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Critical Review

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Critical Review of Eutrophication Models for Life Cycle Assessment

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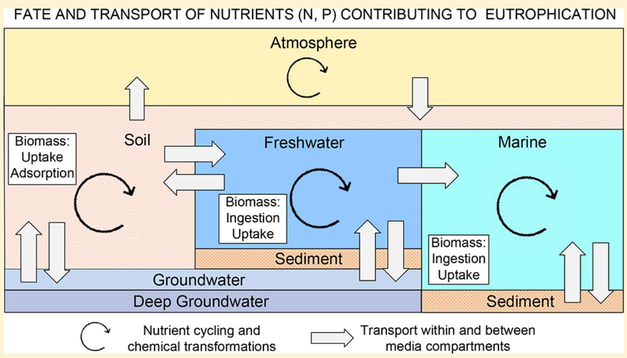
Supporting Information

ABSTRACT: This paper evaluates the current state of life cycle impact assessment (LCIA) methods used to estimate potential eutrophication impacts in freshwater and marine ecosystems and presents a critical review of the underlying surface water quality, watershed, marine, and air fate and transport (F&T) models. Using a criteria rubric, we assess the potential of each method and model to contribute to further refinements of life cycle assessment (LCA) eutrophication mechanisms and nutrient transformation processes as well as model structure, availability, geographic scope, and spatial and temporal resolution. We describe recent advances in LCIA modeling and provide guidance on the best available sources of fate and exposure factors, with a focus on midpoint indicators. The critical review identifies gaps in LCIA characterization modeling regarding the availability and spatial resolution of fate factors in the soil compartment and identifies strategies to characterize emissions from soil. Additional opportunities are identified to leverage detailed F&T models that strengthen existing approaches to LCIA or that have the potential to link LCIA modeling more closely with the spatial and temporal realities of the effects of eutrophication.



1. INTRODUCTION

Human contributions to the increased cycling of nitrogen (N) and phosphorus (P) through the biosphere threaten the health of freshwater and marine ecosystems and the economic and life-support functions they have.[1] Harmful algal blooms (HABs) are caused by the rapid or exponential growth of algae and cyanobacteria and can result from excess nutrient availability (i.e., eutrophication). Algal blooms can have a number of harmful effects, such as species shifts that alter food webs, depletion of oxygen due to algal decay, nuisance algae that physically affect other organisms, and, in some cases, the production of cyanotoxins that are harmful to fish, wildlife, pets, and humans.[2] HABs are also responsible for billions of dollars in economic impacts associated with recreational activities, commercial fishing, property values, human health, and drinking water systems.[3] They are linked to eutrophication resulting from human activities (hereafter eutrophication) and usually result from elevated nutrient inputs to the system.[4] The 2014 algal bloom in Lake Erie demonstrated the potential for impairment of the United States water supply as a result of anthropogenic nutrient loading and subsequent eutrophication impacts.[5] Human N inputs to the national landscapes and surface waters are dominated by fertilizer application, atmospheric deposition, and agricultural N fixation.[6] Scientists and managers alike need improved and reliable quantitative tools to address the challenges of eutrophication.

Life cycle assessment (LCA) supports sustainable decision-making by providing a comprehensive and structured accounting of the potential environmental and human health impacts associated with a product, service, or policy.[7] To ensure that LCA methods reflect the best science available, the methods and

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their underlying models must be updated. Historically, LCA studies have estimated eutrophication impacts based on global or continental average models. However, the science is advancing toward methods that utilize location-specific characteristics [e.g., soil and water data layers in geographic information systems (GIS)] to better characterize and quantify nutrient fate and transport (F&T) through air, land, and water as well as the associated ecosystem responses. In this paper, we review F&T models that can be used to improve estimates of nutrient-related impacts in LCA and thereby advance efforts to mitigate eutrophication of surface waters.

