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A CHEMICAL TRANSPORT MODEL OF INTERNAL LOADING IN LAKE ERIE

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RATIONALE

Internal recycling of nutrients and contaminants from sediments is a well-recognized and important chemical load to the Lake Erie water column. However, recent ecosystem changes (Mills et al. 1993) and P load reductions have led to significant changes in nutrient cycling and to the oligotrophication of the off-shore regions of Lake Erie (Fahnenstiel et al. 1998). In addition, as more sophisticated ecosystem models are developed, such as the Lake Erie Ecosystem Model (LEEM; Locci and Koonce 1999; Koonce 2000) current models of the chemical exchange between sediments and water are inadequate. The objective of the project was to adapt an existing model of sediment-water exchange developed for marine systems to the freshwater environment of the Great Lakes

APPROACH

The objective of the project was to develop a model of the nutrient and metal exchange between sediment and the water column to improve predictions of the internal chemical loading to Lake Erie. The model CANDI (Boudreau 1996) which was developed for marine sediments was modified for use in Lake Erie. CANDI was selected because it was developed as a comprehensive and generic model of sediment and nutrient diagenetic processes. The computer model couples organic matter degradation with sediment oxygen consumption, nitrate reduction, the dissolution and reduction of manganese dioxide and ferric hydroxide, and sulfate reduction which results in the release of phosphate, ammonia, sulfide, dissolved manganese, dissolved iron, carbonate and methane (Table 1). The model also considers the reoxidation of upwardly mobile reduced substances, and bioturbation and irrigation of bottom sediments by solving a series of non-linear, coupled differential equations (Table 2):

ıle 1. Irreversible Reactions (A-1 to A-19) and Alkalinity Conservation (A-20). Reactions A-1 to A-6 represent the net degradation of organic matter deposited from the water column. Reactions A-7 to A-16 describe the reoxidation of secondary species produced during the oxidation of organic matter. Reactions A-17 to A-19 correspond to the non-reductive precipitation of carbonate and sulfide mineral phases. The irreversible production or consumption of protons is buffered by the dissolved carbonate/sulfide acid-base interconversions (A-20).

$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (x+2y)O_2 + (y+2z)HCO_3^- \xrightarrow{R_1} (x+y+2z)CO_2 + yNO_3^- + zHPO_4^{2-} + (x+2y+2z)H_2O$	A-1
$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + \left(\frac{4x+3y}{5}\right)NO_3^- \xrightarrow{R_2} \left(\frac{2x+4y}{5}\right)N_2 + \left(\frac{x-3y+10z}{5}\right)CO_2 + \left(\frac{4x+3y-10z}{5}\right)HCO_3^- + zHPO_4^{2-} + \left(\frac{3x+6y+10z}{5}\right)H_2O$	A-2
$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 2xMnO_2 + (3x+y-2z)CO_2 + (x+y-2z)H_2O \xrightarrow{R_3} 2xMn^{2+} + (4x+y-2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-}$	A-3
$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 4xFe(OH)_3 + (7x+y-2z)CO_2 \xrightarrow{R_4} 4xFe^{2+} + (8x+y-2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-} + (3x-y+2z)H_2O$	A-4
$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + \frac{x}{2}SO_4^{2-} + (y-2z)CO_2 + (y-2z)H_2O \xrightarrow{R_5} \frac{x}{2}H_2S + (x+y-2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-}$	A-5
$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (y-2z)H_2O \xrightarrow{R_6} \frac{x}{2}CH_4 + \left(\frac{x-2y+4z}{2}\right)CO_2 + (y-2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-}$	A-6
$Mn^{2+} + \frac{1}{2}O_2 + 2HCO_3^- \xrightarrow{R_7} MnO_2 + 2CO_2 + H_2O$	A-7
$Fe^{2+} + \frac{1}{4}O_2 + 2HCO_3^- + \frac{1}{2}H_2O \xrightarrow{R_8} Fe(OH)_3 + 2CO_2$	A-8
$2Fe^{2+} + MnO_2 + 2HCO_3^- + 2H_2O \xrightarrow{R_9} 2Fe(OH)_3 + Mn^{2+} + 2CO_2$	A-9
$NH_4^+ + 2O_2 + 2HCO_3^- \xrightarrow{R_{10}} NO_3^- + 2CO_2 + 3H_2O$	A-10
$H_2S + 2O_2 + 2HCO_3^- \xrightarrow{R_{11}} SO_4^{2-} + 2CO_2 + 2H_2O$	A-11
$H_2S + 2CO_2 + MnO_2 \xrightarrow{R_{12}} Mn^{2+} + S^o + 2HCO_3^-$	A-12
$H_2S + 4CO_2 + 2Fe(OH)_3 \xrightarrow{R_{13}} 2Fe^{2+} + S^o + 4HCO_3^- + 2H_2O$	A-13
$FeS + 2O_2 \xrightarrow{R_{14}} Fe^{2+} + SO_4^{2-}$	A-14
$CH_4 + 2O_2 \xrightarrow{R_{15}} CO_2 + 2H_2O$	A-15
$CH_4 + CO_2 + SO_4^{2-} \xrightarrow{R_{16}} 2HCO_3^- + H_2S$	A-16
$Mn^{2+} + 2HCO_3^- \xrightarrow{R_{17}} MnCO_3 + CO_2 + H_2O$	A-17
$Fe^{2+} + 2HCO_3^- \xrightarrow{R_{18}} FeCO_3 + CO_2 + H_2O$	A-18
$Fe^{2+} + 2HCO_3^- + H_2S \xrightarrow{R_{19}} FeS + 2CO_2 + 2H_2O$	A-19
$CO_3^{2-} + \delta CO_2 + \delta H_2O + (1-\delta)H_2S \leftrightarrows (1+\delta)HCO_3^- + (1-\delta)HS^- \qquad 0 \le \delta \le 1$	A-20

