al. (2015)           | CuO        | *Oryza sativa* L. grown, exposed in nutrient solution | Increase in Cu concentration in plant tissue  
- Leaves = 4.3x  
- Stems = 2.3x  
- Young leaves = 1.9x  
- Roots = 24x  
Higher partial dissolution in young leaves than mature leaves, roots |
| Raliya et al. (2016)         | Gold       | *C. lanatus* grown in soil     | 100 nm stomatal openings give large spaces for nanoparticles to enter through  
Drop-cast translocation efficacy:  
- Rods = 49%  
- Spheres = 13%  
- RD = 8%  
- Cubes = 7%  
Aerosol translocation efficacy:  
- Cubes = 37%  
- RD = 28%  
- Spheres = 18%  
- Rods = 17%  
Evidence of translocation from leaves to roots |
| Taylor et al. (2014)         | Gold       | *Arabidopsis thaliana* grown on agar plates, exposed in flasks of growing media | 5-30 nm nanoparticles found in root tissue, shoot chloroplasts, cytoplasm  
Uptake at 100 mg Au/L = 24 mg Au/g  
Uptake dependent on concentration below 200 mg/L, independent above  
Translocation from roots to shoots within 20 hours  
Root length decreased with increasing nanoparticle concentrations |
| Zhu et al. (2012)            | Gold       | *Oryza sativa, Lolium perenne, Raphanus sativus, Cucurbita mixta* grown, exposed in hydroponics system | Positively charged nanoparticles accumulate most on roots, but have worst translocation |
Negatively charged nanoparticles accumulate more slowly, translocated from roots at greater rates. Impact of plant species:
- Radishes = high uptake
- Rice = low uptake, high translocation
- Pumpkins = low uptake, translocation
- Ryegrass = low uptake, high translocation

Nanoparticles can create 15-40 nm holes in cell membranes.

MENPs may also serve as a transport mechanism for other contaminants in a system. If nanoparticles have high enough mobility, compounds that sorb to them may receive appreciable transport. MENPs have been observed sorbing metallic oxyanions such as arsenic and chromium, heavy metals such as lead and cadmium\textsuperscript{12}, and organic compounds such as polyaromatic hydrocarbons\textsuperscript{13}. Significant uptake by MENPs has been seen in systems saturated with a contaminant (see Table 4\textsuperscript{14},\textsuperscript{15},\textsuperscript{16},\textsuperscript{17},\textsuperscript{18},\textsuperscript{19}). MENPs in previously contaminated systems could remobilize immobile contamination, making clean up a larger and more complex task.

**Table 4 – Summary of selected papers on the uptake of contaminants by MENPs**

<table>
<thead>
<tr>
<th>Study</th>
<th>Nanoparticle Type</th>
<th>Contaminant Type</th>
<th>Experimental Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Babaee et al. (2018)</td>
<td>Iron/Copper</td>
<td>Arsenic(III) &amp; Arsenic (V)</td>
<td>pH = 7 (excluding pH experiment) Temperature = 20° C Contact Time Experiment: - Adsorbate concentration = 100, 500, or 1000 μg/L - Adsorbent concentration = 50 mg/L - Duration = 48 hours Competing Ions Experiment: - Adsorbate concentration = 0.5 mg/L</td>
<td>As(III) Adsorption - 1000 μg/L = 69% sorbed - 500 μg/L = 78% sorbed - 100 μg/L = 80% sorbed As(V) Adsorption - 1000 μg/L = 89% sorbed - 500 μg/L = 96% sorbed - 100 μg/L = 97% sorbed Competing ions in solution had no effect on As sorption Sorption decreased with increasing pH - As(III) = sharp decline at pH 5</td>
</tr>
<tr>
<td>Study</td>
<td>Adsorbent</td>
<td>Adsorbate</td>
<td>Adsorbate Concentrations</td>
<td>K_d (L/kg)</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>----------------------------------------</td>
<td>----------------------------------------</td>
<td>--------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Fang et al. (2008)</td>
<td>Nano Zero Valen Iron (NZVI), Nano Zero Valen Copper (NZVC), Nano Silicon Oxide (SiO_2)</td>
<td>Phenanthrene (Phen)</td>
<td>NZVI = 5556 mg/L, NZVC = 5556 mg/L, SiO_2 = 6944 mg/L</td>
<td>278 for 20 μg/L Phen, 110 for 100 μg/L Phen, 37.7 for 800 μg/L Phen</td>
</tr>
<tr>
<td>Ghasmezadeh &amp; Bostani (2017)</td>
<td>Raw compost, compost fermented with beet molasses, leachate (all containing lead and nickel)</td>
<td></td>
<td>Raw compost = 24.46 mg/kg Pb, 1.52 mg/kg Ni, Fermented compost = 24.49 mg/kg Pb, 2.08 mg/kg Ni, Leachate = 16.99 mg/kg Pb, 0.69 mg/kg Ni</td>
<td>143% Pb sorbed, 23% Ni sorbed, 141% Pb sorbed, 16% Ni sorbed</td>
</tr>
<tr>
<td>Martinez et al. (2015)</td>
<td>Magnetite</td>
<td>Chromium (VI)</td>
<td>Adsorbent concentration = 0.5-2.0 mg/mL, Adsorbate concentration = 5, 10, 20, 40, 80, 160 mg/L</td>
<td>13.5 to 6 mg/g, 25 mg/g, 12 mg/g, 75° C</td>
</tr>
</tbody>
</table>

Increasing pH from 1.5 to 4.5 decreased removal efficiency from ~13.5 to 6 mg/g.
Increasing temperature increased removal efficiency from 0 to 25 mg/g, with a plateau at 12 mg/g between 20 and 40° C.
Increasing initial concentration of Cr increased removal efficiency until ~80 mg/L, at pH 9.2.
which point efficiencies plateaued at 12 mg/g
Increasing nanoparticle size decreased removal efficiencies from 10 to 13 mg/g at 16 nm to 4.5 to 5.5 mg/g at 43 nm

| Wang et al. (2014) | Titanium Dioxide (TiO₂) | Phenanthrene | Nanoparticle types
| - Pristine rutile TiO₂
- Rutile TiO₂ with hydrophobic treatment
- Rutile TiO₂ with hydrophilic treatment
- Anatase TiO₂ |
| pH = 7
T = Room Temperature
Solute-to-Sorbent ratio adjusted to have 20-80% phenanthrene uptake by various sorbents
Particles tested with and without DOM coating |
| Kₜ without DOM coating
- Bulk TiO₂ = 0.9
- Anatase TiO₂ = 1.5
- Pristine rutile TiO₂ = 1.1
- Hydrophilic rutile TiO₂ = 0.8
- Hydrophobic rutile TiO₂ = 162.5 |
| Kₜ with DOM coating
- Bulk TiO₂ = 6.1-288.3
- Anatase TiO₂ = 12.5-1428.3
- Pristine rutile TiO₂ = 9.8-442.1
- Hydrophilic rutile TiO₂ = 2.2-342.3
- Hydrophobic rutile TiO₂ = 310.9-2529.2 |

| Xiong et al. (2015) | Magnesium Oxide (MgO) | Cadmium(II) and Lead(II) |
| Adsorbent concentration = 100 mg/L
Adsorbate concentration = 0, 50, 100, 150, 200, 250, 300, 350, or 400 mg/L
pH = 2, 3, 4, or 5
Temperature = 25°C
Cd(II) and Pb(II) tested together for competitive sorption |
| Gradual increase in adsorption capacity with increasing initial concentration, then plateau above 250 mg/L
Maximum adsorption capacity
- Cd(II) = 2294 mg/g
- Pb (II) = 2614 mg/g
Pb(II) preferentially sorbed over Cd(II)
Adsorption capacity increased with pH – rapid increase for Pb(II), slow increase for Cd(II) |
3.0 BACKGROUND

3.1 Colloid Attachment Theory

Given the concerns over nanoparticles in the environment, it is important to understand their movement through the environment and their interactions. Nanoparticles can be modeled similarly to colloids using colloid attachment theory, giving insight into how nanoparticles interact with each other and their surrounding environment. Attraction or repulsion between colloids, according to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, is a combination of van der Waals and electric double layer (EDL) forces. Particles carrying opposite charge will experience attractive forces in relation to each other and no barrier to attachment. Particles carrying like charges will experience repulsive forces, which inhibit attachment. Repulsion forces are a function of distance, with a peak energy barrier occurring close to the surface of the particle (see Figure 2). For two particles with like charges to attach, the system must have enough energy to overcome that barrier and allow particles to interact. In this zone, strong attachments can be formed. A second energy minimum occurs past the energy barrier, due to van der Waals and EDL forces being different functions of distance. Within this secondary energy minimum particles can interact, forming weak attachments with each other[20].
23

Figure 2 – Interaction energy profile. $V_R$ represents EDL forces, and $V_A$ represents van der Waals forces. The sum of the two ($V_T$) is the energy required for interaction between particles. An energy barrier must be exceeded for particles to form strong attachments in the primary minimum ($V_P$). Weaker attachments may form in the secondary energy minimum ($V_S$), where lower energy is needed for interaction to take place. Taken from Piacenza et al. (2018)\textsuperscript{23}

The energy barrier can be altered by changes to particles, ionic strength, and pH. For example, energy barrier height and the primary energy minimum decrease with increasing ionic strength. As a result, stronger attachments can happen in the secondary energy minimum, and less energy is needed to overcome the energy barrier and cause strong attachments between particles. If ionic strength is raised to a critical point, the zero point of charge will be reached, where the charge difference between the particle and the surrounding electrolyte becomes zero\textsuperscript{20}. At the zero point of charge no energy barrier exists to prevent interactions between particles, making attachment between like charged particles favorable. pH can act similarly to encourage particles to reach their zero point of charge\textsuperscript{21}. Particle size also has a role: increasing
colloid diameter will increase the energy barrier height and the energy minimum depth. As a result, more energy is required to form strong attachments, but weaker attachments form more easily in the secondary energy minimum[22].

While theoretical attachment models are useful in understanding interactions between particles, they do not perfectly predict attachment efficiencies. Discrepancies can be attributed to

- Deposition in the secondary minimum, where particles can weakly aggregate without passing the energy barrier;
- Particle straining, where attachment occurs due to particles being physically strained by the matrix, rather than through electrostatic forces;
- Surface charge heterogeneity, causing the formation of areas of high or low charge that can then interact with opposite charged moieties on another particle;
- Or collector surface roughness, which increases surface area onto which particles can attach[22].

3.2 Transport and Fate of Nanoparticles in the Environment

3.2.1 Subsurface Transport and Fate

Nanoparticles are transported through subsurface waters by a combination of advection and diffusion, and may be removed from transport via straining, settling or sorption (see Figure 3[22]). Nanoparticles in the subsurface show potential for high mobility, with breakthrough in column tests occurring in one to four pore volume flushes. However, overall mobility of an MENP plume varies greatly, with normalized effluent concentrations ranging from approximately 0 to 0.9[24][25][26][27]. Mobility is highly dependent on the characteristics of individual MENPs and the surrounding environment. Straining and sedimentation are largely
dependent on size – straining occurs when particles become entrapped in pore throats of the surrounding matrix, and sedimentation is the removal of particles from flow by gravity. Size itself can depend on surface coatings and loading with other contaminants\cite{25,27}, stability of MENPs and their likelihood to form aggregations\cite{24}, and environmental conditions such as ionic strength and pH\cite{28}.

**Figure 3 – Subsurface nanoparticle transport.** Nanoparticles may be removed from subsurface transport via straining, settling or sorption. Straining is the physical entrapment of particles in the matrix. Settling is the movement of particles to the bottom of a flow path via gravity. Sorption is the adherence of particles to the surface of another phase within the soil matrix.

Sorption of nanoparticles to another phase within the soil matrix depends on particle and matrix qualities, as well as environmental conditions. Research has been conducted to characterize the mobility of various MENPs in different conditions (see Table 5). NVLO theory predicts that smaller particles will have a smaller energy barrier, and therefore require less
energy for attachments\textsuperscript{[22]}\textsuperscript{[22]}. Findings of several studies seem to support this, such as Bai et al. (2019)\textsuperscript{[29]}, who observed that smaller particles were more likely to sorb to the surrounding matrix and therefore had decreased mobility. Different types of MENPs will have different reactivities and will uniquely react to matrix and environmental conditions. Li et al. (2019)\textsuperscript{[24]} found that increasing ionic strength decreased the mobility of silicon-Fe particles but increased the mobility of humic acid-Fe particles. As discussed previously, pH and ionic strength can alter attractive and repulsive forces and have been shown to affect MENP mobility in different ways\textsuperscript{[24]},\textsuperscript{[25]},\textsuperscript{[26]}\textsuperscript{[26]}. Other factors have been observed effecting mobility as well, such as dissolved organic carbon\textsuperscript{[29]}\textsuperscript{[29]}. As a result, mobility of MENPs in the subsurface, especially in a mixture of particle types, can be difficult to predict. Some MENPs may experience long term sorption, resulting in chronic contamination of groundwater. Other, more mobile MENPs may freely move about the subsurface, and even transport previously immobile contamination plumes (a concern discussed in section 2.0).

**Table 5 – Summary of selected papers on transport of MENPs in the subsurface**

<table>
<thead>
<tr>
<th>Study</th>
<th>Nanoparticle Type</th>
<th>Experimental Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terzi et al. (2016)</td>
<td>Nano Zero Valent Iron (NZVI)</td>
<td>Glass plate pore network Porosity = 0.65 Flow = 0.025 or 0.05 mL/min Feed solution = distilled, degassed water Some nanoparticles were encased in lipsome barriers</td>
<td>10-20% of Iron nanoparticles sorbed to matrix Lipsomes prevented nanoparticles from interacting with network until lipid barrier was disturbed Empty liposomes were totally immobilized in the system</td>
</tr>
<tr>
<td>He et al. (2019)</td>
<td>Silver</td>
<td>1.2 cm diameter, 10 cm long soil column 30% sand, 43% silt, 27% clay soil Soil surface charge = -15.0 ± 1.1 mV Flow = 0.25 mL/min Ionic Strength = 1.0 mM KNO₃ Particle sizes = 15.0 or 27.4 nm</td>
<td>Breakthrough occurred for all concentrations at 20 pore volumes Decreasing concentration increased relative effluent concentration Decreasing size increased effluent concentration Adding surface coatings increased effluent concentrations</td>
</tr>
<tr>
<td>Study</td>
<td>Material</td>
<td>Column Details</td>
<td>Conditions</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------</td>
<td>-----------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Rahmatpour et al. (2018)</td>
<td>Silver</td>
<td>7 cm diameter, 15 cm long soil columns</td>
<td>Quartz sand, sandy loam soil and loam soil</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Columns saturated and unsaturated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Flow = 0.03-0.70 cm/min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ionic Strength = 6 mM Ca(NO$_3$)$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Particle size = 29 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Input concentration = 50 mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Surface coating = polyvinylpyrrolidone</td>
</tr>
<tr>
<td>Yu et al. (2019)</td>
<td>NZVI</td>
<td>3.6 cm diameter, 15 cm long soil column</td>
<td>Quartz sand</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Flow = 2 mL/min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH = 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ionic Strength = 5 mM NaCl, 0.8 mM CaCl$_2$, 3 mM NaHCO$_3$, 1 mM Na$_2$SO$_4$, 5 mg/L humic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Input concentration = 150 mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Modifications = chitosan or polyaniline</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Particles loaded with As and unloaded tested</td>
</tr>
<tr>
<td>Li et al. (2019)</td>
<td>FeCl$_3$</td>
<td>2 cm diameter, 10 cm long soil column</td>
<td>Glass beads, quartz sand, and natural sand tested</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Flow = 0.25 or 0.5 mL/min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ionic Strength = &lt;0.0005, 0.02, or 0.05 M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Input concentration = 0, 10 or 20 mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Monovalent (NaCl) and divalent (CaCl$_2$) cations tested</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe particles, Fe-colloidal humic acid, and Fe-colloidal silicon tested</td>
</tr>
<tr>
<td>Zhou &amp; Cheng (2018)</td>
<td>n-TiO$_2$</td>
<td>2.5 cm diameter, 15 cm long soil column</td>
<td>Quartz sand</td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peat Moss Used</td>
<td>0 mg, 65 mg, 260 mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow</td>
<td>1 mL/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic Strength</td>
<td>~1 mM NaCl (adjusted w/additions of 1 M and 0.1 M NaOH and HCl to adjust pH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input concentration</td>
<td>20 mg/L nTiO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>5 or 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>At pH 9, increasing peat moss decreases n-TiO₂ recovery</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Theorized mechanisms:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Positively charged n-TiO₂ attracted to negatively charged quartz and peat</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- DOC sorbs onto n-TiO₂ and creates negative charge, repelling quartz and peat</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow</td>
<td>1 mL/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic Strength</td>
<td>Artificial Rainwater (21 mg/L Ca⁺, 13 mg/L Cl⁻, 3 mg/L Mg²⁺, 12.5 mg/L SO₄²⁻, 13 mg/L Na⁺, 35 mg/L HCO₃⁻, 15.5 mg/L NO₃⁻) or 10x Concentration in Artificial Rainwater</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input concentration</td>
<td>100 or 200 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Some solutions were stable, others showed colloid formation until particles reached critical size, followed by sedimentation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Increasing ionic strength decreased recovery (different degrees for different nanoparticles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Transportation mechanisms in fractures are straining, diffusion, settling, interception</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>No clogging, significant amounts of straining observed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Madhi et al. (2018)</td>
<td>Silver</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow</td>
<td>1 pore volume per day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top layer</td>
<td>50 ug Ag/kg soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 nm sized particles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Limited transport in high OM loam, limited but higher transport in low OM loam, some transport in sand</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Effluent concentrations highest at 24 hours, decreased at 48, 72 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particle size decreased down column</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Transport from layer 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- High OM Loam = 10.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Low OM Loam = 13.3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Sand = 24.6%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.2.2 Surface Transport and Fate

MENPs are already being observed in surface waters. Models predicting average environmental concentrations between 2008 and 2016 ranged in estimates from 0.00004 to 0.619 μg/L silver, <0.0001 to 0.1 μg/L cesium oxide, and 0.0002 to 24.5 μg/L titanium dioxide.\[^{30}]\[1]
These concentrations are relatively low, making chronic exposure a small risk. In addition, clean up in surface waters is much easier than in the subsurface. However, there are still some concerns. MENPs can be transported great distances via surface water, which could present a danger in instances of large loadings. MENPs can also sorb to the sediments and suspended media or settle to the bottom and slowly release over time, as with groundwater and the subsurface soil matrix (see Figure 4). Significant sorption will require slow or standing water, as higher linear velocities are more likely to keep particles entrained in the water column.