The process of eutrophication begins with increases in nutrient loading to ecosystems, typically limited by N or P. The availability of these formerly limiting nutrients stimulates primary production leading to adverse effects, including the accumulation of algal toxins and taste and odor problems in drinking water.[8] The death and microbial respiration of algae leads to decreases in dissolved oxygen (DO), resulting in hypoxia, mortality of benthic organisms, and habitat compression, all of which can have negative consequences for higher trophic level species.[9] Over time, as nutrients and organic matter accumulate, hypoxic events can become seasonal, leading to long-term changes in ecosystem structure and function.[9] Each of these changes can have implications for human health, recreation, fisheries, property values, and other economic activities.

LCA and life cycle impact assessment (LCIA) aim to estimate this cause-effect chain for freshwater and marine ecosystems. However, without quantifying site-specific fate, transport, and loading of nutrients at appropriate spatial scales, the calculated relevance for eutrophication may be limited. Furthermore, current LCA characterization models combine marine and freshwater environments into a single impact category (e.g., eutrophication potential) or employ the simplifying assumption that P is limiting in freshwater ecosystems and N is limiting in marine ecosystems. However, these assumptions do not hold true in all situations, and current studies indicate that it is important to provide management for both N and P.[10−12] It is also commonly assumed that atmospheric transport of P is negligible and, thus, that it is safe to exclude this pathway from characterization models. However, several recent studies demonstrate that atmospheric P transport occurs,[13−16] indicating that this assumption is worth revisiting.

Our study aims to improve the characterization of eutrophication impacts in LCA with a focus on identifying opportunities to improve LCIA's representation of nutrient F&T through air, land, and water. To do this, a review of current models that address eutrophication-impact categories in LCA and LCIA, and the nutrient fate and transport models that inform them, is critical.

Our specific goals are to:

(1) explore and document the current state of the science regarding the eutrophication impact category in LCA and LCIA methods, providing short-term guidance for method selection among practitioners;
(2) review and compare selected nutrient F&T models that can be used for assessing eutrophication in LCA and LCIA;
(3) discuss potential linkages of these models to LCIA for eutrophication; and
(4) make recommendations for improving the eutrophication impact category in LCA and LCIA.

Our review of select nutrient F&T models focuses on sources of nutrient loading to each environmental compartment (e.g., water compartments, soil, and air), representation of nutrient speciation, and F&T mechanisms. We distinguish four model categories: (1) surface water quality models, (2) watershed models, (3) marine models, and (4) air-quality models. Through structured model comparison and analysis, we identify candidate models for improving the representation of nutrient-related impacts in LCA, delineate which parameters are most important, and suggest ways to improve methods for characterizing eutrophication impacts in LCA while minimizing the practitioner's burden of data collection.

2. METHODS

Abundant models are available that address different aspects of estimating the eutrophication impact category for LCA and LCIA. Therefore, to limit the scope of the paper and provide a succinct review, criteria were developed to select models for this analysis. A list of candidate F&T and LCIA models was created based on the results of Google Scholar and Google Web searches for peer-reviewed publications and model documentation published between 2007 and 2017. The searches combined the keywords "eutrophication" and "(nitrogen OR phosphorus OR nutrient) AND (pollution OR fate OR impact OR hypoxia)". Sources were added if they were referenced by multiple authors in the original search. Priority was given to models actively maintained and updated, regularly used, especially in the United States, applied by the U.S. Environmental Protection Agency (EPA), and considered to have potential to contribute to LCIA of eutrophication.

Each model was documented using a spreadsheet to assess its suitability for estimating eutrophication-related impacts in LCA. Refer to the Supporting Information for rubric details. General metadata documented included model type, institutional origin and ongoing support, public availability, and aspects of scope, including geographic coverage, time step, and spatial resolution. Nutrient-related metadata included model representations of nutrient loading sources, nutrient species or groupings tracked, transport and removal mechanisms (i.e., processes that facilitate or minimize transport, respectively, through the biosphere), and nutrient transformation processes (which change the form or speciation of a nutrient). Figure 1 illustrates the relationship between nutrient input, transport, removal, and transformation as N and P cycle through the biosphere. Ideally, F&T models and LCIA methods would reflect accurately and precisely all relationships shown in Figure 1. Due to practical factors, however, such as lack of model sophistication, lack of site specificity, and technical challenges associated with determining spatial and temporal distribution of releases and emissions, simplifying assumptions must be made. The approach taken in this Review is to include as much scientific detail as necessary and available and continually work toward methods and models that more-realistically reflect observed environmental processes.