Table 2. Summary of transport-reaction equations included in the model CANDI (from Boudreau 1996).

(a) for each organic matter type (solid)

$$\frac{\partial(G_i)}{\partial t} = \frac{1}{\varphi_s}\frac{\partial}{\partial x}\left[\underbrace{\varphi_s D_B(x)\frac{\partial(G_i)}{\partial x}}_{\text{Biotubation}} - \underbrace{\varphi_s w(G_i)}_{\text{Burial}}\right] - \underbrace{k_i(G_i)R_{Ox}}_{\text{Reactions (1)–(6)}} \quad i = 1, 2;$$

(b) oxygen (solute)

$$\frac{\partial(O_2)}{\partial t} = \frac{1}{\varphi}\frac{\partial}{\partial x}\left[\underbrace{\varphi D'_{O_2}\frac{\partial(O_2)}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{\varphi u(O_2)}_{\text{Burial}}\right] + \underbrace{\alpha(x)[(O_2)_o - (O_2)]}_{\text{Irrigation}} - \underbrace{\frac{\varphi_s(A+2B)}{\delta A}\left\{\sum k_i G_i\right\}R_{O_2}}_{\text{Reaction (1)}}$$

$$-\left\{\underbrace{2R_{NHO_3}}_{\text{Reaction (11)}} + \underbrace{2R_{SO_4}}_{\text{Reaction (10)}} + \underbrace{R_{MnOx}}_{\text{Reaction (9)}} + \underbrace{R_{FeOx}}_{\text{Reaction (8)}} + \underbrace{R_{CHAOx}}_{\text{Reaction (12)}} + \underbrace{2R_{FeSO_4}}_{\text{Reaction (15)}}\right\};$$

(c) nitrate (solute)

$$\frac{\partial(NO_3^-)}{\partial t} = \frac{1}{\varphi}\frac{\partial}{\partial x}\left[\underbrace{\varphi D'_{NO_3}\frac{\partial(NO_3^-)}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{\varphi u(NO_3^-)}_{\text{Burial}}\right] + \underbrace{\alpha(x)[(NO_3^-)_o - (NO_3^-)]}_{\text{Irrigation}}$$

$$-\underbrace{\frac{\varphi_s}{\varphi}\left\{\sum k_i G_i\right\}\left(\frac{4}{5}R_{NO_3} - \frac{B}{A}R_{O_2}\right)}_{\text{Reactions (1) and (2)}} + \underbrace{R_{NHOx}}_{\text{Reaction (11)}};$$