Figure 4 – Surface nanoparticle transport. Nanoparticles may be removed from surface transport via settling and sorption.

These areas of slow or standing water can be achieved in various surface bodies, including wetlands. Constructed wetlands used for wastewater treatment are especially vulnerable, as they receive a higher loading in wastewater than natural wetlands receive from surface water. Choi et al. (2018)[31] found that municipal waste throughout the year contained
between 22 and 319 μg/L titanium dioxide, and 20-212 μg/L zinc oxide. Wetlands also have high concentrations of dissolved organic matter, which may encourage sorption and retention of large quantities of MENPs\textsuperscript{[32],[33]}. Plants are also a potential significant compartment for MENPs in wetlands. Various MENPs have been found to collect at relatively high concentrations in and around plant roots (see Table 2)\textsuperscript{[34],[35],[36],[37]}. MENPs can either be taken up whole into a plant via pore openings on the roots or leaves\textsuperscript{[35],[36],[37]}, or dissolve on the root surface, enter the plant as metal ions, then reform into nanoparticles within plant tissue\textsuperscript{[34],[38],[39],[40]}. Exact uptake likely depends on the type of MENP and plant species. Uptake has been observed as low as <1\%\textsuperscript{[8]} and as high as 60-80\%\textsuperscript{[41]}.

When thinking about chronic exposure of constructed wetlands to MENPs, the primary concern is the toxicity to microbes and plants and the consequential reduction in nutrient consumption. However, MENPs may also enhance the removal of toxins from water via reduction or sorption and sedimentation. The balance between these two factors must be considered when designing and modeling constructed wetlands, to better understand how they will affect treatment efficiencies. This study will seek to perform basic modeling of a constructed wetland, incorporating reductions in nutrient removal and uptake of contaminants by nanoparticles to quantify how MENPs inhibit or enhance treatment.
4.0 MODEL DESIGN

4.1 Model Description

A simplified numerical model of a constructed wetland will be used to evaluate the impact of MENPs on the removal of nutrients and contaminants. Titanium dioxide (TiO$_2$) was selected as the model MENP, due to its common use and discharge into urban wastewater$^{[31]}$, as well as the existence of literature describing its impact on microbial communities$^{[4]}$ and phytoplankton$^{[42]}$ and its interactions with other contaminants. Cadmium was selected as the contaminant of interest contaminant due to its presence in urban wastewater and literature on its interactions with TiO$_2$ nanoparticles$^{[43]}$. The model will calculate concentrations of nitrogen, phosphorus, biochemical oxygen demand, total suspended solids, phytoplankton, dissolved oxygen, and cadmium in systems with and without the presence of TiO$_2$ nanoparticles. In systems with nanoparticles, the concentration of particulate TiO$_2$ will be calculated as well.

The modeled wetland will be rectangular in shape, 350 m wide by 1000 m long, and have a depth of 1 m. Inflow into the wetland will be 19,000 m$^3$/d. These values are based off the dimensions of the constructed wetland at the Fern Hill wastewater treatment plant in Forest Grove, Oregon$^{[44]}$. Inflow will be evenly distributed across one width of the wetland, and outflow will be evenly distributed across the opposite width (see Figure 5). Table 5 shows influent concentrations and initial conditions in the wetland.
Table 6 - Model Influent and Initial Conditions

<table>
<thead>
<tr>
<th>Water Quality Parameter</th>
<th>Wastewater Influent</th>
<th>Wetland Existing Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Nitrogen (OrgN)</td>
<td>2 mg/L[^45]</td>
<td>0.25 mg/L[^46]</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td>2.8 mg/L[^45]</td>
<td>0.25 mg/L[^46]</td>
</tr>
<tr>
<td>Nitrite (NO₂⁻)</td>
<td>0.74 mg/L[^45]</td>
<td>0.25 mg/L[^46]</td>
</tr>
<tr>
<td>Nitrate (NO₃⁻)</td>
<td>6.66 mg/L[^45]</td>
<td>1.25 mg/L[^46]</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>3.1 mg/L[^45]</td>
<td>0.3 mg/L[^46]</td>
</tr>
<tr>
<td>Biological Oxygen Demand (BOD)</td>
<td>10 mg/L[^46]</td>
<td>5 mg/L[^46]</td>
</tr>
<tr>
<td>Nitrogenous Biological Oxygen Demand (NBOD)</td>
<td>110 mg/L</td>
<td>14.9 mg/L</td>
</tr>
<tr>
<td>Total Suspended Solids (TSS)</td>
<td>15 mg/L[^47]</td>
<td>3 mg/L[^46]</td>
</tr>
<tr>
<td>Phytoplankton (A)</td>
<td>0.009 mg Chl-a/L[^48]</td>
<td>0.009 mg Chl-a/L[^48]</td>
</tr>
<tr>
<td>Dissolved Oxygen (DO)</td>
<td>6 mg/L[^47]</td>
<td>8.5 mg/L[^48]</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>1x10⁻³ mg/L[^47]</td>
<td>0 mg/L</td>
</tr>
</tbody>
</table>

Figure 5 – Schematic showing physical parameters of modeled wetland. Not drawn to scale.
4.2 General Governing Equations

All continuity equations and reactions are based on those described for various parameters in Chapra (2008)\textsuperscript{[49]}. The model will use a version of the Advection-Dispersion Equation shown below:

**Equation 1**

\[
\frac{dC}{dt} = -u \frac{dC}{dx} \pm rxn
\]

where \( C \) is the constituent of interest, \( u \) is linear velocity, and \( rxn \) are any reaction occurring in the system. This partial differential equation assumes that the system is well mixed in the \( y \)- and \( z \)-direction, no diffusion occurs in any direction, and the flow rate and volume are constant. For some constituents, a modified version of this general equation will be used to account for movement of the constituent of interest between phases:

**Equation 2**

\[
\frac{d(C_a + C_b + \cdots)}{dt} = -u \frac{d(C_a + C_b + \cdots)}{dx} \pm rxn
\]

where \( C_a \) and \( C_b \) are concentrations of the constituent in compartments a and b, respectively.

4.3 General Finite Difference Approximations

The numerical solution to these general equations begins with the division of the wetland into a grid of a finite number of nodes, arranged at intervals of \( \Delta x \) along the \( x \)-direction of the wetland (see Figure 6). Unknown concentrations will be calculated at each node and assumed to be the concentration within a box of size width by depth by \( \Delta x \) around the node. Using a finite difference approximation (FDA) to the general equation, the initial conditions (initial wetland...
concentrations) and a boundary condition (influent concentrations), these concentrations can be calculated over space and time. The FDA for the basic general equation is:

**Equation 3**

\[
C_i^{n+1} = C_i^n - \frac{u\Delta t}{\Delta x} (C_i^n - C_{i-1}^n) \pm \Delta t R_{xn}
\]

where \(C_i^n\) is the concentration of a constituent at node i and timestep n, u is linear velocity, \(\Delta t\) is the timestep, \(\Delta x\) is the distance between nodes, and \(R_{xn}\) are any reactions that occur involving the constituent. FDAs for constituents using the modified general equation as their basis will be derived with the specific parameters of each constituent in mind.

![Figure 6 – Division of wetland into series of n nodes. Nodes are centered in boxes of size width by depth by \(\Delta x\).](image)

4.4 Constituent General Equations and Finite Difference Approximations

4.4.1 Nitrogen

The general continuity equations for organic nitrogen (OrgN), ammonia (NH\(_3\)), nitrite (NO\(_2^-\)) and nitrate (NO\(_3^-\)) are as follows:

**Equation 4**

\[
\frac{dNo}{dt} = -u \frac{dNo}{dx} - k_{oa}No_{nitr}
\]

**Equation 5**

\[
\frac{dNa}{dt} = -u \frac{dNa}{dx} + a_{na}k_{death}A + k_{oa}No_{nitr} - k_{al}Na_{nitr}
\]
Equation 6
\[
\frac{dN_i}{dt} = -u \frac{dN_i}{dx} + k_{ai} N_n f_{nitr} - k_{in} N_i f_{nitr}
\]

Equation 7
\[
\frac{dN_n}{dt} = -u \frac{dN_n}{dx} - a_{na} k_{growth} \frac{N_n}{k_{SN} + N_n} A + k_{in} N_i f_{nitr}
\]

where

- No ~ organic nitrogen (g N/m^3)
- Na ~ ammonia (g N/m^3)
- Ni ~ nitrite (g N/m^3)
- Nn ~ nitrate (g N/m^3)
- u ~ linear velocity (m/d)
- k_{oa} ~ organic nitrogen to ammonia rate constant (1/d)
- k_{ai} ~ ammonia to nitrite rate constant (1/d)
- k_{in} ~ nitrite to nitrate rate constant (1/d)
- f_{nitr} ~ oxygen limitation factor for nitrification
- a_{na} ~ ratio of nitrogen to chlorophyll a in phytoplankton (g N/ g Chl-a)
- k_{death} ~ death rate of phytoplankton (1/d)
- k_{growth} ~ maximum growth rate of phytoplankton (1/d)
- k_{SN} ~ half-saturation constant for nitrogen limitation of phytoplankton growth (mg/L)
- A ~ concentration of phytoplankton as chlorophyll-a (mg Chl-a/L)

The reactions for the transformation of OrgN to NH3, NH3 to NO₂⁻, and NO₂⁻ to NO₃⁻, as well as the consumption of NO₃⁻ by phytoplankton and the production of NH₃ by the decay of deceased phytoplankton are all first-order. k_{oa} is set at 0.05 /d. k_{ai} at 0.075 /d, k_{in} at 0.2 /d, a_{na} at 10.8 g N/g
Chl-a, \( k_{\text{growth}} \) at 2 /d, \( k_{\text{death}} \) at 0.2 /d, and \( k_{\text{sn}} \) at 0.0125 mg N/L without nanoparticles present\(^{[49]}\). It is assumed that, with nanoparticles, the rate of nitrification will decrease. Based on decreased total nitrogen removal rates reported by Yang et al. (2018)\(^{[4]}\) for lower TiO\(_2\) concentration, \( k_{\text{oa}}, k_{\text{ai}} \) and \( k_{\text{in}} \) are lowered to 0.029, 0.054 and 0.179 /d, respectively.

The oxygen limitation factor is given by:

**Equation 8**

\[
 f_{nitr} = 1 - e^{-k_{nitr}DO}
\]

where DO is the dissolved oxygen concentration, and \( k_{nitr} \) is the first-order nitrification inhibition coefficient, set at 0.6 L/mg\(^{[49]}\). The numerical forms of these equations are:

**Equation 9**

\[
 N_{o_i}^{n+1} = N_{o_i}^n - \frac{u \Delta t}{\Delta x} (N_{o_i}^n - N_{o_{i-1}}^n) - k_{oa}N_{o_i}^n \Delta t f_{nitr,i}^n
\]

**Equation 10**

\[
 N_{a_i}^{n+1} = N_{a_i}^n - \frac{u \Delta t}{\Delta x} (N_{a_i}^n - N_{a_{i-1}}^n) + a_{na}k_{death}A_i^n \Delta t + k_{oa}N_{o_i}^n \Delta t f_{nitr,i}^n - k_{ai}N_{a_i}^n \Delta t f_{nitr,i}^n
\]

**Equation 11**

\[
 N_{i_i}^{n+1} = N_{i_i}^n - \frac{u \Delta t}{\Delta x} (N_{i_i}^n - N_{i_{i-1}}^n) + k_{ai}N_{a_i}^n \Delta t f_{nitr,i}^n - k_{in}N_{i_i}^n \Delta t f_{nitr,i}^n
\]

**Equation 12**

\[
 N_{n_i}^{n+1} = N_{n_i}^n - \frac{u \Delta t}{\Delta x} (N_{n_i}^n - N_{n_{i-1}}^n) - a_{na}k_{growth} \frac{N_{n}}{k_{sn} + N_{n}} A_i^n + k_{in}N_{i_i}^n \Delta t f_{nitr,i}^n
\]

Under anoxic conditions, \( f_{nitr} \) equals 0, indicating that all nitrogen transformation ceases. In addition, decaying phytoplankton will contribute to BOD rather than ammonia, giving the numerical equations:

**Equation 13**

\[
 N_{o_i}^{n+1} = N_{o_i}^n - \frac{u \Delta t}{\Delta x} (N_{o_i}^n - N_{o_{i-1}}^n)
\]
Equation 14

\[ N_{a_i}^{n+1} = N_{a_i}^n - \frac{u \Delta t}{\Delta x} (N_{a_i}^n - N_{a_i}^{n-1}) \]

Equation 15

\[ N_{i_i}^{n+1} = N_{i_i}^n - \frac{u \Delta t}{\Delta x} (N_{i_i}^n - N_{i_i}^{n-1}) \]

Equation 16

\[ N_{n_i}^{n+1} = N_{n_i}^n - \frac{u \Delta t}{\Delta x} (N_{n_i}^n - N_{n_i}^{n-1}) - a_{na} k_{growth} \frac{N_n}{k_{sn} + N_n} A_i^m \]

4.4.2 Phosphorus

The general continuity equation for dissolved phosphorus is:

Equation 17

\[ \frac{dP}{dt} = -u \frac{dP}{dx} - a_{pa} k_{growth} \frac{P}{k_{sp} + P} A + a_{pa} k_{death} A \]

where

- \( P \) ~ dissolved phosphorus (mg/L)
- \( u \) ~ linear velocity (m/d)
- \( a_{pa} \) ~ ratio of phosphorus to chlorophyll a in phytoplankton (g P/g Chl-a)
- \( k_{death} \) ~ death rate of phytoplankton (/d)
- \( k_{growth} \) ~ maximum growth rate of phytoplankton (/g)
- \( k_{sp} \) ~ half-saturation constant for phosphorus limitation of phytoplankton growth (mg/L)
- \( A \) ~ concentration of phytoplankton as chlorophyll-a (mg Chl-a/L^3)

The reactions for consumption of phosphorus by phytoplankton and the production of phosphorus via the decay of deceased phytoplankton are both first order. It is assumed that there
are no other reactions that add or remove phosphorus to or from the system, such as precipitation or dissolution. \( a_{pa} \) is set at 1.5 g P/g Chl-a, and \( k_{sp} \) at 0.003 mg P/L\(^4\). The numerical form of this equation is:

Equation 18

\[
P_{i}^{n+1} = P_{i}^{n} - \frac{u \Delta t}{\Delta x} (P_{i}^{n} - P_{i-1}^{n}) - a_{pa} k_{\text{growth}} \frac{P_{i}^{n}}{k_{\text{sn}}} + P_{i}^{n} A_{i}^{n} \Delta t + a_{pa} k_{\text{death}} A_{i}^{n} \Delta t
\]

4.4.3 Biochemical Oxygen Demand

The general continuity equation for biochemical oxygen demand with oxygen present is:

Equation 19

\[
\frac{dL}{dt} = -u \frac{dL}{dx} - k_{d} L
\]

where

- \( L \sim \) biochemical oxygen demand (BOD) remaining in the system (mg/L)
- \( u \sim \) linear velocity (m/d)
- \( k_{d} \sim \) BOD decay rate (/d)

The reactions for the consumption of BOD by bacterial decay is first order. This equation assumes that no other organic matter will enter the system to contribute to BOD, and that BOD will not be removed through other processes such as settling. \( k_{d} \) is set at 0.075 /d without nanoparticles present\(^4\). With nanoparticles present, \( k_{d} \) is lowered to 0.0735 /d based on decreased chemical oxygen demand removal rates reported by Yang et al. (2018)\(^4\). The numerical form of this equation is:

Equation 20

\[
L_{i}^{n+1} = L_{i}^{n} - \frac{u \Delta t}{\Delta x} (L_{i}^{n} - L_{i-1}^{n}) - k_{d} L_{i}^{n} \Delta t
\]
This first series of equations assumes that oxygen is present in the system. However, once dissolved oxygen in the system falls to zero, BOD decay can no longer proceed at a rate of $k_d$. Instead, BOD decay will occur as quickly as oxygen in being replenished in the system. In this case, oxygen is being replenished by advection, reaeration, and net photosynthesis. In addition, any decay of organic matter from phytoplankton will cease, and that phytoplankton will instead replenish BOD in the system. As a result, the general continuity equation for BOD decay becomes:

**Equation 21**

$$\frac{dL}{dt} = -u \frac{dL}{dx} + u \frac{dDO}{dx} + a_{oa}k_{death}A - k_aDO_{sat} - P_{net}$$

where:

- $DO$ ~ dissolved oxygen (mg/L)
- $a_{oa}$ ~ ratio of oxygen consumed by decomposition of organic matter to mass of chlorophyll-a (g O/g Chl-a)
- $k_{death}$ ~ death rate of phytoplankton
- $A$ ~ phytoplankton concentration as chlorophyll-a (mg Chl-a/L)
- $k_a$ ~ reaeration constant (/d)
- $DO_{sat}$ ~ water saturation concentration of dissolved oxygen (mg/L)
- $P_{net}$ ~ oxygen produced by net photosynthesis, where $P_{net} = 0.225A$

The values of $k_a$, $DO_{sat}$, and $P_{net}$ will be further discussed down below. The numerical form of this equation is:

**Equation 22**

$$L_{i+1}^n = L_i^n - \frac{u\Delta t}{\Delta x} (L_i^n - L_{i-1}^n) - \frac{u\Delta t}{\Delta x} DO_{i-1}^n + a_{oa}k_{death}A_i^n - k_aDO_{sat} - 0.225A_i^n$$
Once rates of advection, net photosynthesis and oxygen advection exceed the decay rate of BOD, the original set of equations again applies.