2.1. Assessment of Eutrophication in Life Cycle Assessment: State of the Practice. LCIA models are used to characterize environmental and human health impacts associated with the release of substances to the environment and the use of natural resources. For a given impact category (here, eutrophication), LCIA estimates the relative severity of releases and emissions to various environmental compartments.

Environmental impacts in LCA are characterized at the endpoint or midpoint level. Endpoint are the ultimate impacts of interest, e.g., human health effects measured in disability-adjusted life years (DALYs) or ecological impacts measured as

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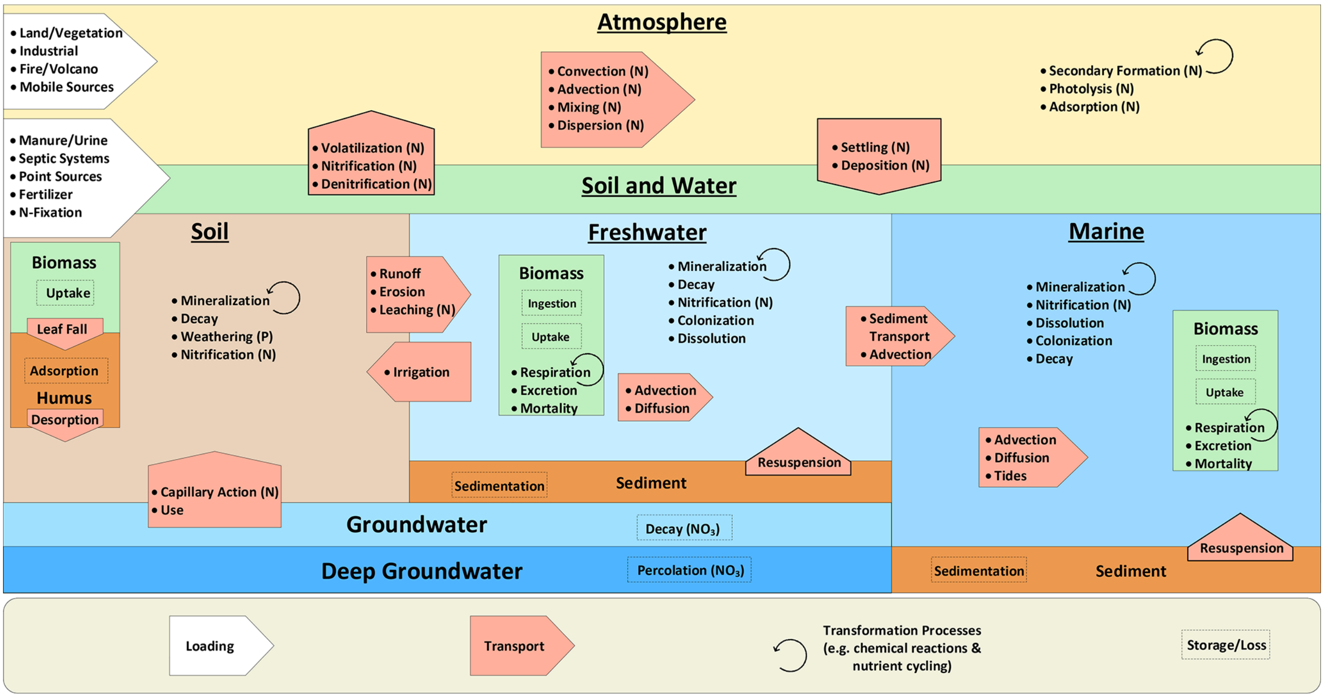

Figure 1. Fate and transport considerations relevant for eutrophication modeling.