(d) MnO_2 (solid)

$$\frac{\partial(MnO_2)}{\partial t} = \frac{1}{\varphi_s}\frac{\partial}{\partial x}\left[\underbrace{\varphi_s D_B(x)\frac{\partial(MnO_2)}{\partial x}}_{\text{Biotubation}} - \underbrace{\varphi_s w(MnO_2)}_{\text{Burial}}\right] - \underbrace{\left\{\sum k_i G_i\right\}R_{MnO_2}}_{\text{Reaction (3)}}$$

$$-\left\{\underbrace{R_{MnFe}}_{\text{Reaction (16)}} + \underbrace{R_{MnO_2\,TS}}_{\text{Reaction (17)}} + \underbrace{4R_{FeSMn4}}_{\text{Reaction (18)}}\right\} + \underbrace{\frac{\varphi_s}{\varphi}R_{MnOx}}_{\text{Reaction (9)}};$$

(e) Fe(III)-solid

$$\frac{\partial(Fe(OH)_3)}{\partial t} = \frac{1}{\varphi_s}\frac{\partial}{\partial x}\left[\underbrace{\varphi_s D_B(x)\frac{\partial(Fe(OH)_3)}{\partial x}}_{\text{Biotubation}} - \underbrace{\varphi_s w(Fe(OH)_3)}_{\text{Burial}}\right] - \underbrace{4\left\{\sum k_i G_i\right\}R_{Fe(III)}}_{\text{Reaction (4)}}$$

$$+\frac{\varphi_s}{\varphi}\underbrace{4R_{FeOx}}_{\text{Reaction (8)}} + \underbrace{2R_{MnFe}}_{\text{Reaction (14)}} - \underbrace{R_{TSFe3}}_{\text{Reaction (16)}} - \underbrace{2R_{FeSFe3}}_{\text{Reaction (17)}};$$

(f) sulfate (solute)

$$\frac{\partial(SO_4^=)}{\partial t} = \frac{1}{\varphi}\frac{\partial}{\partial x}\left[\underbrace{\varphi D'_{SO_4}\frac{\partial(SO_4^=)}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{\varphi u(SO_4^=)}_{\text{Burial}}\right] + \underbrace{\alpha(x)[(SO_4^=)_o - (SO_4^=)]}_{\text{Irrigation}}$$

$$-\underbrace{\frac{\varphi_s}{2\varphi}\left\{\sum k_i G_i\right\}R_{SO_4}}_{\text{Reactions (5)}} + \underbrace{R_{SOx}}_{\text{Reaction (10)}} + \frac{\varphi_s}{\varphi}\left\{\underbrace{R_{FeSMn4}}_{\text{Reactions (18)}} + \underbrace{R_{FeSOx}}_{\text{Reactions (19)}}\right\};$$

Table 2 Continued.

(g) total dissolved phosphate (solute)

$$\frac{\partial(\Sigma PO_4)}{\partial t} = \frac{1}{\varphi_P}\frac{\partial}{\partial x}\left[\underbrace{(\varphi D'_{\Sigma PO_4} + \varphi_s D_B(x) K_{PA})\frac{\partial(\Sigma PO_4)}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{(\varphi u + \varphi_s w K_{PA})(\Sigma PO_4)}_{\text{Burial}}\right]$$

$$+ \underbrace{\frac{\varphi}{\varphi_P}\alpha(x)[(\Sigma PO_4)_o - (\Sigma PO_4)]}_{\text{Irrigation}} - \underbrace{\frac{\varphi_s C}{\varphi_P A}\{\sum k_i G_i\} R_{Os}}_{\text{Reactions (1)–(8)}};$$

(h) total ammonia (solute)

$$\frac{\partial(\Sigma NH_4)}{\partial t} = \frac{1}{\varphi_N}\frac{\partial}{\partial x}\left[\underbrace{(\varphi D'_{\Sigma NH_4} + \varphi_s D_B(x) K_{NA})\frac{\partial(\Sigma NH_4)}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{(\varphi u + \varphi_s w K_{NA})(\Sigma NH_4)}_{\text{Burial}}\right]$$

$$+ \frac{1}{\varphi_N}\left[\underbrace{\alpha(x)[(\Sigma NH_4)_o - (\Sigma NH_4)]}_{\text{Irrigation}} - \underbrace{R_{NHOx}}_{\text{Reaction (11)}}\right]$$

$$- \underbrace{\frac{\varphi_s B}{\varphi_N A}\{\sum k_i G_i\}(R_{NO_3} + R_{MnO_2} + R_{Fe(OH)} + R_{SO_4})}_{\text{Reactions (2)–(6)}};$$