4.4.4 Nitrogenous Biochemical Oxygen Demand

Nitrogenous biochemical oxygen demand (NBOD) is calculated based on concentrations of organic nitrogen, ammonia and nitrite, all of which consume oxygen in the nitrification process. The numerical equation for NBOD is:

**Equation 23**

\[ Ln_i^{n+1} = r_{on}(N_o_i^{n+1} + N_a_i^{n+1} + N_i_i^{n+1}) \]

where

- \( Ln \sim \) NBOD remaining in system (mg N/L)
- \( r_{on} \sim \) ratio of mass of oxygen consumed per mass of organic nitrogen oxidized into nitrate (g O/g N)
- \( N_o \sim \) organic nitrogen concentration (mg N/L)
- \( N_a \sim \) ammonia concentration (mg N/L)
- \( N_i \sim \) nitrite concentration (mg N/L)

Assuming organic nitrogen can be approximated using the Redfield ratio presented in Chapra (2008), \( r_{on} \) is set at 19.86 g O/g N\(^{[49]}\). Note that NBOD is not used in any other equations in the model and is instead meant as another quantification of nitrogen in the system.

4.4.5 Total Suspended Solids

The general continuity equation for total suspended solids is:
Equation 24

\[
\frac{dTSS}{dt} = -u \frac{dTSS}{dx} - \frac{v_{s,TSS}A_s}{V} TSS
\]

where

- TSS ~ total suspended solids (mg/L)
- \( u \) ~ linear velocity (m/d)
- \( v_{s,TSS} \) ~ settling velocity for total suspended solids (m/d)
- \( A_s \) ~ settling area (m²)
- \( V \) ~ system volume (m³)

\( v_{s,TSS} \) was calculated using Stokes’ Law:

Equation 25

\[
v_s = \alpha \frac{g}{18} \left( \frac{\rho_s - \rho_w}{\mu} \right) d_p^2
\]

where

- \( d_p \) ~ particle diameter (2 μm, based on particle sizes for silty clay)
- \( \rho_s \) ~ particle density (2.65 g/cm³ for silty clay)
- \( \rho_w \) ~ water density (1 g/m³)
- \( \mu \) ~ water viscosity (0.014 g/cm·s)
- \( g \) ~ gravitational constant (9.81 m/s²)
- \( \alpha \) ~ form factor (1 for sphere)

This yields a settling velocity of 0.22 m/d. This equation assumes that settled solids will not be re-entrained into the water column. The numerical form of this equation is:

Equation 26

\[
TSS_{l}^{n+1} = TSS_{l}^{n} - \frac{u \Delta t}{\Delta x} (TSS_{l}^{n} - TSS_{l-1}^{n}) - \frac{v_{s} \Delta t}{d} TSS_{l}^{n}
\]
4.4.6 Phytoplankton

The general continuity equation for phytoplankton is:

**Equation 27**

\[
\frac{dA}{dt} = -u \frac{dA}{dx} + k_{ga}A - k_{death}A
\]

where

- \( A \) ~ phytoplankton concentration as Chlorophyll-\( \alpha \) (mg Chl-\( \alpha \)/L)
- \( u \) ~ linear velocity (m/d)
- \( k_{ga} \) ~ phytoplankton growth rate (/d)
- \( k_{death} \) ~ phytoplankton death rate (/d)

Phytoplankton growth and death are both first order reactions. The phytoplankton growth rate was modeled using the growth-rate model developed by Chapra (2008)[49]. Assuming growth is only nutrient limited, \( k_{ga} \) is:

**Equation 28**

\[
k_{ga} = k_{growth \min} \left( \frac{AN_i^n}{k_{sn} + AN_i^n}, \frac{AP_i^n}{k_{sp} + AP_i^n} \right)
\]

where

- \( k_{growth} \) ~ maximum phytoplankton growth rate (/d)
- \( AN \) ~ concentration of available nitrate (mg/L)
- \( AP \) ~ concentration of available phosphorus (mg/L)
- \( k_{sn} \) ~ half-saturation constant for nitrogen limitation of phytoplankton growth (mg/L)
- \( k_{sp} \) ~ half-saturation constant for phosphorus limitation of phytoplankton growth (mg/L)
It is assumed that other factors such as light and temperature have a negligible impact on the growth rate of phytoplankton, and that phytoplankton depletion is due to non-predatory factors such as respiration and excretion. The assumption has also been made that, because phytoplankton have a net positive oxygen production, they will not be affected by anoxic conditions. A protocol is also in place to prevent excess phytoplankton blooms that create anoxic conditions: if phytoplankton concentrations rise above 0.02 mg Chl-a/L, the death rate is increased to 10 /d. Once phytoplankton concentrations fall below that value, the death rate drops back down to 0.2 /d.

Nanoparticles also have an impact on phytoplankton, but as mentioned in section 2.0 it is unclear whether nanoparticles are beneficial or detrimental to plants, phytoplankton included. Two cases will be modeled – one in which nanoparticles increase the growth rate of phytoplankton,

*Equation 29*

\[
k_{growth}' = k_{growth} + 0.003NP
\]

and one in which they decrease the growth rate,

*Equation 30*

\[
k_{growth}' = k_{growth} - 0.0005NP
\]

The slopes of these two equations were chosen based on slopes of linear approximation of changing growth rate with increasing nanoparticle concentration for different species of phytoplankton found in Kulacki and Cardinale (2012)[42]. The numerical form of this equation is:

*Equation 31*

\[
A_i^{n+1} = A_i^n - \frac{u\Delta t}{\Delta x} (A_i^n - A_{i-1}^n) + k_{ga}^n A_i^n \Delta t - k_{da} A_i^n \Delta t
\]
4.4.7 Dissolved Oxygen

The general continuity equation for dissolved oxygen is:

**Equation 32**

\[
\frac{dDO}{dt} = -u \frac{dDO}{dx} + k_a (DO_{sat} - DO) + P_{net} - k_d L - a_{oa} k_{death} A - r_{oa} k_{ai} N_a - r_{oi} k_{in} N_i
\]

where:

- \( DO \) ~ dissolved oxygen (mg/L)
- \( u \) ~ linear velocity (m/d)
- \( k_a \) ~ reaeration coefficient (/d)
- \( DO_{sat} \) ~ dissolved oxygen water saturation concentration (mg/L)
- \( P_{net} \) ~ net photosynthesis (mg/L)
- \( k_d \) ~ BOD decay rate (/d)
- \( L \) ~ BOD remaining in system (mg/L)
- \( a_{oa} \) ~ ratio between oxygen consumed by phytoplankton decomposition and chlorophyll-a concentrations (g O/g Chl-a)
- \( k_{death} \) ~ phytoplankton death rate (/d)
- \( r_{oa} \) ~ conversion from ammonia consumed to oxygen consumed (g O/g N)
- \( r_{oi} \) ~ conversion from nitrite consumed to oxygen consumed (g O/g N)
- \( k_{na} \) ~ organic nitrogen to ammonia rate constant (/d)
- \( k_{ai} \) ~ ammonia to nitrite rate constant (/d)
- \( k_{in} \) ~ nitrite to nitrate rate constant (/d)
- \( N_o \) ~ organic nitrogen concentration (mg N/L)
- \( N_a \) ~ ammonia concentration (mg N/L)
- \( N_i \) ~ nitrite concentration (mg N/L)
Reaeration is a first order reaction, and net photosynthesis and the decay of BOD and transformation of nitrogen are zero order reactions. DO_{sat} is set at 9.09 mg/L, based on the value for oxygen solubility of pure water at 20° C and sea level. r_{oa} is set at 3.43 g O/g N, and r_{oi} at 1.14 g O/g N⁴⁹.

\( k_a \) was first approximated using the O’Connor-Dobbins formula:

**Equation 33**

\[
k_a = 3.93 \frac{\sqrt{q}}{d^{1.5}}
\]

where q is the average linear velocity (m/s), d is water depth (m), and k_a has units /d. This yielded a \( k_a \) of 0.0985 /d. However, upon initial testing of the model, this value was found to be too low to maintain aerobic conditions. As a result, the \( k_a \) was increased to 2 /d. This is still within the realm of possibility for reaeration coefficients⁴⁹, assuming some kind of human intervention to increase reaeration takes place and prevents the wetland from becoming and remaining anoxic.

Net photosynthesis will be calculated using the biomass estimate from Chapra (2008)⁴⁹, which assumes that nutrients are not limited, as will likely be the case in a constructed wetland receiving wastewater. By this method:

**Equation 34**

\[
P = r_o G_{max} 1.066 T^{-20} \varphi t A
\]

**Equation 35**

\[
R = r_o k_{ra} 1.08 T^{-20} A
\]

where

- P ~ daily average plant photosynthesis rate
- R ~ daily average plant respiration rate
• $r_o$ ~ oxygen generated per unit mass of plant biomass produced (g/mg Chl-a)
• $G_{max}$ ~ maximum plant growth rate for optimal light conditions and excess nutrients (/d)
• $T$ ~ water temperature ($^\circ$ C)
• $A$ ~ concentration of plant biomass (mg Chl-a/m$^3$)
• $\varphi_i$ ~ attenuation of growth due to light
• $k_{ra}$ ~ respiration rate of plants (/d)

These equations are often simplified to a rule of thumb value, where $r_o = 0.125$ g/mg, $T = 20^\circ$ C, $G_{max} = 2$ /d, and $k_{ra} = 0.2$ /d, giving

**Equation 36**

$$P = 0.25a$$

**Equation 37**

$$R = 0.025a$$

**Equation 38**

$$P_{net} = P - R = 0.225a$$

$k_d, k_{ai},$ and $k_{in}$ are the same values used in the BOD and nitrogen calculations.

The numerical form of this equation is:

**Equation 39**

$$DO_{i+1}^n = DO_i^n - \frac{u \Delta t}{\Delta x} (DO_i^n - DO_{i-1}^n) + \Delta t k_a (DO_{sat} - DO_i^n) + 0.225 \Delta t A_i^n - \Delta t k_d L_i^n$$

$$- \Delta t a_{oa} k_{death} A_i^n - \Delta t r_{ai} k_{ai} N_{ai}^n - \Delta t r_{in} k_{in} N_{in}^n$$

In cases in which dissolved oxygen has dropped to zero, the rate of BOD decay is assumed to be equal to the rate of advection, reaeration and net photosynthesis. In addition, nitrogen transformation ceases. As a result, changes in DO over time fall to zero. Once advection,
reaeration and net photosynthesis rates exceed BOD decay and nitrification rates, the original set of equations applies again.

4.4.8 Nanoparticles

The general continuity equation for nanoparticles is:

**Equation 40**

\[
\frac{d (NP_w + NP_{TSS})}{dt} = -u \frac{d (NP_w + NP_{TSS})}{dx} - \frac{v_{s,NP}}{d} NP_w - \frac{v_{s,TSS}}{d} NP_{TSS}
\]

where:

- \( NP_w \) ~ concentration of TiO\(_2\) nanoparticles suspended in water (mg TiO\(_2\)/L)
- \( NP_{TSS} \) ~ concentration of TiO\(_2\) nanoparticles sorbed to suspended solids (g TiO\(_2\)/g TSS)
- \( u \) ~ linear velocity (m/d)
- \( v_{s,NP} \) ~ settling velocity of nanoparticles entrained in water (m/d)
- \( v_{s,TSS} \) ~ settling velocity of nanoparticles sorbed to total suspended solids (m/d)

Using a linear free energy relationship, nanoparticles sorbed to total suspended solids can be expressed in terms of the total suspended solids concentration and the concentration of nanoparticles suspended in water:

**Equation 41**

\[
\frac{d(NP + NP_{TSS} k_{NP-TSS})}{dt} = -u \frac{d(NP + NP_{TSS} k_{NP-TSS})}{dx} - \frac{v_{s,NP}}{d} NP - \frac{v_{s,TSS}}{d} NP_{TSS} k_{NP-TSS}
\]

where:

- \( NP \) ~ concentration of TiO\(_2\) nanoparticles suspended in water (mg TiO\(_2\)/L)
- \( TSS \) ~ concentration of total suspended solids in water (mg TSS/L)
• \( k_{NP-TSS} \) ~ sorption coefficient between titanium dioxide nanoparticles and total suspended solids (L/mg)

This general equation assumes that nanoparticles will only reside suspended in water and sorbed to suspended matter, and that nanoparticles will not be removed via reactions such as dissolution. \( k_{NP-TSS} \) is set at 495 L/mg\(^{[50]}\). \( v_{s,NP} \) was calculated to be 0.36 m/d using Stokes’ Law (see section 4.4.5) assuming a particle diameter of 100 nm and a particle density of 4.26 g/cm\(^3\).