time-integrated species loss.[17] Midpoints estimate the relative contribution of releases to an endpoint at an earlier point (i.e., midpoint) on the cause-effect chain where an equivalency between substances can be established.[17] Examples of eutrophication midpoints include concentration equivalents of phosphate for freshwater environments and concentration equivalents of nitrogen compounds for marine environments. Midpoint CFs are the product of fate factors (FF) and an optional exposure factor (XF). Endpoint CFs are the product of midpoint CFs, effect factors (EFs), and an optional damage factor (DF).[18]

Eq 1 describes the basic framework used in LCA to calculate environmental and human health impacts:[19]

$$I_i = \sum_{xmn} F^i_{xmn} P^i_{xn} M_{xm} \qquad (1)$$

where I_i is the potential impact of all chemicals (x) released to all media compartments (m) with all modeled exposure routes (n) for a given impact category (e.g., eutrophication potential). For a given chemical, x, F^i_{xmn} represents the F&T pathway; P^i_{xn} represents the potency; and M_{xm} represents the mass.

This paper focuses on models that quantify the FFs for N and P. Biological or chemical oxygen demand (BOD and COD) are also often characterized in LCIA methods.[20] Consideration of BOD and COD F&T is excluded from this analysis due to limited treatment in the reviewed models.

Development or selection of an appropriate LCIA eutrophication method should also consider the capacity to spatially differentiate impact potential based on location and the environmental compartment(s) involved. The feasibility and importance of spatial differentiation has been demonstrated for other impact categories and is partially employed within existing LCIA eutrophication methods.[20−22] An ideal LCIA method will achieve practical simplicity while being scientifically robust and globally applicable. During the selection of models for a specific application, a trade-off often exists between model fidelity and available project resources.[23] Flexibility and adaptability are also advantageous, given the spectrum of life cycle inventory (LCI) data quality, product system definitions, and scopes of study.

2.2. Model Introduction. We consider four common LCIA methods and a new marine LCIA eutrophication method as a basis for discussing the advancement of F&T models in midpoint assessment of eutrophication. A total of 15 F&T models are reviewed that consider nutrient F&T in multiple environmental compartments. The application of nutrient F&T models for multiple environmental compartments could improve the quantification of LCIA eutrophication midpoint assessment by providing site-specific and mechanistic estimates of N and P loadings. This section introduces the LCIA and F&T models and describes their structure and essential features. Table 1 documents these features, allowing a quick comparison of structure and function of all reviewed models. This section frames the modeling landscape considered in this analysis, providing a foundation for further review and discussion. Additional descriptions of all models are provided in Table S2.

2.2.1. Life Cycle Impact Assessment Methods Included in the Review. TRACI, the Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI), provides eutrophication midpoint CFs representative of average U.S. conditions,[24−26] combining P-related freshwater and N-related marine impacts based on the Redfield ratio. The Redfield ratio describes a generic elemental composition of algae that is used to develop an equivalency between elements and nutrient forms based on stoichiometric relationships. Atmospheric FFs are developed from source receptor matrices based on the ASTRAP model.[20] Estimated F&T of N in surface freshwaters and of atmospherically deposited N is based on the fraction of river basin precipitation reaching the ocean. All P releases to surface freshwater systems are assumed to reach a P-limited waterbody.

ReCiPe 2016 provides midpoint CFs for freshwater eutrophication for 157 countries using cumulative P FFs developed