(i) total dissolved sulfide (solute)

$$\frac{\partial(\Sigma H_2S)}{\partial t} = \frac{1}{\varphi}\frac{\partial}{\partial x}\left[\underbrace{\varphi D'_{\Sigma H_2S}\frac{\partial \Sigma(H_2S)}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{\varphi u(\Sigma H_2S)}_{\text{Burial}}\right] + \underbrace{\alpha(x)[(\Sigma H_2S)_o - (\Sigma H_2S)]}_{\text{Irrigation}}$$

$$+ \frac{\varphi_s}{2\varphi}\underbrace{\{\sum k_i G_i\} R_{SOx}}_{\text{Reaction (1)}} - \underbrace{R_{SOx}}_{\text{Reaction (10)}} + \underbrace{R_{CH_4SO_4}}_{\text{Reaction (13)}}$$

$$- \frac{\varphi_s}{\varphi}\left\{\underbrace{R_{FeSpyr}}_{\text{Reaction (7)}} + \underbrace{R_{TSFeS}}_{\text{Reaction (14)}} + \underbrace{R_{MnO_2TS}}_{\text{Reaction (15)}}\right\}.$$

(j) dissolved manganese (solute)

$$\frac{\partial(Mn^{2+})}{\partial t} = \frac{1}{\varphi}\frac{\partial}{\partial x}\left[\underbrace{\varphi D'_{Mn}\frac{\partial(Mn^{2+})}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{\varphi u(Mn^{2+})}_{\text{Burial}}\right] + \underbrace{\alpha(x)[(Mn^{2+})_o - (Mn^{2+})]}_{\text{Irrigation}}$$

$$+ \underbrace{\frac{2\varphi_s}{\varphi}\{\sum k_i G_i\} R_{MnO_2}}_{\text{Reaction (5)}} - \underbrace{2R_{MnOx}}_{\text{Reaction (9)}} + \frac{\varphi_s}{\varphi}\left[\underbrace{R_{MnFe}}_{\text{Reaction (14)}} + \underbrace{R_{MnO_2TS}}_{\text{Reaction (15)}} + \underbrace{4R_{FeSMnx}}_{\text{Reaction (18)}}\right];$$

Table 2 Continued.

(k) dissolved iron (solute)

$$\frac{\partial(Fe^{2+})}{\partial t} = \frac{1}{\varphi}\frac{\partial}{\partial x}\left[\underbrace{\varphi D'_{Fe}\frac{\partial(Fe^{2+})}{\partial x}}_{\text{Molecular Diffusion}} - \underbrace{\varphi u(Fe^{2+})}_{\text{Burial}}\right] + \underbrace{\alpha(x)[(Fe^{2+})_o - (Fe^{2+})]}_{\text{Irrigation}}$$

$$+ \frac{4\varphi_s}{\varphi}\underbrace{\left\{\sum k_i G_i\right\} R_{Fe(III)}}_{\text{Reaction (4)}} - \underbrace{4R_{FeOx}}_{\text{Reaction (8)}} - \frac{\varphi_s}{\varphi}\underbrace{2R_{MnFe}}_{\text{Reaction (14)}}$$

$$+ \frac{\varphi_s}{\varphi}\left\{\underbrace{R_{FeSOx}}_{\text{Reaction (19)}} + \underbrace{2R_{TSFe3}}_{\text{Reaction (16)}} + \underbrace{3R_{FeSFe3}}_{\text{Reaction (17)}} - \underbrace{R_{FeSppt}}_{\text{Reaction (6)}} + \underbrace{R_{FeSMn4}}_{\text{Reaction (18)}}\right\};$$

(l) FeS, iron monosulfide (solid)

$$\frac{\partial(FeS)}{\partial t} = \frac{1}{\varphi_s}\frac{\partial}{\partial x}\left[\underbrace{\varphi_s D_B(x)\frac{\partial(FeS)}{\partial x}}_{\text{Bioturbation}} - \underbrace{\varphi_s w(FeS)}_{\text{Burial}}\right] - \underbrace{R_{FeSOx}}_{\text{Reaction (19)}}$$

$$- \underbrace{R_{FeSFe3}}_{\text{Reaction (17)}} - \underbrace{R_{FeSMn4}}_{\text{Reaction (18)}} + \underbrace{R_{FeSppt}}_{\text{Reaction (7)}} - \underbrace{R_{pyrox}}_{\text{Reaction (20)}};$$