The numerical form of this equation is:

**Equation 42**

\[
NP_{i}^{n+1} = \frac{1}{1 + TSS_{i}^{n+1} k_{NP-TSS}} \left( NP_{i}^{n} [1 + TSS_{i}^{n} k_{NP-TSS}] - \frac{u \Delta t}{\Delta x} \left[ NP_{i}^{n} (1 + TSS_{i}^{n} k_{NP-TSS}) - NP_{i-1}^{n} (1 + TSS_{i-1}^{n} k_{NP-TSS}) \right] - \frac{v_{s,NP} \Delta t}{d} NP_{i}^{n} \right)
\]

\[- \frac{v_{s,TSS} \Delta t}{d} k_{NP-TSS} TSS_{i}^{n} NP_{i}^{n} \]

4.4.9 Cadmium

The general continuity equation for cadmium is:

**Equation 43**

\[
\frac{d(Cd_{w} + Cd_{TSS} + Cd_{NP})}{dt} = -u \frac{d(Cd_{w} + Cd_{TSS} + Cd_{NP})}{dx} - \frac{v_{s,TSS}}{d} Cd_{TSS} - \frac{v_{s,NP}}{d} Cd_{NP} - \frac{v_{s,TSS}}{d} Cd_{NP+TSS}
\]

where:

• \( Cd_{w} \) ~ concentration of cadmium dissolved in water (mg Cd/L)

• \( Cd_{TSS} \) ~ concentration of cadmium sorbed to suspended solids (g Cd/g TSS)

• \( Cd_{NP} \) ~ concentration of cadmium sorbed to suspended nanoparticles (g Cd/g TiO\(_2\))
• \( u \) ~ linear velocity (m/d)

• \( \text{Cd}_{\text{NP+TSS}} \) ~ concentration of cadmium sorbed to suspended nanoparticles that are sorbed to total suspended solids (g Cd/g TiO\(_2\))

Using a linear free energy relationship, cadmium sorbed to total suspended solids and nanoparticles can be expressed in terms of the total suspended solids or nanoparticle concentrations and the concentration of cadmium dissolved in water:

**Equation 44**

\[
\frac{d(Cd + Cd \times \text{TSS} \times k_{\text{Cd-TSS}} + Cd \times \text{NP} \times k_{\text{Cd-NP}})}{dt} = -u \frac{d(Cd + Cd \times \text{TSS} \times k_{\text{Cd-TSS}} + Cd \times \text{NP} \times k_{\text{Cd-NP}})}{dx} - \frac{v_{s,\text{TSS}}}{d} k_{\text{Cd-TSS}} \times \text{TSS} \times Cd
\]

\[
- \frac{v_{s,\text{NP}}}{d} k_{\text{Cd-NP}} \times \text{NP} \times Cd - \frac{v_{s,\text{TSS}}}{d} k_{\text{Cd-NP}} f_{\text{NP-TSS}} \times \text{NP} \times Cd
\]

where:

• \( \text{Cd} \) ~ concentration of cadmium dissolved in water (mg Cd/L)

• \( \text{TSS} \) ~ concentration of total suspended solids in water (mg TSS/L)

• \( k_{\text{Cd-TSS}} \) ~ sorption coefficient between cadmium and total suspended solids (L/mg)

• \( \text{NP} \) ~ concentration of nanoparticles in water (mg TiO\(_2\)/L)

• \( k_{\text{Cd-NP}} \) ~ sorption coefficient between cadmium and nanoparticles (-)

• \( f_{\text{NP-TSS}} \) ~ fraction of nanoparticles sorbed to total suspended solids (-)

This general equation assumes that cadmium will only reside dissolved in water and sorbed to suspended matter and nanoparticles. It also assumes cadmium will not be removed via other reactions such as precipitation. \( k_{\text{Cd-TSS}} \) is set at 4.7 L/mg\(^{[51]}\), and \( k_{\text{Cd-NP}} \) is set at 0.37 L/mg\(^{[43]}\). The numerical form of this equation is:
Equation 45

\[
Cd_i^{n+1} = \frac{1}{1 + TSS_i^{n+1}k_{Cd-TSS} + NP_i^{n+1}k_{Cd-NP}} \left( Cd_i^n \left[ 1 + TSS_i^n k_{Cd-TSS} + NP_i^n k_{Cd-NP} \right] \right)
\]

\[\frac{u\Delta t}{\Delta x} \left[ Cd_i^n \left[ 1 + TSS_i^n k_{Cd-TSS} + NP_i^n k_{Cd-NP} \right] \right]
\]

\[- C_d_{i-1}^n \left( 1 + TSS_{i-1}^n k_{Cd-TSS} + NP_i^n k_{Cd-NP} \right) - \frac{v_s TSS \Delta t}{d} k_{Cd-TSS} TSS_i^n Cd_i^n \]

\[- \frac{v_s NP \Delta t}{d} k_{Cd-NP} NP_i^n Cd_i^n - \frac{v_s TSS \Delta t}{d} k_{Cd-NP} f_{NP-TSS} NP_i^n Cd_i^n \]

where

Equation 46

\[f_{NP-TSS} = \frac{k_{NP-TSS} TSS_i^n}{1 + k_{NP-TSS} TSS_i^n} \]

Note that, in the model scheme without nanoparticles, the nanoparticle concentration will fall to zero, making the general equation for cadmium

Equation 47

\[\frac{d(Cd + Cd TSS k_{Cd-TSS})}{dt} = -u \frac{d(Cd + Cd NP k_{Cd-NP})}{dx} \]

and the numerical solution

Equation 48

\[
Cd_i^{n+1} = \frac{1}{1 + TSS_i^{n+1}k_{Cd-TSS}} \left( Cd_i^n \left[ 1 + TSS_i^n k_{Cd-TSS} \right] \right)
\]

\[\frac{u\Delta t}{\Delta x} \left[ Cd_i^n \left[ 1 + TSS_i^n k_{Cd-TSS} \right] - Cd_{i-1}^n \left( 1 + TSS_{i-1}^n k_{Cd-TSS} \right) \right]
\]

\[- \frac{v_s \Delta t}{d} k_{Cd-TSS} TSS_i^n Cd_i^n \]
4.5 Model Run Parameters

The model was run over the course of 1000 days, to allow wetland effluent concentrations to reach steady-state conditions. A control scenario without nanoparticles was run to establish base system outputs. Five different concentrations of nanoparticles were selected: 0.01778 mg/L, representing the average concentration of TiO$_2$ in wastewater$^{[31]}$, as well as concentrations of 0.01, 0.1, 1 and 10 mg/L TiO$_2$ to examine responses to increasing nanoparticle levels. Each of these concentrations was run in a scenario in which nanoparticles increase the growth rate of phytoplankton, as well as a scenario in which nanoparticles decrease the growth rate of phytoplankton.
5.0 RESULTS AND DISCUSSION

5.1 Impact of Background Nanoparticle Concentrations

Table 6 shows final effluent concentrations of constituents of interest with TiO$_2$ concentrations of 0 mg/L and 0.01778 mg/L. Note that in all cases other than phytoplankton and dissolved oxygen there was no difference between concentrations assuming a positive or a negative correlation between nanoparticle concentration and growth rate. Phytoplankton saw a 0.5% increase with a positive correlation, and no change with a negative correlation. As a result, changes to these concentrations were assumed to be negligible (see Figure 9). Dissolved oxygen saw a 2.7% increase with a positive correlation, and a 2.3% increase with a negative correlation. Since the difference between these two is negligible, the percent increase was averaged to 2.5% (see Figure 8). Phosphorus and total suspended solids final effluent concentrations were also unaffected by the presence of nanoparticles in wastewater effluent (see Figures 9 and 10, respectively). BOD and cadmium showed negligible changes in effluent concentration with the addition of nanoparticles – BOD increased by 2.8% and cadmium decreased by 1% (see Figures 11 and 12, respectively). NBOD overall increased by 13% (see Figure 13), with changes in species concentration ranging from a 47% increase in organic nitrogen to a 17% decrease in nitrate (see Figures 14 and 15).
The nitrification process is the most vulnerable to impacts of nanoparticles in this model. However, while TiO₂ nanoparticles are known to preferentially lower populations of nitrifying bacteria and decrease nitrification rates, the exact relationship is currently unknown. Yang et al. (2018)⁴ reported total nitrogen removal of 78.2% with no nanoparticles present, 38% removal with 1 mg/L TiO₂, and 50.3% removal with 50 mg/L TiO₂. It is difficult to draw conclusions on the relationship between nitrogen transformation rates and nanoparticles from three data points, but they at least suggest that the relationship between nitrogen transformation rates and TiO₂ concentrations is not linear. As a result, in this case it was assumed that the drop in nitrification rates would be like the decrease in TN removal rates at the lower concentration, 1 mg/L TiO₂. As the background concentration used in the model is two orders of magnitude smaller than this concentration, the change in nitrification rates will likely be different.

---

Table 7 - Effluent concentrations of constituents of interest at 1000 days

<table>
<thead>
<tr>
<th>Constituent</th>
<th>No Nanoparticles</th>
<th>Nanoparticles</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Nitrogen (mg N/L)</td>
<td>0.792</td>
<td>1.17</td>
<td>47.7%</td>
</tr>
<tr>
<td>Ammonia (mg N/L)</td>
<td>4.52</td>
<td>5.20</td>
<td>+15.0%</td>
</tr>
<tr>
<td>Nitrite (mg N/L)</td>
<td>1.48</td>
<td>1.32</td>
<td>-10.8%</td>
</tr>
<tr>
<td>Nitrate (mg N/L)</td>
<td>5.28</td>
<td>4.39</td>
<td>-16.9%</td>
</tr>
<tr>
<td>Phosphorus (mg N/L)</td>
<td>3.08</td>
<td>3.08</td>
<td>0%</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>2.50</td>
<td>2.57</td>
<td>+2.8%</td>
</tr>
<tr>
<td>NBOD (mg/L)</td>
<td>135</td>
<td>153</td>
<td>+13.3%</td>
</tr>
<tr>
<td>Total Suspended Solids (mg/L)</td>
<td>0.271</td>
<td>0.271</td>
<td>0%</td>
</tr>
<tr>
<td>Phytoplankton (mg Chl-a/L)</td>
<td>19.9</td>
<td>20</td>
<td>+0.5%</td>
</tr>
<tr>
<td>Dissolved Oxygen (mg/L)</td>
<td>5.13</td>
<td>5.27</td>
<td>+2.5%</td>
</tr>
<tr>
<td>Nanoparticles (μg/L)</td>
<td>0</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>Cadmium (μg/L)</td>
<td>1</td>
<td>0.99</td>
<td>-1%</td>
</tr>
</tbody>
</table>
While there are indications that TiO$_2$ nanoparticles impact phytoplankton, it is unlikely that there will be a noticeable impact at typical concentrations in wastewater effluent. With the relationship given by Kulacki and Cardinale (2018)$^{[42]}$, nanoparticle concentrations must be on the order of $10^2$ before significant changes to the growth rate of phytoplankton are seen. In addition, this model tested two extreme cases for nanoparticle impact on phytoplankton growth: growth is always increased, and growth is always decreased. Different phytoplankton species respond to TiO$_2$ nanoparticles differently, and increased growth rates in some will be balanced out by decreased growth rates in others$^{[42]}$. As a result, it is possible nanoparticles will have a net zero impact on the total phytoplankton concentrations in a system.

5.2 Nanoparticle Concentration Sensitivity Analysis

5.2.1 Nitrogen, Dissolved Oxygen and Phytoplankton

Model trials were run to analyze the sensitivity of each constituent of interest to nanoparticle concentrations, with TiO$_2$ input concentrations of 0, 0.01, 0.1, 1, and 10 mg/L (see Figure 16 for TiO$_2$ effluent concentrations). Organic nitrogen, phosphorus, BOD, and total suspended solids showed no change with increasing TiO$_2$ concentrations. The models indicate that, while the presence of nanoparticles has some impact on the effluent concentrations of ammonia, nitrite, nitrate, NBOD, phytoplankton, and dissolved oxygen, increasing the concentration of nanoparticles gives negligible changes(see Figures 17 through 21, respectively). Ammonia, nitrite, nitrate, NBOD and dissolved oxygen all see slightly lower peaks in concentration oscillations at the beginning of the model with increasing nanoparticle concentrations, but the steady state effluent concentrations remain largely unchanged. These amplitude changes are seen with nanoparticles increasing the growth rate of phytoplankton and
are likely a result of higher net photosynthesis and nitrate removal by phytoplankton. Phytoplankton see a higher dip in concentration within the first 25 days as nanoparticle concentrations increase, but only a significant change at 10 mg/L with a positive correlation between nanoparticle concentration and growth rate (see Figure 22). This is likely because the average nitrate concentration in this modeled scenario is the lowest, limiting the growth of phytoplankton. As with the other parameters, the steady state concentration of phytoplankton in the wetland effluent remained unchanged.

5.2.2 Cadmium

Cadmium results showed that dissolved and total cadmium are very sensitive to nanoparticle concentrations within the system (see Table 7). As nanoparticle concentrations in the wastewater effluent increase, the final dissolved concentration of cadmium decreases significantly (see Figure 23), as does the total cadmium concentration leaving the wetland, where total cadmium is the sum of dissolved cadmium, cadmium sorbed to total suspended solids, and cadmium sorbed to nanoparticles.

Table 8 – Cadmium concentrations in final wetland effluent

<table>
<thead>
<tr>
<th>TiO₂ (mg/L)</th>
<th>Cd Dissolved (μg/L)</th>
<th>Fraction dissolved (%)</th>
<th>Fraction sorbed to TSS (%)</th>
<th>Fraction sorbed to nanoparticles (%)</th>
<th>Total Cd in wetland effluent (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>44.0%</td>
<td>56.0%</td>
<td>0%</td>
<td>2.27</td>
</tr>
<tr>
<td>0.01</td>
<td>0.995</td>
<td>43.9%</td>
<td>55.9%</td>
<td>0.2%</td>
<td>2.27</td>
</tr>
<tr>
<td>0.1</td>
<td>0.947</td>
<td>43.3%</td>
<td>55.1%</td>
<td>1.6%</td>
<td>2.19</td>
</tr>
<tr>
<td>1</td>
<td>0.605</td>
<td>37.9%</td>
<td>48.3%</td>
<td>13.9%</td>
<td>1.60</td>
</tr>
<tr>
<td>10</td>
<td>0.0486</td>
<td>16.9%</td>
<td>21.5%</td>
<td>61.7%</td>
<td>0.288</td>
</tr>
</tbody>
</table>
At low concentration expected in wastewater, nanoparticles do not represent a significant compartment for cadmium, and as a result are not necessarily a concern for either cadmium removal or cadmium transport downstream. However, at 1 mg/L and 10 mg/L the nanoparticles become a significant sink for cadmium and enhance removal of cadmium from the wastewater effluent. At 1 mg/L, dissolved cadmium is reduced by 39.5%, and total cadmium by 29.5%. At 10 mg/L, dissolved cadmium is reduced by 95.1%, and total cadmium by 87.3%. These concentrations are not levels expected to be seen in wastewater effluent. However, TiO₂ nanoparticles could be added to wastewater treatment effluent to enhance removal of cadmium and other contaminants.
Figure 7 – Phytoplankton concentration profile at 1000 days (top) and phytoplankton wetland effluent concentration (bottom) with 0 mg/L TiO$_2$ and background TiO$_2$ concentrations. The addition of nanoparticles causes negligible changes.
Figure 8 – Dissolved oxygen concentration profile at 1000 days (top) and dissolved oxygen wetland effluent concentration (bottom) with 0 mg/L TiO$_2$ and background TiO$_2$ concentrations. The addition of nanoparticles causes negligible changes.
Figure 9 - Phosphorus concentration profile at 1000 days (top) and phosphorus wetland effluent concentration (bottom) with 0 mg/L TiO$_2$ and background TiO$_2$ concentrations. The addition of nanoparticles causes negligible changes.
Figure 10 – Total suspended solids concentration profile at 1000 days (top) and total suspended solids wetland effluent concentration (bottom) with 0 mg/L TiO$_2$ and background TiO$_2$ concentrations. The addition of nanoparticles causes negligible changes.
Figure 11 - BOD concentration profile at 1000 days (top) and BOD wetland effluent concentration (bottom) with 0 mg/L TiO\(_2\) and background TiO\(_2\) concentrations. The addition of nanoparticles causes negligible changes.
Figure 12 - Cadmium concentration profile at 1000 days (top) and cadmium wetland effluent concentration (bottom) with 0 mg/L TiO$_2$ and background TiO$_2$ concentrations. The addition of nanoparticles causes negligible changes.
Figure 13 - NBOD concentration profile at 1000 days (top) and NBOD wetland effluent concentration (bottom) with 0 mg/L TiO$_2$ and background TiO$_2$ concentrations. The addition of nanoparticles increased NBOD in the wetland effluent by 13.3%. 
Figure 14 – Organic nitrogen, ammonia, nitrite and nitrate concentration profiles at 1000 days.
Figure 15 – Organic nitrogen, ammonia, nitrite and nitrate wetland effluent concentration with 0 mg/L TiO\(_2\) and background TiO\(_2\) concentrations. The addition of nanoparticles increased organic nitrogen and ammonia by 47.7% and 15% respectively, and decreased nitrite and nitrate by 10.8% and 16.9%, respectively.
Figure 16 – Sensitivity analysis wetland effluent concentrations.
Figure 17 – Ammonia sensitivity analysis wetland effluent concentrations. Concentrations were calculated with both positive and negative correlations between nanoparticle concentrations and phytoplankton growth rates.
Figure 18 - Nitrite sensitivity analysis wetland effluent concentrations. Concentrations were calculated with both positive and negative correlations between nanoparticle concentrations and phytoplankton growth rates.
Figure 19 - Nitrate sensitivity analysis wetland effluent concentrations. Concentrations were calculated with both positive and negative correlations between nanoparticle concentrations and phytoplankton growth rates.
Figure 20 - NBOD sensitivity analysis wetland effluent concentrations. Concentrations were calculated with both positive and negative correlations between nanoparticle concentrations and phytoplankton growth rates.
Figure 21 – Dissolved oxygen sensitivity analysis wetland effluent concentrations. Concentrations were calculated with both positive and negative correlations between nanoparticle concentrations and phytoplankton growth rates.
Figure 22 - Phytoplankton sensitivity analysis wetland effluent concentrations. Concentrations were calculated with both positive and negative correlations between nanoparticle concentrations and phytoplankton growth rates.
Figure 23 – Cadmium sensitivity analysis wetland effluent concentrations.
6.0 CONCLUDING REMARKS

Titanium dioxide nanoparticles impact various water quality parameters of wastewater treatment wetlands to varying degrees. Nitrogen was the most significantly impacted by concentrations expected in wastewater effluent, with slower rates of nitrification as a result. This in turn has an impact on the efficacy of the wetland. Removal of organic nitrogen and ammonia may not be high enough that effluent concentrations comply with water quality standards as a result of reduced rates of nitrification. However, the reduction in removal rates may be lower for concentrations typically seen in wastewater effluent. Batch experiments on reductions in nitrogen removal were conducted with nanoparticle concentrations a few orders of magnitude above concentrations typically seen in wastewater. Further quantification of these reductions is needed to better model the impact on nitrification rates in treatment wetlands.