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Table 1. Summary of Coverage Offered by Surveyed Models across Multiple Media Types[a]

category	characteristic	CML[h]	TRACI 2.1	ReCiPe 2016	IMPACT World+	CARMEN	He et al. 2011	NEWS 2	SWAT	IMAGE-GNM	SPARROW	WASP	AQUATOX	Cosme et al.	NCOM-CGEM	FVCOM-WQM	FVCOM-GEM	EFDC-WQM	CMAQ	CAMx	GEOS-Chem
				LCIA					watershed				water quality			marine				atmosphere	
geographic scope	global[c]			●[b]	●		●	●		●				●					○	○	●
	regional		●			●		●	●		●	●	●		●	●	●	●	●	●	
spatial resolution	country		●	●	●																
	watershed							●			●			●							
	reach										●	●	●								
	grid, degrees					●	●		●	●					●	●	●	●	●	●	●
modeling approach	mechanistic	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	empirical[d]					○	○	●	○	●	●	○	○								
uncertainty	deterministic	●	●	●	●	●	●	●	●			●	●	●	●	●	●	●	●	●	●
	probabilistic									●	●										
total form chemical coverage	N	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	P	●	●		●	●		●	●	●	●	●	●		●	●	●	●		●	
	DO								●			●	●	●	●	●		●			
compartments	surface freshwater	◐	●	●	●	●	●	●	●	●	●	●	●	●				●			
	soil and groundwater[e]	◐	○	●		●	●	●	●	●	●			●							
	marine[f]	◐	◐		◐								◐[g]	●	●	●	●	●			
	atmosphere	◐	●		●														●	●	●

[a]Geographic scope refers to the spatial extent of the model's application. Superscripts refer to the row (i.e., model criteria); circle symbols refer to the particular model in the row. [b]●: Criterion included in model. [c]○: Have global capacity when nested with global models. [d]○: Incorporate minor empirical elements. [e]○: Provide guidance but no characterization factors.. [f]◐: Provide characterization factors but incorporate no compartment-specific F&T. [g]◐: AQUATOX has a submodule specific to the estuarine environment. [h]CML pertains to the global average. Geographic scope and spatial resolution do not apply.

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by Helmes et al.[21] Releases to soil are characterized by assuming 10% of the P reaches freshwater.[27,28] Endpoint CFs are based on an emission-weighted global average effect factor.[29,30] Marine eutrophication is not included. The previous version, ReCiPe 2008, provided CFs for freshwater and marine eutrophication at the midpoint and endpoint levels. ReCiPe 2008 represents average European conditions using the CARMEN model[31,32] for soil, groundwater, and surface freshwater F&T of N and P and EUTREND for F&T of N releases to air. ReCiPe 2008 users are encouraged to report freshwater and marine eutrophication results separately,[33] although combined CFs are provided based on the Redfield ratio. Endpoint CFs are presented in terms of species loss.

IMPACT World+ provides eutrophication midpoint CFs using cumulative fate factors for P in freshwater using those from Helmes et al.,[21] similar to ReCiPe 2016. The fate of N in surface freshwater is based on CARMEN's estimate of the European average, as was used in ReCiPe 2008 and EDIP 2003.[34] No FFs are provided for the soil compartment, leaving these estimations to the LCI phase. Endpoint impacts are estimated in terms of partially disappeared fraction (PDF) of species per unit area over a given period.[35,36] IMPACT World+ will replace the IMPACT 2002 LCIA method[37] once it is released.

Cosme et al. provides marine eutrophication midpoint and endpoint CFs based on inland N F&T as estimated by the NEWS 2 model. Novel simplified F&T models are developed and applied within 66 large marine ecosystems (LMEs) to develop the first set of global, spatially differentiated marine CFs. The research expands the existing LCIA eutrophication cause−effect chain, developing a new midpoint indicator based on oxygen depletion.[18,38−40] An early version of this work was presented as part of the LC-IMPACT project.[22]

CML provides aquatic midpoint CFs for releases to soil, air, and water based on the Redfield ratio and the stoichiometric ratio of N and P in the releases.[41] The CFs for release of a given substance to soil and water are equivalent because F&T is not considered and terrestrial and aquatic eutrophication are combined. CFs for air emissions were last updated in 2002 and incorporate atmospheric F&T using the RAINS model.[42] The CML method does not distinguish freshwater and marine eutrophication, nor does it include endpoint metrics.

2.2.2. Nutrient Fate and Transport Models Included in the Review. Based on our model-selection criteria, we describe a select set of surface water quality models, watershed models, marine models, and air-quality models with the potential for integration into LCIA (Table 1). Additional model details are provided in Table S2.