(m) Total CO_2 (solute)

$$\frac{\partial(\Sigma CO_2)}{\partial t} = \frac{1}{\varphi}\frac{\partial}{\partial x}\left[\underbrace{\varphi D'_{\Sigma CO_2}\frac{\partial(\Sigma CO_2)}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{\varphi u(\Sigma CO_2)}_{\text{Burial}}\right] + \underbrace{\alpha(x)[(\Sigma CO_2)_o - (\Sigma CO_2)]}_{\text{Irrigation}}$$

$$+ \frac{\varphi_s}{\varphi}\left\{\sum k_i G_i\right\}\left\{\underbrace{R_{O_2}}_{\text{Reaction (1)}} + \underbrace{R_{NO_3}}_{\text{Reaction (2)}} + \underbrace{R_{MnO_2}}_{\text{Reaction (3)}} + \underbrace{R_{Fe(III)}}_{\text{Reaction (4)}}\right.$$

$$\left. + \underbrace{R_{SO_4}}_{\text{Reaction (5)}} + \underbrace{0.5R_{CH_4}}_{\text{Reaction (6)}}\right\} + \underbrace{R_{CH_4Ox}}_{\text{Reaction (12)}} + \underbrace{R_{CH_4SO_4}}_{\text{Reaction (13)}};$$

(n) Methane (solute)

$$\frac{\partial(CH_4)}{\partial t} = \frac{1}{\varphi}\frac{\partial}{\partial x}\left[\underbrace{\varphi D'_{CH_4}\frac{\partial(CH_4)}{\partial x}}_{\text{Molecular diffusion}} - \underbrace{\varphi u(CH_4)}_{\text{Burial}}\right] + \underbrace{\alpha(x)[(CH_4)_o - (CH_4)]}_{\text{Irrigation}}$$

$$+ \underbrace{\frac{\varphi_s}{2\varphi}\left\{\sum k_i G_i\right\} R_{CH_4}}_{\text{Reaction (6)}} - \underbrace{R_{CH_4Ox}}_{\text{Reaction (12)}} - \underbrace{R_{CH_4SO_4}}_{\text{Reaction (13)}}.$$

Model inputs include salinity, temperature pressue, the bioturbation rate, the sedimentation rate, the porosity, C:N:P ratio, initial pore water concentrations of the ions, depositional fluxes, reaction rate constants, Monod constants, time, depth, and spatial (vertical) resolution. Model outputs are depth profiles of dissolved and solid species, depth profiles of rates of organic matter oxidation, and percent carbon oxidized by various oxidants. Although the model has been successfully debugged and currently does run, there appear to be some problems with the charge balance which predict an unrealistic pH. Current model runs are based entirely on a data set of parameter values obtained from both marine and Lake Erie environments. These limitations will be explored in future applications with real data from Lake Erie.

ADDITIONAL BENEFITS

This small grant project has led to the application of a larger proposal to EPA GLNPO to obtain the sediment samples and pore waters needed to calibrate the model. Further, that proposal, 'Lake Erie Trophic Status', is a multi-institutional, multi-collaborator, multi-national study to understand nutrient cycling and the onset of anoxia in Lake Erie. This model will be well-integrated into those results if that project is funded.

The Project Director's post-doctoral student, William Fornes, participated in this project and has now secured permanent employment with an oceanographic and public educational outreach organization, CORE, in Washington D.C.

DISSEMINATION

The project director (Matisoff) organized a special session on 'Advances in the Biogeochemisty of Sediment Pore Waters' at the IAGLR 2001 meeting in Green Bay. At that session he presented the paper 'A Model for Sediment Biogeochemical Cycling and Chemical Loading in the Great Lakes'. The abstract for the paper is given below:

> Internal recycling of nutrients and contaminants from sediments is a well-recognized and important input to the water column. However, models of biogeochemical cycling are not well developed. To directly address this deficiency, we apply the CANDI model to improve predictions of internal chemical loading to the Great Lakes. The model considers kinetically controlled reactions including degradation of organic carbon by oxygen, Fe and Mn oxides, nitrate, sulfate and methanogenesis, carbonate dissolution, and pyrite formation and equilibrium reactions that govern pH. Results to be presented include the proportional effects of suboxic and anoxic reactions on organic carbon diagenesis, the effects of bioturbation on the release on nutrients to the water column, and the changes in nutrient fluxes from the sediments in response to changes in nutrient deposition fluxes.

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