While several parameters saw some fluctuations with increasing nanoparticle concentrations in the wastewater effluent, only cadmium saw significant changes. At TiO$_2$ concentrations like those seen in wastewater effluent, the impacts on dissolved and total cadmium concentrations were low. However, at higher concentrations there were appreciable reductions in dissolved and total cadmium in the wetland effluent. This raises the question of whether nanoparticles could be used in wastewater treatment for contaminant removal. At high concentrations there is high contaminant removal, but also impacts on other processes in the system, namely nutrient reduction and removal. In addition, the concentrations of nanoparticles leaving in the wetland effluent increases with influent concentrations. These factors must be weighed against the potential contaminant removal enhancement, in order to decide whether nanoparticles create a net benefit in wastewater treatment.
Several things could be done to improve on this model and gain a better understanding of the impact of nanoparticles. Several processes were left out, including the nutrient uptake and decay of aquatic and terrestrial plants, denitrification and nitrogen fixation, population dynamics of nitrifying bacteria, and removal of cadmium by other processes such as precipitation. These and other factors would increase the complexity, and as a result the real-world applicability of the model. In addition, several parameters, such as the reduction in nitrification, were early experimental values that need further verification to improve accuracy. Nanoparticles may or may not play a significant role in water quality models at low concentrations, and likely can be discounted from most water quality models. However, models of systems with high nanoparticle input, whether incidental or deliberately added, should incorporate their impacts on the whole system to properly capture the nutrient and contaminant dynamics.
7.0 REFERENCES


APPENDIX A1: WETLAND MODEL WITHOUT NANOPARTICLES

% Madeline Hubbard
% December 15, 2019
% Master's Degree Project

clear all; close all; clc;

%% Define Constants

% wetland parameters
width = 350; %m
depth = 1; %m
length = 1000; %m
flow = 19000; %m^3/d
u = flow/(width*depth); %velocity, m/d
duration = 1000; %days

% N parameters
koa = 0.05; %OrgN to NH3 rxn constant, /d
kai = 0.075; %NH3 to NO2- rxn constant, /d
kin = 0.2; %NO2- to NO3- rxn constant, /d
ana = 10.8; %ratio of nitrogen to chlorophyll a in phytoplankton, g N/g Chl-a
ksn = 0.0125; %half-saturation constant for N limitation (g N/m^3)
knitr = -0.6; %first-order nitrification inhibition coefficient (m^3/g)

% P parameters
apa = 1.5; %ratio of phosphorus to chlorophyll a in phytoplankton, g P/g Chl-a
ksp = 0.003; %half-saturation constant for P limitation (g N/m^3)

% BOD parameters
roc = 2.69; %ratio of mass of O consumed per mass of OrgC decomposed, g O/g C
aoa = 165.7; %ratio of oxygen consumed to decompose phytoplankton to chlorophyll a in phytoplankton, g O/g Chl-a
kd = 0.075; %BOD decay rate, /d

% NBOD parameters
ron = 19.86; %ratio of mass of oxygen consumed per mass of OrgN+NH3+NO2- transformed

% TSS parameters
vsTSS = 0.22; %settling velocity of TSS, m/d

%A parameters
kgrowth = 2; %ideal growth rate of phytoplankton, /d
kdeath = 0.2; %death rate of phytoplankton, /d

% DO parameters
ka = 2; %reaeration coefficient, /d
DOsat = 9.09; %oxygen saturation, g/m^3
roo = 15.29; %ratio of O2 consumed to OrgN consumed, g O/g N
roa = 3.43; %ratio of O2 consumed to NH3 consumed, g O/g N
roi = 1.14; %ratio of O2 consumed to NO2- consumed, g O/g N
%NP parameters
kNPTSS = 495; %NP-TSS sorption coefficient, m3 water/g TSS
vsNP = 0.36; %settling velocity of NPs, m/d

%Cd parameters
kCdTSS = 4.7; %Cd-TSS sorption coefficient, m3 water/g TSS
kCdNP = 0.37; %Cd-NP sorption coefficient, m3 water/g TSS

%influent conditions
OrgN_in = 2; %organic nitrogen, g N/m3
NH3_in = 2.8; %ammonia, g N/m3
NO2_in = 0.74; %nitrite, g N/m3
NO3_in = 6.66; %nitrate, g N/m3
P_in = 3.1; %phosphorus, g /m3
BOD_in = 10; %BOD, g/m3
NBOD_in = 775.5; %nitrogenous BOD, g/m3
TSS_in = 15; %total suspended solids, g/m3
A_in = 0.009; %phytoplankton as Chl-a, g Chl-a/m3
DO_in = 6; %dissolved oxygen, g/m3
NP_in = 0; %TiO2 NPs, g TiO2/m3
Cd_in = 1e-3; %cadmium, g/m3

%initial wetland conditions
OrgN0 = 0.25; %organic nitrogen, g N/m3
NH30 = 0.25; %ammonia, g N/m3
NO20 = 0.25; %nitrite, g N/m3
NO30 = 1.25; %nitrate, g N/m3
P0 = 0.3; %phosphorus, g P/m3
BOD0 = 2; % BOD, g/m3
NBOD0 = 14.9; %nitrogenous BOD, g/m3
TSS0 = 3; %total suspended solids
A0 = 0.009; %phytoplankton as chlorophyll-a, g Chl-a/m3
DO0 = 8.5; %dissolved oxygen, g/m3
NP0 = 0; %TiO2 NPs, g TiO2/m3
Cd0 = 0; %cadmium, g/m3

% Define variables
dx = 10; %m
dt = 100; %s
dt = dt/86400; %convert dt from s to d
Nx = (length/dx)+1; %# of points over x
Nt = (duration/dt)+1; %# of points over t

% Define matrices, initial boundary conditions
OrgN = zeros(1,Nx);
Ammonia = zeros(1,Nx);
Nitrite = zeros(1,Nx);
Nitrate = zeros(1,Nx);
Phosphorus = zeros(1,Nx);
BOD = zeros(1,Nx);
NBOD = zeros(1,Nx);
TotalSuspendedSolids = zeros(1,Nx);
Phytoplankton = zeros(1,Nx);
DissolvedOxygen = zeros(1,Nx);
Nanoparticles = zeros(1,Nx);
Cadmium = zeros(1,Nx);

OrgN(:, :) = OrgN0;
Ammonia(:, :) = NH30;
Nitrite(:, :) = NO20;
Nitrate(:, :) = NO30;
Phosphorus(:, :) = P0;
BOD(:, :) = BOD0;
NBOD(:, :) = NBOD0;
TotalSuspendedSolids(:, :) = TSS0;
Phytoplankton(:, :) = A0;
DissolvedOxygen(:, :) = DO0;
Nanoparticles(:, :) = NP0;
Cadmium(:, :) = Cd0;

% data processing variables
Effluent_OrgN = zeros(1,Nt);
Effluent_NH3 = zeros(1,Nt);
Effluent_NO2 = zeros(1,Nt);
Effluent_NO3 = zeros(1,Nt);
Effluent_P = zeros(1,Nt);
Effluent_BOD = zeros(1,Nt);
Effluent_NBOD = zeros(1,Nt);
Effluent_TSS = zeros(1,Nt);
Effluent_A = zeros(1,Nt);
Effluent_DO = zeros(1,Nt);
Effluent_NP = zeros(1,Nt);
Effluent_Cd = zeros(1,Nt);

%% Calculations
for index1 = 2:Nt

% state index point
if rem(index1,100000) == 0
    disp(index1)
else
end

% define place holder matrices
Nonew = zeros(1,Nx);
Nanew = zeros(1,Nx);
Ninew = zeros(1,Nx);
Nnnew = zeros(1,Nx);
Pnew = zeros(1,Nx);
Lnew = zeros(1,Nx);
LNnew = zeros(1,Nx);
TSSnew = zeros(1,Nx);
Anew = zeros(1,Nx);
DOnew = zeros(1,Nx);
NPnew = zeros(1,Nx);
Cndnew = zeros(1,Nx);

% if index1 == 250
% break
% else
% end

% calculate new BOD, Nitrogen, DO, TSS, Cd
for index2 = 1:Nx
    if index2 == 1 % left barrier
        No1 = OrgN(index2);
        No2 = OrgN_in;
        Na1 = Ammonia(index2);
        Na2 = NH3_in;
        Ni1 = Nitrite(index2);
        Ni2 = NO2_in;
        Nn1 = Nitrate(index2);
        Nn2 = NO3_in;
        P1 = Phosphorus(index2);
        P2 = P_in;
        L1 = BOD(index2);
        L2 = BOD_in;
        TSS1 = TotalSuspendedSolids(index2);
        TSS2 = TSS_in;
        A1 = Phytoplankton(index2);
        A2 = A_in;
        DO1 = DissolvedOxygen(index2);
        DO2 = DO_in;
        NP1 = Nanoparticles(index2);
        NP2 = NP_in;
        Cd1 = Cadmium(index2);
        Cd2 = Cd_in;
    else
        No1 = OrgN(index2);
        No2 = OrgN(index2-1);
        Na1 = Ammonia(index2);
        Na2 = Ammonia(index2-1);
        Ni1 = Nitrite(index2);
        Ni2 = Nitrite(index2-1);
        Nn1 = Nitrate(index2);
        Nn2 = Nitrate(index2-1);
        P1 = Phosphorus(index2);
        P2 = Phosphorus(index2-1);
        L1 = BOD(index2);
        L2 = BOD(index2-1);
TSS1 = TotalSuspendedSolids(index2);
TSS2 = TotalSuspendedSolids(index2-1);
A1 = Phytoplankton(index2);
A2 = Phytoplankton(index2-1);
DO1 = DissolvedOxygen(index2);
DO2 = DissolvedOxygen(index2-1);
NP1 = Nanoparticles(index2);
NP2 = Nanoparticles(index2-1);
Cd1 = Cadmium(index2);
Cd2 = Cadmium(index2-1);

end

fnitr = 1 - exp(knitr*DO1); %nitrification limitation

if (DO1 - ((dt*u/dx)*(DO1-DO2)) + (ka*(DOsat-DO1)*dt) +
(0.225*A1*dt)) < ...
    (kd*L1*dt) + (aoa*kdeath*A1*dt) + (roa*kai*Na1*fnitr*dt) +
(roi*kin*Ni1*fnitr*dt))
    %dissolved oxygen drops below zero - anaerobic environment
    Nonew(index2) = No1 - ((dt*u/dx)*(No1-No2)) - (koa*No1*dt*fnitr);
    Nanew(index2) = Na1 - ((dt*u/dx)*(Na1-Na2)) + (koa*No1*dt*fnitr) -
(kai*Na1*dt*fnitr);
    Ninew(index2) = Ni1 - ((dt*u/dx)*(Ni1-Ni2)) + (kai*Na1*dt*fnitr) -
(kin*Ni1*dt*fnitr);
    Nnnew(index2) = Nn1 - ((dt*u/dx)*(Nn1-Nn2)) -
(ana*kgrowth*(Nn1/(ksn+Nn1))*A1*dt) + (kin*Ni1*dt*fnitr);
    Pnew(index2) = P1 - ((dt*u/dx)*(P1-P2)) -
(apoa*kgrowth*(P1/(ksp+P1))*A1*dt);
    Lnew(index2) = L1 - ((dt*u/dx)*(L1-L2)) + ((dt*u/dx)*(DO1-DO2)) +
(aoa*kdeath*A1*dt) - (ka*DOsat*dt) - (0.225*A1*dt);
    LNnew(index2) = ron*(Nonew(index2)+Nanew(index2)+Ninew(index2)) +
Nnnew(index2);
    TSSnew(index2) = TSS1 - ((dt*u/dx)*(TSS1-TSS2)) -
((vsTSS*dt/depth)*TSS1);
    kga = kgrowth*min([[(Na1/(ksn+Na1)),(P1/(ksp+P1))]]);
    Anew(index2) = A1 - ((dt*u/dx)*(A1-A2)) + (kga*A1*dt) -
(kdeath*A1*dt);
    DOnew(index2) = 0; % DO remains constant at zero
    coeff1 = 1/(1 + (kNPTSS*TSSnew(index2)));

86
coeff2 = NP1*(1 + (kNPTSS*TSS1));
coeff3 = NP2*(1 + (kNPTSS*TSS2));
coeff4 = kNPTSS*TSS1*NP1;

NPnew(index2) = coeff1*(coeff2 - ((u*dt/dx)*(coeff2-coeff3)) - ((vsNP*dt/depth)*NP1) - ((vsTSS*dt/depth)*coeff4));

coeff5 = 1/(1 + (kCdTSS*TSSnew(index2)) + (kCdNP*NPnew(index2)));
coeff6 = Cd1*(1 + (kCdTSS*TSS1) + (kCdNP*NP1));
coeff7 = Cd2*(1 + (kCdTSS*TSS2) + (kCdNP*NP2));
fNPTSS = (kNPTSS*TSS1)/(1+(kNPTSS*TSS1));
coeff8 = (kCdTSS*TSS1*Cd1) + (kCdNP*fNPTSS*NP1*Cd1);

Cdnew(index2) = coeff5*(coeff6 - ((u*dt/dx)*(coeff6-coeff7)) - ((vsTSS*dt/depth)*coeff8) - ((vsNP*dt/depth)*(kCdNP*NP1*Cd1)));

else %aerobic environment

Nonew(index2) = No1 - ((dt*u/dx)*(No1-No2)) - (koa*No1*dt);
Nanew(index2) = Na1 - ((dt*u/dx)*(Na1-Na2)) + (ana*kdeath*Al*dt) + (koa*Na1*dt) - (kai*Na1*dt*fnitr);
Ninew(index2) = Ni1 - ((dt*u/dx)*(Ni1-Ni2)) + (kai*Na1*dt*fnitr) - (kin*Ni1*dt*fnitr);
Nnnew(index2) = Nn1 - ((dt*u/dx)*(Nn1-Nn2)) - (ana*kgrowth*(Nn1/(ksn+Nn1))*Al*dt) + (kin*Ni1*dt*fnitr);
Pnew(index2) = P1 - ((dt*u/dx)*(P1-P2)) - (apa*kgrowth*(P1/(ksp+P1))*Al*dt) + (apa*kdeath*Al*dt);
Lnew(index2) = L1 - ((dt*u/dx)*(L1-L2)) - (kd*L1*dt);
LNnew(index2) = ron*(Nonew(index2)+Nanew(index2)+Ninew(index2)+Nnnew(index2));

TSSnew(index2) = TSS1 - ((dt*u/dx)*(TSS1-TSS2)) - ((vsTSS*dt/depth)*TSS1);
kga = kgrowth*min([[(Na1/(ksn+Na1)),(P1/(ksp+P1))]]);
Anew(index2) = A1 - ((dt*u/dx)*(A1-A2)) + (kga*Al*dt) - (kdeath*Al*dt);

DONew(index2) = DO1 - ((dt*u/dx)*(DO1-DO2)) + (ka*(DOsat-DO1)*dt) + (0.225*Al*dt) - (kd*L1*dt)... - (aoa*kdeath*Al*dt) - (roa*kai*Na1*fnitr*dt) - (roi*kin*Ni1*fnitr*dt);

coeff1 = 1/(1 + (kNPTSS*TSSnew(index2)));
coeff2 = NP1*(1 + (kNPTSS*TSS1));
coeff3 = NP2*(1 + (kNPTSS*TSS2));
coeff4 = kNPTSS*TSS1*NP1;

NPnew(index2) = coeff1*(coeff2 - ((u*dt/dx)*(coeff2-coeff3)) - ((vsNP*dt/depth)*NP1) - ((vsTSS*dt/depth)*coeff4));
coeff5 = 1/(1 + (kCdTSS*TSSnew(index2)) + (kCdNP*NPnew(index2)));  
coeff6 = Cd1*(1 + (kCdTSS*TSS1) + (kCdNP*NP1));  
coeff7 = Cd2*(1 + (kCdTSS*TSS2) + (kCdNP*NP2));  
fNPTSS = (kNPTSS*TSS1)/(1+(kNPTSS*TSS1));  
coeff8 = (kCdTSS*TSS1*Cd1) + (kCdNP*fNPTSS*NP1*Cd1));  
Cdnew(index2) = coeff5*(coeff6 - ((u*dt/dx)*(coeff6 - coeff7)) - ((vsTSS*dt/depth)*coeff8) - ((vsNP*dt/depth)*(kCdNP*NP1*Cd1)));  
end
end

% test break
% if index1 == 50000
% break
% else
% end

% assign new initial conditions
OrgN = Nonew;
Ammonia = Nanew;
Nitrite = Ninew;
Nitrate = Nnnew;
Phosphorus = Pnew;
BOD = Lnew;
NBOD = LNnew;
TotalSuspendedSolids = TSSnew;
Phytoplankton = Anew;
DissolvedOxygen = DOnew;
Nanoparticles = NPnew;
Cadmium = Cdnew;