AQUATOX[43,44] and WASP[45] are surface water quality models, which differ from watershed models in that they only model surface freshwater systems at the reach or river network scale. Both models facilitate more-detailed representation of F&T processes within surface freshwater bodies than typical watershed or LCIA models. WASP and AQUATOX track nutrient transformations within the water column including biological cycling, dual-nutrient growth limitation, light limitation, and temperature-dependent reaction kinetics. Both AQUATOX and WASP are U.S. EPA models used to estimate water quality concentrations and fluxes in individual stream reaches and river networks for monitoring and regulatory purposes. Further details on the F&T models are provided in the Supporting Information.

CARMEN,[31,32] He et al. (2011),[46,47] SPARROW,[48] NEWS 2,[49] SWAT,[50] and IMAGE-GNM[51,52] are watershed models that simulate runoff and F&T processes in soil, groundwater, and surface freshwater compartments within topography-delimited watersheds. Terrestrial biological processes are considered as they relate to the loading or retention of nutrients. SPARROW and NEWS 2 are hybrid models relying on mechanistic and empirical approaches to F&T modeling. SPARROW and IMAGE-GNM both facilitate uncertainty analysis of model results, whereas other models are primarily deterministic. IMAGE-GNM is a module within the IMAGE integrated assessment model. He et al. and SWAT are on the more-mechanistic end of the spectrum, and the latter generally allows for the incorporation of a wider suite of agricultural management practices than other models.

NCOM-CGEM,[53] FVCOM-GEM,[54] FVCOM-WQM,[55] and EFDC-WQM[56−58] are examples of linked hydrodynamic water quality models. The hydrodynamic component of each model simulates fluid flow in estuarine and coastal regions, considering the influence of complex coastal geometry, tides, and forcing factors such as solar radiation and wind. Water-quality modules simulate the response of biological communities to nutrient loading.

CMAQ,[59−61] GEOS-Chem,[62] and CAMx[63] are all multiscale air-quality models that track the F&T of N compounds, ozone, particulate matter, toxins, and other airborne pollutants through the atmosphere. Multiscale models utilize a nested grid structure to allow for higher grid resolution in select regions. Boundary conditions are established using a coarser regional or global grid resolution. All described models facilitate the simultaneous modeling of multiple pollutants in an integrated "one-atmosphere" model.[60] The one-atmosphere structure facilitates interactions between chemical species and mechanisms.

3. RESULTS

3.1. Fate and Transport Approaches to Assisting LCIA for Eutrophication. It is well-recognized that a wide range of F&T models can be used to support LCIA for eutrophication, and this is true across water quality, watershed, marine, and air F&T model types. However, current midpoint eutrophication methods generally lack site-specific F&T factors and precise modeling of nutrient loading at appropriate spatial scales and domains (e.g., global coverage) is often preferable but not available.

To fully explore how F&T models can be used most efficiently in the context of LCIA and provide recommendations to improve (and ultimately revise) the LCIA eutrophication category, a review and description of pertinent model elements and processes is first required. This section describes and evaluates how F&T is estimated in four primary environmental compartments and the example models that are used to simulate the respective F&T, as documented in the criteria rubric (see Table S4). The F&T compartments, and associated subsections presented here, include surface freshwater systems, soils and groundwater, marine systems, and the atmosphere.

3.2. Fate and Transport in Surface Freshwaters. The surface water quality models and watershed models that best inform LCIA methods include diverse sources of nutrient loading and approaches to modeling in-stream transport. A total of three of these models (SWAT, WASP, and AQUATOX) also simulate nutrient transformation processes (Table 2). Most F&T models including surface freshwaters do not simulate nutrient transformation but are useful for transport and retention processes.