% set negative conditions to zero
for index3 = 1:Nx
    if OrgN(index3) < 0
        OrgN(index3) = 0;
    elseif Ammonia(index3) < 0
        Ammonia(index3) = 0;
    elseif Nitrite(index3) < 0
        Nitrite(index3) = 0;
    elseif Nitrate(index3) < 0
        Nitrate(index3) = 0;
    elseif Phosphorus(index3) < 0
        Phosphorus(index3) = 0;
    elseif BOD(index3) < 0
        BOD(index3) = 0;
    elseif NBOD(index3) < 0
        NBOD(index3) = 0;
    elseif TotalSuspendedSolids(index3) < 0
        TotalSuspendedSolids(index3) = 0;
    elseif Phytoplankton(index3) < 0
        Phytoplankton(index3) = 0;
    elseif DissolvedOxygen(index3) < 0
        DissolvedOxygen(index3) = 0;
    end
end
elseif Nanoparticles(index3) < 0
    Nanoparticles(index3) = 0;
elseif Cadmium(index3) < 0
    Cadmium(index3) = 0;
end
end

% set kdeath

CheckKdeath = max(Anew);
if CheckKdeath > 0.02 %protocol for high phytoplankton conditions
    kdeath = 10;
else
    kdeath = 0.2;
end

% check for instability
CheckBOD = isnan(Lnew);
CheckOrgN = isnan(Nonew);
CheckAmmonia = isnan(Nanew);
CheckNitrite = isnan(Ninew);
CheckNitrate = isnan(Nnnew);
CheckPhosphorus = isnan(Pnew);
CheckPhytoplankton = isnan(Anew);
CheckDO = isnan(DOnew);
CheckTSS = isnan(TSSnew);
CheckNP = isnan(NPnew);
CheckCd = isnan(Cdnew);

CheckBOD = max(max(CheckBOD));
CheckOrgN = max(max(CheckOrgN));
CheckAmmonia = max(max(CheckAmmonia));
CheckNitrite = max(max(CheckNitrite));
CheckNitrate = max(max(CheckNitrate));
CheckPhosphorus = max(max(CheckPhosphorus));
CheckPhytoplankton = max(max(CheckPhytoplankton));
CheckDO = max(max(CheckDO));
CheckTSS = max(max(CheckTSS));
CheckNP = max(max(CheckNP));
CheckCd = max(max(CheckCd));

if CheckBOD == 1
    disp('broken BOD');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckOrgN == 1
    disp('broken organic N');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckAmmonia == 1
    disp('broken ammonia');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
break
else if CheckNitrite == 1
    disp('broken nitrite');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else if CheckNitrate == 1
    disp('broken nitrate');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else if CheckPhosphorus == 1
    disp('broken phosphorus');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else if CheckPhytoplankton == 1
    disp('broken phytoplankton');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else if CheckDO == 1
    disp('broken dissolved oxygen');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else if CheckTSS == 1
    disp('broken total suspended solids');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else if CheckNP == 1
    disp('broken nanoparticles');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else if CheckCd == 1
    disp('broken cadmium');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else
    end
end

% save effluent concentrations
Effluent_OrgN(index1) = OrgN(Nx);
Effluent_NH3(index1) = Ammonia(Nx);
Effluent_NO2(index1) = Nitrite(Nx);
Effluent_NO3(index1) = Nitrate(Nx);
Effluent_P(index1) = Phosphorus(Nx);
Effluent_BOD(index1) = BOD(Nx);
Effluent_NBOD(index1) = NBOD(Nx);
Effluent_TSS(index1) = TotalSuspendedSolids(Nx);
Effluent_A(index1) = Phytoplankton(Nx);
Effluent_DO(index1) = DissolvedOxygen(Nx);
Effluent_NP(index1) = Nanoparticles(Nx);
Effluent_Cd(index1) = Cadmium(Nx);
end

%% Save Data

cd 'E:\Grad Project\Data'

timestep data
save('Effluent_OrgN_0.mat','Effluent_OrgN');
save('Effluent_NH3_0.mat','Effluent_NH3');
save('Effluent_NO2_0.mat','Effluent_NO2');
save('Effluent_NO3_0.mat','Effluent_NO3');
save('Effluent_P_0.mat','Effluent_P');
save('Effluent_BOD_0.mat','Effluent_BOD');
save('Effluent_NBOD_0.mat','Effluent_NBOD');
save('Effluent_TSS_0.mat','Effluent_TSS');
save('Effluent_A_0.mat','Effluent_A');
save('Effluent_DO_0.mat','Effluent_DO');
save('Effluent_NP_0.mat','Effluent_NP');
save('Effluent_Cd_0.mat','Effluent_Cd');

profile data
save('OrgN_Profile_0.mat','OrgN');
save('NH3_Profile_0.mat','Ammonia');
save('NO2_Profile_0.mat','Nitrite');
save('NO3_Profile_0.mat','Nitrate');
save('P_Profile_0.mat','Phosphorus');
save('BOD_Profile_0.mat','BOD');
save('NBOD_Profile_0.mat','NBOD');
save('TSS_Profile_0.mat','TotalSuspendedSolids');
save('A_Profile_0.mat','Phytoplankton');
save('DO_Profile_0.mat','DissolvedOxygen');
save('NP_Profile_0.mat','Nanoparticles');
save('Cd_Profile_0.mat','Cadmium');
APPENDIX A2: WETLAND MODEL WITH NANOPARTICLES AND A POSITIVE CORRELATION TO PHYTOPLANKTON GROWTH RATE

% Madeline Hubbard
% December 15, 2019
% Master's Degree Project

clear all; close all; clc;

%% Define Constants

% wetland parameters
width = 350; % m
depth = 1; % m
length = 1000; % m
flow = 19000; % m3/d
u = flow/(width*depth); % velocity, m/d
duration = 1000; % days

% N parameters
koa = 0.029; % OrgN to NH3 rxn constant, /d
kai = 0.054; % NH3 to NO2- rxn constant, /d
kin = 0.179; % NO2- to NO3- rxn constant, /d
ana = 10.8; % ratio of nitrogen to chlorophyll a in phytoplankton, g N/g Chl-a
ksn = 0.0125; % half-saturation constant for N limitation (g N/m3)
knitr = -0.6; % first-order nitrification inhibition coefficient (m3/g)

% P parameters
apa = 1.5; % ratio of phosphorus to chlorophyll a in phytoplankton, g P/g Chl-a
ksp = 0.003; % half-saturation constant for P limitation (g N/m3)

% BOD parameters
roc = 2.69; % ratio of mass of O consumed per mass of OrgC decomposed, g O/g C
aoa = 165.7; % ratio of oxygen consumed to decompose phytoplankton to chlorophyll a in phytoplankton, g O/g Chl-a
kd = 0.0735; % BOD decay rate, /d

% NBOD parameters
ron = 19.86; % ratio of mass of oxygen consumed per mass of OrgN+NH3+NO2- transformed

% TSS parameters
vsTSS = 0.22; % settling velocity of TSS, m/d

% A parameters
kgrowth0 = 2; % base ideal growth rate of phytoplankton, /d
kdeath = 0.2; % death rate of phytoplankton, /d

% DO parameters
ka = 2; % reaeration coefficient, /d
DOsat = 9.09; % oxygen saturation, g/m3
roo = 15.29; % ratio of O2 consumed to OrgN consumed, g O/g N
roa = 3.43; % ratio of O2 consumed to NH3 consumed, g O/g N
roi = 1.14; % ratio of O2 consumed to NO2- consumed, g O/g N
%NP parameters
k_{NPTSS} = 495; %NP-TSS sorption coefficient, m^3 water/g TSS
vs_{NP} = 0.36; %settling velocity of NPs, m/d

%Cd parameters
k_{CdTSS} = 4.7; %Cd-TSS sorption coefficient, m^3 water/g TSS
k_{CdNP} = 0.37; %Cd-NP sorption coefficient, m^3 water/g TSS

%influent conditions
OrgN_{in} = 2; %organic nitrogen, g N/m^3
NH3_{in} = 2.8; %ammonia, g N/m^3
NO2_{in} = 0.74; %nitrite, g N/m^3
NO3_{in} = 6.66; %nitrate, g N/m^3
P_{in} = 3.1; %phosphorus, g P/m^3
BOD_{in} = 10; %BOD, g/m^3
NBOD_{in} = 775.5; %nitrogenous BOD, g/m^3
TSS_{in} = 15; %total suspended solids, g/m^3
A_{in} = 0.009; %phytoplankton as Chl-a, g Chl-a/m^3
DO_{in} = 6; %dissolved oxygen, g/m^3
NP_{in} = 0.01778; %TiO2 NPs, g TiO2/m^3

%initial wetland conditions
OrgN0 = 0.25; %organic nitrogen, g N/m^3
NH30 = 0.25; %ammonia, g N/m^3
NO20 = 0.25; %nitrite, g N/m^3
NO30 = 1.25; %nitrate, g N/m^3
P0 = 0.3; %phosphorus, g P/m^3
BOD0 = 2; %BOD, g/m^3
NBOD0 = 14.9; %nitrogenous BOD, g/m^3
TSS0 = 3; %total suspended solids
A0 = 0.009; %phytoplankton as chlorophyll-a, g Chl-a/m^3
DO0 = 8.5; %dissolved oxygen, g/m^3
NP0 = 0; %TiO2 NPs, g TiO2/m^3
Cd0 = 0; %cadmium, g/m^3

%% Define variables
dx = 10; %m
dt = 100; %s
dt = dt/86400; %convert dt from s to d
Nx = (length/dx)+1; %# of points over x
Nt = (duration/dt)+1; %# of points over t

%% Define matrices, initial boundary conditions
OrgN = zeros(1,Nx);
Ammonia = zeros(1,Nx);
Nitrite = zeros(1,Nx);
Nitrate = zeros(1,Nx);
Phosphorus = zeros(1,Nx);
BOD = zeros(1,Nx);
NBOD = zeros(1,Nx);
TotalSuspendedSolids = zeros(1,Nx);
Polyplankton = zeros(1,Nx);
DissolvedOxygen = zeros(1,Nx);
Nanoparticles = zeros(1,Nx);
Cadmium = zeros(1,Nx);

OrgN(:, :) = OrgN0;
Ammonia(:, :) = NH30;
Nitrite(:, :) = NO20;
Nitrate(:, :) = NO30;
Phosphorus(:, :) = P0;
BOD(:, :) = BOD0;
NBOD(:, :) = NBOD0;
TotalSuspendedSolids(:, :) = TSS0;
Polyplankton(:, :) = A0;
DissolvedOxygen(:, :) = DO0;
Nanoparticles(:, :) = NP0;
Cadmium(:, :) = Cd0;

% data processing variables
Effluent_OrgN = zeros(1,Nt);
Effluent_NH3 = zeros(1,Nt);
Effluent_NO2 = zeros(1,Nt);
Effluent_NO3 = zeros(1,Nt);
Effluent_P = zeros(1,Nt);
Effluent_BOD = zeros(1,Nt);
Effluent_NBOD = zeros(1,Nt);
Effluent_TSS = zeros(1,Nt);
Effluent_A = zeros(1,Nt);
Effluent_DO = zeros(1,Nt);
Effluent_NP = zeros(1,Nt);
Effluent_Cd = zeros(1,Nt);

% Calculations
for index1 = 2:Nt

% state index point
if rem(index1,100000) == 0
    disp(index1); disp(index1)
else
end

% define place holder matrices
Nonew = zeros(1,Nx);
Nanew = zeros(1,Nx);
Ninew = zeros(1,Nx);
Nnnew = zeros(1,Nx);
Pnew = zeros(1,Nx);
Lnew = zeros(1,Nx);
LNnew = zeros(1,Nx);
TSSnew = zeros(1,Nx);
Anew = zeros(1,Nx);
DOnew = zeros(1,Nx);
NPnew = zeros(1,Nx);
Cdnew = zeros(1,Nx);
% if index1 == 250
%   break
% else
% end

%calculate new BOD, Nitrogen, DO, TSS, Cd
for index2 = 1:Nx
  if index2 == 1 %left barrier
    No1 = OrgN(index2);
    No2 = OrgN_in;
    Na1 = Ammonia(index2);
    Na2 = NH3_in;
    Ni1 = Nitrite(index2);
    Ni2 = NO2_in;
    Nn1 = Nitrate(index2);
    Nn2 = NO3_in;
    P1 = Phosphorus(index2);
    P2 = P_in;
    L1 = BOD(index2);
    L2 = BOD_in;
    TSS1 = TotalSuspendedSolids(index2);
    TSS2 = TSS_in;
    A1 = Phytoplankton(index2);
    A2 = A_in;
    DO1 = DissolvedOxygen(index2);
    DO2 = DO_in;
    NP1 = Nanoparticles(index2);
    NP2 = NP_in;
    Cd1 = Cadmium(index2);
    Cd2 = Cd_in;
  else
    No1 = OrgN(index2);
    No2 = OrgN(index2-1);
    Na1 = Ammonia(index2);
    Na2 = Ammonia(index2-1);
    Ni1 = Nitrite(index2);
    Ni2 = Nitrite(index2-1);
    Nn1 = Nitrate(index2);
    Nn2 = Nitrate(index2-1);
    P1 = Phosphorus(index2);
    P2 = Phosphorus(index2-1);
  end
L1 = BOD(index2);
L2 = BOD(index2-1);

TSS1 = TotalSuspendedSolids(index2);
TSS2 = TotalSuspendedSolids(index2-1);

A1 = Phytoplankton(index2);
A2 = Phytoplankton(index2-1);

DO1 = DissolvedOxygen(index2);
DO2 = DissolvedOxygen(index2-1);

NP1 = Nanoparticles(index2);
NP2 = Nanoparticles(index2-1);

Cd1 = Cadmium(index2);
Cd2 = Cadmium(index2-1);

end

fnitr = 1 - exp(knitr*DO1); %nitrification limitation
kgrowth = kgrowth0 + (0.003*NP1); %kgrowth based on nanoparticle concentration

if (DO1 - ((dt*u/dx)*(DO1-DO2)) + (ka*(DOsat-DO1)*dt) +
(0.225*A1*dt)) < ...
  ((kd*L1*dt) + (aoa*kdeath*A1*dt) + (roa*kai*Nal*fnitr*dt) +
  (roi*kin*Nal*fnitr*dt))
  %dissolved oxygen drops below zero - anaerobic environment

  Nonew(index2) = No1 - ((dt*u/dx)*(No1-No2)) - (koa*No1*dt*fnitr);

  Nanew(index2) = Na1 - ((dt*u/dx)*(Na1-Na2)) + (koa*No1*dt*fnitr)
  - (kai*Nal*dt*fnitr);

  Ninew(index2) = Nl1 - ((dt*u/dx)*(Nl1-Nl2)) + (kai*Nal*dt*fnitr)
  - (kin*Nal*dt*fnitr);

  Nnnew(index2) = Nn1 - ((dt*u/dx)*(Nn1-Nn2)) -
  (ana*kgrowth*(Nnl/(ksn+Nnl))*A1*dt) + (kin*Nil*dt*fnitr);

  Pnew(index2) = P1 - ((dt*u/dx)*(P1-P2)) -
  (apa*kgrowth*(P1/(ksp+P1))*A1*dt);

  Lnew(index2) = L1 - ((dt*u/dx)*(L1-L2)) + ((dt*u/dx)*(DO1-DO2)) +
  (aoa*kdeath*A1*dt) - (ka*DOsat*dt) - (0.225*A1*dt);

  LNnew(index2) = ron*(Nonew(index2)+Nanew(index2)+Ninew(index2))+Nnnew(index2);

  TSSnew(index2) = TSS1 - ((dt*u/dx)*(TSS1-TSS2)) -
  ((vsTSS*dt/depth)*TSS1);

  kga = kgrowth*min(([Nal/(ksn+Nal)],(P1/(ksp+P1))));

  Anew(index2) = A1 - ((dt*u/dx)*(A1-A2)) + (kga*A1*dt) -
  (kdeath*A1*dt);
DOnew(index2) = 0; % DO remains constant at zero

coeff1 = 1/(1 + (kNPTSS*TSSnew(index2)));
coeff2 = NP1*(1 + (kNPTSS*TSS1));
coeff3 = NP2*(1 + (kNPTSS*TSS2));
coeff4 = kNPTSS*TSS1*NP1;

NPnew(index2) = coeff1*(coeff2 - ((u*dt/dx)*(coeff2-coeff3)) - ((vsNP*dt/depth)*NP1) - ((vsTSS*dt/depth)*coeff4));

coeff5 = 1/(1 + (kCdTSS*TSSnew(index2)) + (kCdNP*NPnew(index2)));
coeff6 = Cd1*(1 + (kCdTSS*TSS1) + (kCdNP*NP1));
coeff7 = Cd2*(1 + (kCdTSS*TSS2) + (kCdNP*NP2));

fNPTSS = (kNPTSS*TSS1)/(1+(kNPTSS*TSS1));
coeff8 = (kCdTSS*TSS1*Cd1) + (kCdNP*fNPTSS*NP1*Cd1);

Cdnew(index2) = coeff5*(coeff6 - ((u*dt/dx)*(coeff6-coeff7)) - ((vsTSS*dt/depth)*coeff8) - ((vsNP*dt/depth)*(kCdNP*NP1*Cd1)));

else % aerobic environment

Nonew(index2) = No1 - ((dt*u/dx)*(No1-No2)) - (koa*No1*dt);

Nanew(index2) = Na1 - ((dt*u/dx)*(Na1-Na2)) + (ana*kdeath*A1*dt) + (koa*Na1*dt) - (kai*Na1*dt*fnitr);

Ninew(index2) = Ni1 - ((dt*u/dx)*(Ni1-Ni2)) + (kai*Na1*dt*fnitr) - (kin*Ni1*dt*fnitr); 

Nnnew(index2) = Nn1 - ((dt*u/dx)*(Nn1-Nn2)) - (ana*kgrowth*(Nn1/(ksn+Nn1))*A1*dt) + (kin*Ni1*dt*fnitr);

Pnew(index2) = P1 - ((dt*u/dx)*(P1-P2)) - (apa*kgrowth*(P1/(ksp+P1))*A1*dt) + (apa*kdeath*A1*dt);

Lnew(index2) = L1 - ((dt*u/dx)*(L1-L2)) - (kd*L1*dt);

LNnew(index2) = ron*(Nonew(index2)+Nanew(index2)+Ninew(index2)+Nnnew(index2));

TSSnew(index2) = TSS1 - ((dt*u/dx)*(TSS1-TSS2)) - ((vsTSS*dt/depth)*TSS1);

kga = kgrowth*min([(Na1/(ksn+Na1)),(P1/(ksp+P1))]);

Anew(index2) = A1 - ((dt*u/dx)*(A1-A2)) + (kga*A1*dt) - (kdeath*A1*dt);

DOnew(index2) = DO1 - ((dt*u/dx)*(DO1-DO2)) + (ka*(DOsat-DO1)*dt) + (0.225*A1*dt) - (kd*L1*dt)
- (aoa*kdeath*A1*dt) - (roa*kai*Na1*fnitr*dt) - (roi*kin*Ni1*fnitr*dt);

coeff1 = 1/(1 + (kNPTSS*TSSnew(index2)));
coeff2 = NP1*(1 + (kNPTSS*TSS1));
coeff3 = NP2*(1 + (kNPTSS*TSS2));
coeff4 = kNPTSS*TSS1*NP1;
NPnew(index2) = coeff1*(coeff2 - ((u*dt/dx)*(coeff2-coeff3)) - ((vsNP*dt/depth)*NP1) - ((vsTSS*dt/depth)*coeff4));

coeff5 = 1/(1 + (kCdTSS*TSSnew(index2)) + (kCdNP*NPnew(index2)));
coeff6 = Cd1*(1 + (kCdTSS*TSS1) + (kCdNP*NP1));
coeff7 = Cd2*(1 + (kCdTSS*TSS2) + (kCdNP*NP2));
fNPTSS = (KNPNS*TSS1)/(1+(KNPNS*TSS1));
coeff8 = (kCdTSS*TSS1*Cd1) + (kCdNP*fNPTSS*NP1*Cd1));

Cdnew(index2) = coeff5*(coeff6 - ((u*dt/dx)*(coeff6 - coeff7)) - ((vsTSS*dt/depth)*coeff8) - ((vsNP*dt/depth)*(kCdNP*NP1*Cd1));

end
end

%     % test break
%     if index1 == 50000
%         break
%     else
%     end
%
% assign new initial conditions
OrgN = Nonew;
Ammonia = Nanew;
Nitrite = Ninew;
Nitrate = Nnew;
Phosphorus = Pnew;
BOD = Lnew;
NBOD = LNnew;
TotalSuspendedSolids = TSSnew;
Phytoplankton = Anew;
DissolvedOxygen = DOnew;
Nanoparticles = NPnew;
Cadmium = Cdnew;

% set negative conditions to zero
for index3 = 1:Nx
    if OrgN(index3) < 0
        OrgN(index3) = 0;
    elseif Ammonia(index3) < 0
        Ammonia(index3) = 0;
    elseif Nitrite(index3) < 0
        Nitrite(index3) = 0;
    elseif Nitrate(index3) < 0
        Nitrate(index3) = 0;
    elseif Phosphorus(index3) < 0
        Phosphorus(index3) = 0;
    elseif BOD(index3) < 0
        BOD(index3) = 0;
    elseif NBOD(index3) < 0
        NBOD(index3) = 0;
    elseif TotalSuspendedSolids(index3) < 0
        TotalSuspendedSolids(index3) = 0;
    end
elseif Phytoplankton(index3) < 0
    Phytoplankton(index3) = 0;
elseif DissolvedOxygen(index3) < 0
    DissolvedOxygen(index3) = 0;
elseif Nanoparticles(index3) < 0
    Nanoparticles(index3) = 0;
elseif Cadmium(index3) < 0
    Cadmium(index3) = 0;
end
end

% set kdeath
CheckKdeath = max(Anew);
if CheckKdeath > 0.02
    kdeath = 10;
else
    kdeath = 0.2;
end

% check for instability
CheckBOD = isnan(Lnew);
CheckOrgN = isnan(Nonew);
CheckAmmonia = isnan(Nanew);
CheckNitrite = isnan(Nnew);
CheckNitrate = isnan(Nnnew);
CheckPhosphorus = isnan(Pnew);
CheckPhytoplankton = isnan(Anew);
CheckDO = isnan(DOnew);
CheckTSS = isnan(TSSnew);
CheckNP = isnan(NPnew);
CheckCd = isnan(Cdnew);

CheckBOD = max(max(CheckBOD));
CheckOrgN = max(max(CheckOrgN));
CheckAmmonia = max(max(CheckAmmonia));
CheckNitrite = max(max(CheckNitrite));
CheckNitrate = max(max(CheckNitrate));
CheckPhosphorus = max(max(CheckPhosphorus));
CheckPhytoplankton = max(max(CheckPhytoplankton));
CheckDO = max(max(CheckDO));
CheckTSS = max(max(CheckTSS));
CheckNP = max(max(CheckNP));
CheckCd = max(max(CheckCd));

if CheckBOD == 1
    disp('broken BOD');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckOrgN == 1
    disp('broken organic N');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break

elseif CheckAmmonia == 1
    disp('broken ammonia');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckNitrite == 1
    disp('broken nitrite');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckNitrate == 1
    disp('broken nitrate');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckPhosphorus == 1
    disp('broken phosphorus');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckPhytoplankton == 1
    disp('broken phytoplankton');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckDO == 1
    disp('broken dissolved oxygen');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckTSS == 1
    disp('broken total suspended solids');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckNP == 1
    disp('broken nanoparticles');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
elseif CheckCd == 1
    disp('broken cadmium');
    breakstep = sprintf('timestep = %d',index1);
    disp(breakstep);
    break
else
    end

%save effluent concentrations
Effluent_OrgN(index1) = OrgN(Nx);
Effluent_NH3(index1) = Ammonia(Nx);
Effluent_NO2(index1) = Nitrite(Nx);
Effluent_NO3(index1) = Nitrate(Nx);
Effluent_P(index1) = Phosphorus(Nx);
Effluent_BOD(index1) = BOD(Nx);
Effluent_NBOD(index1) = NBOD(Nx);
Effluent_TSS(index1) = TotalSuspendedSolids(Nx);
Effluent_A(index1) = Phytoplankton(Nx);
Effluent_DO(index1) = DissolvedOxygen(Nx);
Effluent_NP(index1) = Nanoparticles(Nx);
Effluent_Cd(index1) = Cadmium(Nx);

end

%% Save Data

cd 'E:\Grad Project\Data'
%NP_in = NP_in*100000;

%timestep data
file1 = sprintf('Effluent_OrgN_PosA_%d.mat',NP_in);
save(file1,'Effluent_OrgN');
file2 = sprintf('Effluent_NH3_PosA_%d.mat',NP_in);
save(file2,'Effluent_NH3');
file3 = sprintf('Effluent_NO2_PosA_%d.mat',NP_in);
save(file3,'Effluent_NO2');
file4 = sprintf('Effluent_NO3_PosA_%d.mat',NP_in);
save(file4,'Effluent_NO3');
file5 = sprintf('Effluent_P_PosA_%d.mat',NP_in);
save(file5,'Effluent_P');
file6 = sprintf('Effluent_BOD_PosA_%d.mat',NP_in);
save(file6,'Effluent_BOD');
file7 = sprintf('Effluent_NBOD_PosA_%d.mat',NP_in);
save(file7,'Effluent_NBOD');
file8 = sprintf('Effluent_TSS_PosA_%d.mat',NP_in);
save(file8,'Effluent_TSS');
file9 = sprintf('Effluent_A_PosA_%d.mat',NP_in);
save(file9,'Effluent_A');
file10 = sprintf('Effluent_DO_PosA_%d.mat',NP_in);
save(file10,'Effluent_DO');
file11 = sprintf('Effluent_NP_PosA_%d.mat',NP_in);
save(file11,'Effluent_NP');
file12 = sprintf('Effluent_Cd_PosA_%d.mat',NP_in);
save(file12,'Effluent_Cd');

%profile data
file13 = sprintf('OrgN_Profile_PosA_%d.mat',NP_in);
save(file13,'OrgN');
file14 = sprintf('NH3_Profile_PosA_%d.mat',NP_in);
save(file14,'Ammonia');
file15 = sprintf('NO2_Profile_PosA_%d.mat',NP_in);
save(file15,'Nitrite');
file16 = sprintf('NO3_Profile_PosA_%d.mat',NP_in);
save(file16,'Nitrate');
file17 = sprintf('P_Profile_PosA_%d.mat',NP_in);
save(file17,'Phosphorus');
file18 = sprintf('BOD_Profile_PosA_%d.mat',NP_in);
save(file18,'BOD');
file19 = sprintf('NBOD_Profile_PosA_%d.mat',NP_in);
save(file19,'NBOD');
file20 = sprintf('TSS_Profile_PosA_%d.mat',NP_in);
save(file20,'TotalSuspendedSolids');
file21 = sprintf('A_Profile_PosA_%d.mat',NP_in);
save(file21,'Phytoplankton');
file22 = sprintf('DO_Profile_PosA_%d.mat',NP_in);
save(file22,'DissolvedOxygen');
file23 = sprintf('NP_Profile_PosA_%d.mat',NP_in);
save(file23,'Nanoparticles');
file24 = sprintf('Cd_Profile_PosA_%d.mat',NP_in);
save(file24,'Cadmium');
APPENDIX A3: WETLAND MODEL WITH NANOPARTICLES AND A NEGATIVE CORRELATION TO PHYTOPLANKTON GROWTH RATE

% Madeline Hubbard
% December 15, 2019
% Master's Degree Project

clear all; close all; clear;

%% Define Constants

% wetland parameters
width = 350; % m
depth = 1; % m
length = 1000; % m
flow = 19000; % m^3/d
u = flow/(width*depth); % velocity, m/d
duration = 1000; % days

% N parameters
koa = 0.029; % OrgN to NH3 rxn constant, /d
kai = 0.054; % NH3 to NO2- rxn constant, /d
kin = 0.179; % NO2- to NO3- rxn constant, /d
ana = 10.8; % ratio of nitrogen to chlorophyll a in phytoplankton, g N/g Chl-a
ksn = 0.0125; % half-saturation constant for N limitation (g N/m^3)
knitr = -0.6; % first-order nitrification inhibition coefficient (m^3/g)

% P parameters
apa = 1.5; % ratio of phosphorus to chlorophyll a in phytoplankton, g P/g Chl-a
ksp = 0.003; % half-saturation constant for P limitation (g N/m^3)

% BOD parameters
roc = 2.69; % ratio of mass of O consumed per mass of OrgC decomposed, g O/g C
aoa = 165.7; % ratio of oxygen consumed to decompose phytoplankton to chlorophyll a, g O/g Chl-a
kd = 0.0735; % BOD decay rate, /d

% NBOD parameters
ron = 19.86; % ratio of mass of oxygen consumed per mass of OrgN+NH3+NO2- transformed

% TSS parameters
vSTSS = 0.22; % settling velocity of TSS, m/d

% A parameters
kgrowth0 = 2; % base ideal growth rate of phytoplankton, /d
kdeath = 0.2; % death rate of phytoplankton, /d

% DO parameters
ka = 2; % reaeration coefficient, /d
DOsat = 9.09; % oxygen saturation, g/m^3
roo = 15.29; % ratio of O2 consumed to OrgN consumed, g O/g N
roa = 3.43; % ratio of O2 consumed to NH3 consumed, g O/g N
roi = 1.14; % ratio of O2 consumed to NO2- consumed, g O/g N
%NP parameters
kNPTSS = 495; %NP-TSS sorption coefficient, m3 water/g TSS
vsNP = 0.36; %settling velocity of NPs, m/d

%Cd parameters
kCdTSS = 4.7; %Cd-TSS sorption coefficient, m3 water/g TSS
kCdNP = 0.37; %Cd-NP sorption coefficient, m3 water/g TSS

%influent conditions
OrgN_in = 2; %organic nitrogen, g N/m3
NH3_in = 2.8; %ammonia, g N/m3
NO2_in = 0.74; %nitrite, g N/m3
NO3_in = 6.66; %nitrate, g N/m3
P_in = 3.1; %phosphorus, g P/m3
BOD_in = 10; % BOD, g/m3
NBOD_in = 775.5; %nitrogenous BOD, g/m3
TSS_in = 15; %total suspended solids, g/m3
A_in = 0.009; %phytoplankton as Chl-a, g Chl-a/m3
DO_in = 6; %dissolved oxygen, g/m3
%NP_in = 0.01778; %TiO2 NPs, g TiO2/m3
NP_in = 10;
Cd_in = 1e-3; %cadmium, g/m3

%initial wetland conditions
OrgN0 = 0.25; %organic nitrogen, g N/m3
NH30 = 0.25; %ammonia, g N/m3
NO20 = 0.25; %nitrite, g N/m3
NO30 = 1.25; %nitrate, g N/m3
P0 = 0.3; %phosphorus, g P/m3
BOD0 = 2; % BOD, g/m3
NBOD0 = 14.9; %nitrogenous BOD, g/m3
TSS0 = 3; %total suspended solids
A0 = 0.009; %phytoplankton as chlorophyll-a, g Chl-a/m3
DO0 = 8.5; %dissolved oxygen, g/m3
NP0 = 0; %TiO2 NPs, g TiO2/m3
Cd0 = 0; %cadmium, g/m3

%% Define variables
dx = 10; %m
dt = 100; %s
dt = dt/86400; %convert dt from s to d
Nx = (length/dx)+1; %# of points over x
Nt = (duration/dt)+1; %# of points over t

%% Define matrices, initial boundary conditions
OrgN = zeros(1,Nx);
Ammonia = zeros(1,Nx);
Nitrite = zeros(1,Nx);
Nitrate = zeros(1,Nx);
Phosphorus = zeros(1,Nx);
BOD = zeros(1,Nx);
NBOD = zeros(1,Nx);
TotalSuspendedSolids = zeros(1,Nx);
Phytoplankton = zeros(1,Nx);
DissolvedOxygen = zeros(1,Nx);
Nanoparticles = zeros(1,Nx);
Cadmium = zeros(1,Nx);

OrgN(:, :) = OrgN0;
Ammonia(:, :) = NH30;
Nitrite(:, :) = NO20;
Nitrate(:, :) = NO30;
Phosphorus(:, :) = P0;
BOD(:, :) = BOD0;
NBOD(:, :) = NBOD0;
TotalSuspendedSolids(:, :) = TSS0;
Phytoplankton(:, :) = A0;
DissolvedOxygen(:, :) = DO0;
Nanoparticles(:, :) = NP0;
Cadmium(:, :) = Cd0;

% data processing variables
Effluent_OrgN = zeros(1,Nt);
Effluent_NH3 = zeros(1,Nt);
Effluent_NO2 = zeros(1,Nt);
Effluent_NO3 = zeros(1,Nt);
Effluent_P = zeros(1,Nt);
Effluent_BOD = zeros(1,Nt);
Effluent_NBOD = zeros(1,Nt);
Effluent_TSS = zeros(1,Nt);
Effluent_A = zeros(1,Nt);
Effluent_DO = zeros(1,Nt);
Effluent_NP = zeros(1,Nt);
Effluent_Cd = zeros(1,Nt);

%% Calculations
for index1 = 2:Nt
    % state index point
    if rem(index1,100000) == 0
disp(index1)
    else
end