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Table 2. Comparison of Freshwater F&T Mechanisms and Coverage of Nutrient Species for Models That Include Nutrient Cycling[a]

category[b]	characteristic	model name: SWAT	WASP	AQUATOX
sources of aquatic loading	point source: user specified	N, P	N, P	N, P
	non-point source: user specified	–	N, P	N, P
	leaching	NO_3	–	–
	surface runoff	PO_4, NO_3	–	–
	shallow groundwater	NO_3	–	–
	erosion	PIP, POP, PON	–	–
freshwater nutrient pools	nitrogen	ON, NH_4, NO_2/NO_3, BN	NH_3, NO_3, DON, BN, DN	NH_3/NH_4, NO_3, DN, BN
	phosphorus	OP, PO_4, BP	PO_4, DOP, BP, DP, PIP	PO_4, DP, BP, PIP
	DO	DO	DO	DO
transport and removal mechanisms	advection	N, P	N, P	N, P
	diffusion	–	–	N, P
	biological fixation	–	–	BN (+)
	sediment exchange	NH_4 (±), PO_4 (±)	–	NO_3 (+), NH_3 (+), PO_4 (+)
	settling	ON (−), OP (−), BN (−), BP (−)[c]	BN (−), BP (−), DN (−), DP (−), PIP (−)	BN (−), BP (−), DN (−), DP (−)
	resuspension	N (+), P (+)	DN (+), DP (+), PIP (+)	DN (+), DP (+), BN (+), BP (+)
	use	N (−), P (−)	–	–
	denitrification	–	NO_3 (−)	NO_3 (−)
nutrient cycling processes (within grid cells)	mineralization	OP (−), PO_4 (+)	DON (−), NH_3 (+), DOP (−), PO_4 (+)	NH_3 (+), PO_4 (+), DN (−), DP (−), BN (−), BP (−)
	nitrification	NO_3/NO_2 (+), NH_4 (−), DO (−)	NH_3 (−), NO_3 (+), DO (−)	NO_3 (+), NH_3 (−), DO (−)
	dissolution, hydrolysis	ON (−), NH_4 (+)	DN (−), DP (−), DON (+), DOP (+)	–
	decomposition, microbial	DO (−)[d]	–	DN (−), DP (−), NH_3 (+), PO_4 (+), DO (−)
	growth, photosynthesis	BN (+), NO_3 (−), NH_4 (−), PO_4 (−), BP (+), DO (+)	NH_3 (−), NO_3 (−), PO_4 (−), BN (+), BP (+), DO (+)	NH_3 (−), NO_3 (−), PO_4 (−), BN (+), BP (+), DO (+)
	mortality	ON (+), BN (−), OP (+), BP (−)	BN (±), BP (±), DN (+), DP (+), NH_3 (+), PO_4 (+)	BN (−), BP (−), DN (+), DP (+), NH_3 (+), PO_4 (+)
	ingestion	–	BN (±), BP (±), DN (+), DP (+), NH_3 (+), PO_4 (+)	DN (−), DP (−), BN (±), BP (±), NH_3 (+), PO_4 (+)
	excretion	–	–	NH_3 (+), BN (−), BP (−), DN (+), DP (+), PO_4 (+)
	colonization	–	–	DN (−), DP (−), NH_3 (+), PO_4 (+)
	adsorption	–	PO_4 (−), PIP (+)	PO_4 (−), PIP (+)
	respiration, metabolism	ON (+), OP (+), BN (−), BP (−), DO (−)	BN (−), BP (−), NH_3 (+), PO_4 (+), DO (−)	DO (−), NH_3 (+), PO_4 (+), BN (−), BP (−)
	reaeration	DO (+)	DO (+)	DO (+)
	sediment demand	DO (−)	DO (−)	DO (−)

[a]The (+) or (−) notation refers to an increase or decrease, respectively, in concentration of associated species in the water column. [b]P, phosphorus; N, nitrogen; DON, dissolved organic nitrogen; ON, organic nitrogen; OP, organic phosphorus; DOP, dissolved organic phosphorus; DO, dissolved oxygen; PIP, particulate inorganic phosphorus; POP, particulate organic phosphorus; PON, particulate organic nitrogen; NO_2, nitrite; NO_3, nitrate; NH_4, ammonium; NH_3, ammonia; PO_4, phosphate; DN, detrital nitrogen; DP, detrital phosphorus; BN, biological nitrogen; BP, biological phosphorus. [c]SWAT includes specific mechanisms for sediment routing within river channels that are not present in most models. NEWS2 is also considered a form of sediment routing for TSS. [d]Decomposition of carbonaceous biochemical oxygen demand (CBOD) in the water column.