    % define place holder matrices
    Nonew = zeros(1,Nx);
    Nanew = zeros(1,Nx);
    Ninew = zeros(1,Nx);
    Nnnew = zeros(1,Nx);
    Pnew = zeros(1,Nx);
    Lnew = zeros(1,Nx);
    LNnew = zeros(1,Nx);
    TSSnew = zeros(1,Nx);
    Anew = zeros(1,Nx);
    DONew = zeros(1,Nx);
    NPnew = zeros(1,Nx);
    Cdnew = zeros(1,Nx);
% if index1 == 250
%   break
% else
% end

% calculate new BOD, Nitrogen, DO, TSS, Cd
for index2 = 1:Nx
  if index2 == 1 % left barrier
    No1 = OrgN(index2);
    No2 = OrgN_in;
    Na1 = Ammonia(index2);
    Na2 = NH3_in;
    Ni1 = Nitrite(index2);
    Ni2 = NO2_in;
    Nn1 = Nitrate(index2);
    Nn2 = NO3_in;
    P1 = Phosphorus(index2);
    P2 = P_in;
    L1 = BOD(index2);
    L2 = BOD_in;
    TSS1 = TotalSuspendedSolids(index2);
    TSS2 = TSS_in;
    A1 = Phytoplankton(index2);
    A2 = A_in;
    DO1 = DissolvedOxygen(index2);
    DO2 = DO_in;
    NP1 = Nanoparticles(index2);
    NP2 = NP_in;
    Cd1 = Cadmium(index2);
    Cd2 = Cd_in;
  else
    No1 = OrgN(index2);
    No2 = OrgN(index2-1);
    Na1 = Ammonia(index2);
    Na2 = Ammonia(index2-1);
    Ni1 = Nitrite(index2);
    Ni2 = Nitrite(index2-1);
    Nn1 = Nitrate(index2);
    Nn2 = Nitrate(index2-1);
    P1 = Phosphorus(index2);
    P2 = Phosphorus(index2-1);
  end
end
L1 = BOD(index2);
L2 = BOD(index2-1);

TSS1 = TotalSuspendedSolids(index2);
TSS2 = TotalSuspendedSolids(index2-1);

A1 = Phytoplankton(index2);
A2 = Phytoplankton(index2-1);

DO1 = DissolvedOxygen(index2);
DO2 = DissolvedOxygen(index2-1);

NP1 = Nanoparticles(index2);
NP2 = Nanoparticles(index2-1);

Cd1 = Cadmium(index2);
Cd2 = Cadmium(index2-1);

end

fnitr = 1 - exp(knitr*DO1);  % nitrification limitation
kgrowth = kgrowth0 - (0.0005*NP1);  % kgrowth based on nanoparticle concentration

if (DO1 - ((dt*u/dx)*(DO1-DO2)) + (ka*(DOsat-DO1)*dt) + (0.225*A1*dt)) < ...
  (kd*L1*dt) + (aoa*kdeath*A1*dt) + (roa*kai*Nal*fnitr*dt) + (roi*kin*Nil*fnitr*dt))
  % dissolved oxygen drops below zero - anaerobic environment
  Nonew(index2) = No1 - ((dt*u/dx)*(No1-No2)) - (koa*Nol*dt*fnitr);
  Nanew(index2) = Na1 - ((dt*u/dx)*(Na1-Na2)) + (koa*Nol*dt*fnitr) - (kai*Nal*dt*fnitr);
  Ninew(index2) = Ni1 - ((dt*u/dx)*(Ni1-Ni2)) + (kai*Nal*dt*fnitr) - (kin*Nil*dt*fnitr);
  Nnnew(index2) = Nn1 - ((dt*u/dx)*(Nn1-Nn2)) - (anakgrowth*(Nnl/(ksn+Nnl))*A1*dt) + (kin*Nil*dt*fnitr);
  Pnew(index2) = P1 - ((dt*u/dx)*(P1-P2)) - (apa*kgrowth*(P1/(ksp+P1))*A1*dt);
  Lnew(index2) = L1 - ((dt*u/dx)*(L1-L2)) + ((dt*u/dx)*(DO1-DO2)) + (aoa*kdeath*A1*dt) - (ka*DOsat*dt) - (0.225*A1*dt);
  LNnew(index2) = ron*(Nonew(index2)+Nanew(index2)+Ninew(index2))+Nnnew(index2);
  TSSnew(index2) = TSS1 - ((dt*u/dx)*(TSS1-TSS2)) - ((vsTSS*dt/depth)*TSS1);
  kga = kgrowth*min([Nal/(ksn+Nnl),P1/(ksp+P1)]);
  Anew(index2) = A1 - ((dt*u/dx)*(A1-A2)) + (kga*A1*dt) - (kdeath*A1*dt);
DOnew(index2) = 0; % DO remains constant at zero
coeff1 = 1/(1 + (kNPTSS*TSSnew(index2))); coat
coeff2 = NP1*(1 + (kNPTSS*TSS1));
coeff3 = NP2*(1 + (kNPTSS*TSS2));
coeff4 = kNPTSS*TSS1*NP1;

NPnew(index2) = coeff1*(coeff2 - ((u*dt/dx)*(coeff2-coeff3)) - ((vsNP*dt/depth)*NP1) - ((vsTSS*dt/depth)*coeff4));

coeff5 = 1/(1 + (kCdTSS*TSSnew(index2)) + (kCdNP*NPnew(index2)));
coeff6 = Cd1*(1 + (kCdTSS*TSS1) + (kCdNP*NP1));
fNPTSS = (kNPTSS*TSS1)/(1+(kNPTSS*TSS1));
coeff8 = (kCdTSS*TSS1*Cd1) + (kCdNP*fNPTSS*NP1*Cd1);

Cdnew(index2) = coeff5*(coeff6 - ((u*dt/dx)*(coeff6-coeff7)) - ((vsTSS*dt/depth)*coeff8) - ((vsNP*dt/depth)*(kCdNP*NP1*Cd1)));

else % aerobic environment

Nonew(index2) = No1 - ((dt*u/dx)*(No1-No2)) - (koa*No1*dt);

Nanew(index2) = Na1 - ((dt*u/dx)*(Na1-Na2)) + (ana*kdeath*Al*dt) + (kai*Na1*dt*fnitr);

Ninew(index2) = Ni1 - ((dt*u/dx)*(Ni1-Ni2)) + (kai*Na1*dt*fnitr) - (kin*Ni1*dt*fnitr);

Nnnew(index2) = Nn1 - ((dt*u/dx)*(Nn1-Nn2)) - (ana*kgrowth*(Nn1/(ksn+Nn1))*A1*dt) + (kin*Ni1*dt*fnitr);

Pnew(index2) = P1 - ((dt*u/dx)*(P1-P2)) - (apa*kgrowth*(P1/(ksp+P1))*A1*dt) + (apa*kdeath*Al*dt);}

Lnew(index2) = L1 - ((dt*u/dx)*(L1-L2)) - (kd*L1*dt);

LNnew(index2) = ron*(Nonew(index2)+Nanew(index2)+Ninew(index2));

TSSnew(index2) = TSS1 - ((dt*u/dx)*(TSS1-TSS2)) - ((vsTSS*dt/depth)*TSS1);

kga = kgrowth*min([Na1/(ksn+Na1),P1/(ksp+P1)]);

Anew(index2) = A1 - ((dt*u/dx)*(A1-A2)) + (kga*A1*dt) - (kdeath*Al*dt);

DOnew(index2) = DO1 - ((dt*u/dx)*(DO1-DO2)) + (ka*(DOsat-DO1)*dt) + (0.225*A1*dt) - (kd*L1*dt)...
- (aoa*kdeath*Al*dt) - (roa*kai*Na1*fnitr*dt) - (roi*kin*Ni1*fnitr*dt);

coeff1 = 1/(1 + (kNPTSS*TSSnew(index2))); coat
coeff2 = NP1*(1 + (kNPTSS*TSS1));
coeff3 = NP2*(1 + (kNPTSS*TSS2));
coeff4 = kNPTSS*TSS1*NP1;
NPnew(index2) = coeff1*(coeff2 - ((u*dt/dx)*(coeff2-coeff3)) - ((vsNP*dt/depth)*NP1) - ((vsTSS*dt/depth)*coeff4));

coeff5 = 1/(1 + (kCdTSS*TSSnew(index2)) + (kCdNP*NPnew(index2)));
coeff6 = Cd1*(1 + (kCdTSS*TSS1) + (kCdNP*NP1));
coeff7 = Cd2*(1 + (kCdTSS*TSS2) + (kCdNP*NP2));
fNPTSS = (kNPTSS*TSS1)/(1+(kNPTSS*TSS1));
coeff8 = (kCdTSS*TSS1*Cd1) + (kCdNP*fNPTSS*NP1*Cd1));

Cdnew(index2) = coeff5*(coeff6 - ((u*dt/dx)*(coeff6-coeff7)) - ((vsTSS*dt/depth)*coeff8) - ((vsNP*dt/depth)*(kCdNP*NP1*Cd1)));
\texttt{elseif \hspace{1em} Phytoplankton(index3) < 0}
\texttt{Phytoplankton(index3) = 0;}
\texttt{elseif \hspace{1em} DissolvedOxygen(index3) < 0}
\texttt{DissolvedOxygen(index3) = 0;}
\texttt{elseif \hspace{1em} Nanoparticles(index3) < 0}
\texttt{Nanoparticles(index3) = 0;}
\texttt{elseif \hspace{1em} Cadmium(index3) < 0}
\texttt{Cadmium(index3) = 0;}
\texttt{end}
\texttt{end}

\% set \texttt{kdeath}
\texttt{CheckKdeath = max(Anew);} \\
\texttt{if \hspace{1em} CheckKdeath > 0.02 \hspace{1em} \texttt{\%protocol for high phytoplankton conditions}}
\texttt{kdeath = 10;}
\texttt{else}
\texttt{kdeath = 0.2;}
\texttt{end}

\% check for instability
\texttt{CheckBOD = isnan(Lnew);} \\
\texttt{CheckOrgN = isnan(Nonew);} \\
\texttt{CheckAmmonia = isnan(Nanew);} \\
\texttt{CheckNitrite = isnan(Ninew);} \\
\texttt{CheckNitrate = isnan(Nnnew);} \\
\texttt{CheckPhosphorus = isnan(Pnew);} \\
\texttt{CheckPhytoplankton = isnan(Anew);} \\
\texttt{CheckDO = isnan(DOnew);} \\
\texttt{CheckTSS = isnan(TSSnew);} \\
\texttt{CheckNP = isnan(NPnew);} \\
\texttt{CheckCd = isnan(Cdnew);} \\
\texttt{CheckBOD = max(max(CheckBOD));} \\
\texttt{CheckOrgN = max(max(CheckOrgN));} \\
\texttt{CheckAmmonia = max(max(CheckAmmonia));} \\
\texttt{CheckNitrite = max(max(CheckNitrite));} \\
\texttt{CheckNitrate = max(max(CheckNitrate));} \\
\texttt{CheckPhosphorus = max(max(CheckPhosphorus));} \\
\texttt{CheckPhytoplankton = max(max(CheckPhytoplankton));} \\
\texttt{CheckDO = max(max(CheckDO));} \\
\texttt{CheckTSS = max(max(CheckTSS));} \\
\texttt{CheckNP = max(max(CheckNP));} \\
\texttt{CheckCd = max(max(CheckCd));}

\texttt{if \hspace{1em} CheckBOD == 1}
\texttt{disp('broken BOD');} \\
\texttt{breakstep = sprintf('timestep = %d',index1);} \\
\texttt{disp(breakstep);} \\
\texttt{break}
\texttt{elseif \hspace{1em} CheckOrgN ==1}
\texttt{disp('broken organic N');} \\
\texttt{breakstep = sprintf('timestep = %d',index1);} \\
\texttt{disp(breakstep);} \\
\texttt{break}
elseif CheckAmmonia == 1
disp('broken ammonia');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
elseif CheckNitrite == 1
disp('broken nitrite');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
elseif CheckNitrate == 1
disp('broken nitrate');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
elseif CheckPhosphorus == 1
disp('broken phosphorus');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
elseif CheckPhytoplankton == 1
disp('broken phytoplankton');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
elseif CheckDO == 1
disp('broken dissolved oxygen');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
elseif CheckTSS == 1
disp('broken total suspended solids');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
elseif CheckNP == 1
disp('broken nanoparticles');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
elseif CheckCd == 1
disp('broken cadmium');
breakstep = sprintf('timestep = %d',index1);
disp(breakstep);
break
else end

%save effluent concentrations
Effluent_OrgN(index1) = OrgN(Nx);
Effluent_NH3(index1) = Ammonia(Nx);
Effluent_NO2(index1) = Nitrite(Nx);
Effluent_NO3(index1) = Nitrate(Nx);
Effluent_P(index1) = Phosphorus(Nx);
Effluent_BOD(index1) = BOD(Nx);
Effluent_NBOD(index1) = NBOD(Nx);
Effluent_TSS(index1) = TotalSuspendedSolids(Nx);
Effluent_A(index1) = Phytoplankton(Nx);
Effluent_DO(index1) = DissolvedOxygen(Nx);
Effluent_NP(index1) = Nanoparticles(Nx);
Effluent_Cd(index1) = Cadmium(Nx);
end

%% Save Data
cd 'E:\Grad Project\Data'
%NP_in = NP_in*100000;
%timestep data
file1 = sprintf('Effluent_OrgN_NegA_%d.mat',NP_in);
save(file1,'Effluent_OrgN');
file2 = sprintf('Effluent_NH3_NegA_%d.mat',NP_in);
save(file2,'Effluent_NH3');
file3 = sprintf('Effluent_NO2_NegA_%d.mat',NP_in);
save(file3,'Effluent_NO2');
file4 = sprintf('Effluent_NO3_NegA_%d.mat',NP_in);
save(file4,'Effluent_NO3');
file5 = sprintf('Effluent_P_NegA_%d.mat',NP_in);
save(file5,'Effluent_P');
file6 = sprintf('Effluent_BOD_NegA_%d.mat',NP_in);
save(file6,'Effluent_BOD');
file7 = sprintf('Effluent_NBOD_NegA_%d.mat',NP_in);
save(file7,'Effluent_NBOD');
file8 = sprintf('Effluent_TSS_NegA_%d.mat',NP_in);
save(file8,'Effluent_TSS');
file9 = sprintf('Effluent_A_NegA_%d.mat',NP_in);
save(file9,'Effluent_A');
file10 = sprintf('Effluent_DO_NegA_%d.mat',NP_in);
save(file10,'Effluent_DO');
file11 = sprintf('Effluent_NP_NegA_%d.mat',NP_in);
save(file11,'Effluent_NP');
file12 = sprintf('Effluent_Cd_NegA_%d.mat',NP_in);
save(file12,'Effluent_Cd');
%profile data
file13 = sprintf('OrgN_Profile_NegA_%d.mat',NP_in);
save(file13,'OrgN');
file14 = sprintf('NH3_Profile_NegA_%d.mat',NP_in);
save(file14,'Ammonia');
file15 = sprintf('NO2_Profile_NegA_%d.mat',NP_in);
save(file15,'Nitrite');
file16 = sprintf('NO3_Profile_NegA_%d.mat',NP_in);
save(file16,'Nitrate');
file17 = sprintf('P_Profile_NegA_%d.mat',NP_in);
save(file17,'Phosphorus');
file18 = sprintf('BOD_Profile_NegA_%d.mat',NP_in);
save(file18,'BOD');
file19 = sprintf('NBOD_Profile_NegA_%d.mat',NP_in);
save(file19,'NBOD');
file20 = sprintf('TSS_Profile_NegA_%d.mat',NP_in);
save(file20,'TotalSuspendedSolids');
file21 = sprintf('A_Profile_NegA_%d.mat',NP_in);
save(file21,'Phytoplankton');
file22 = sprintf('DO_Profile_NegA_%d.mat',NP_in);
save(file22,'DissolvedOxygen');
file23 = sprintf('NP_Profile_NegA_%d.mat',NP_in);
save(file23,'Nanoparticles');
file24 = sprintf('Cd_Profile_NegA_%d.mat',NP_in);
save(file24,'Cadmium');

%% Plot Data
%% Time = 0:dt:duration;
figure(1)
plot(Time,Effluent_OrgN);
title('Organic Nitrogen Concentration (g N/m^3)');
xlabel('time (s)');
figure(2)
plot(Time,Effluent_NH3);
title('Ammonia Concentration (g N/m^3)');
xlabel('time (s)');
figure(3)
plot(Time,Effluent_NO2);
title('Nitrite Concentration (g N/m^3)');
xlabel('time (s)');
figure(4)
plot(Time,Effluent_NO3);
figure(5)
plot(Time,Effluent_P);
figure(6)
plot(Time,Effluent_BOD);
figure(7)
plot(Time,Effluent_NBOD);
figure(8)
plot(Time,Effluent_TSS);
figure(9)
plot(Time,Effluent_A);
plot(Time, Effluent_NP);
title('Nanoparticle Concentration (g TiO_2/m^3)');
xlabel('time (s)');

figure(11)
plot(Time, Effluent_Cd);
title('Cadmium Concentration (g/m^3)');
xlabel('time (s)');