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SPARROW does not model F&T mechanisms directly (except in-stream retention). However, it does include terrestrial non-point loading via F&T input data describing land-use regimes, management practices, topography, climate, and soil type. It then uses these inputs to fit a nonlinear regression equation to estimate the non-conservative transport of N and P from diffuse and point sources on the land surface to rivers and streams and through river and stream systems. A primary benefit of SPARROW's empirical approach is its limited mechanistic complexity and built-in statistical validation against available monitoring data.

Watershed models simulate nutrient loading from surface runoff, lateral subsurface flow, and erosion. SWAT and IMAGE-GNM differentiate between lateral subsurface flow and groundwater percolation. CARMEN, NEWS 2, SWAT, and IMAGE-GNM include nutrient loading associated with particulate nutrient erosion.

WASP, AQUATOX, TRACI 2.1, and IMPACT World+ accept user-defined point and nonpoint sources of nutrient loading but do not calculate releases to surface freshwater from soil applications. ReCiPe 2016 uses a simplifying assumption that 10% of P released to soil reaches freshwater. More details on nonpoint sources of nutrient loading are provided in the section on soil and groundwater. Model consideration of nutrient loading directly affects life cycle impact assessment. For watershed or water-quality models under consideration for FF development, the approach to nutrient loading has implications for data collection and validation procedures.

Models vary widely in how they track N and P species in surface freshwaters, which relates directly to emission species resolution of FFs that can ultimately be developed. CARMEN, ReCiPe 2016, TRACI 2.1, IMPACT World+, and IMAGE-GNM track total N and total P in the surface freshwater compartment. He et al. aggregates N species tracked in the soil compartment into total N and dissolved inorganic nitrogen (DIN) within surface freshwater. He et al. does not model P compounds. SWAT, WASP, and AQUATOX provide significantly more detail, modeling nutrient classes (e.g., organic N/P and detrital N/P) and specific chemical species (e.g., ammonium and phosphate).

Representation of nutrient transport and retention within bodies of water also varies among models. TRACI calculates N transport to coastal ecosystems based on the fraction of watershed area that drains to the ocean, assuming that N transport is proportional to hydrologic transport.[20] In TRACI, 100% of P input to freshwater is assumed to reach a body of water where it is the limiting nutrient. In contrast (for N), CARMEN assumes that 30% of N released or transported to surface freshwater is lost via denitrification, while the remainder is transported to coastal ecosystems.[33] Rather than assuming a percentage, other models consider specific in-stream transport and retention mechanisms such as advection, settling, sediment exchange, and denitrification. Model coverage of specific mechanisms is listed in Tables 2 and S3. Finally, the model documentation for He et al. notes that nutrient transmission losses are considered, but no rates of detention are given. These considerations primarily impact LCIA development to the extent that they affect model accuracy and the scientific validity of FFs ultimately developed.

In addition to retention mechanisms, SWAT, WASP, and AQUATOX track transformation of nutrients through several organic and inorganic forms. All three models account for advective transport. AQUATOX additionally accounts for diffusion, which can occur both between surface freshwater grid cells and stratified layers of a lake or reservoir.

Each model represents different biological processes that affect activities such as sedimentation. SWAT uses generic algal growth, whereas WASP distinguishes between suspended and attached growth. AQUATOX models a multilevel food web. Biological categories in AQUATOX include algae, macrophytes, invertebrates, fish, and final bioaccumulative species, such as bald eagles or minks.

As organisms die and decompose, they become available for mineralization or dissolution into dissolved inorganic forms. SWAT, WASP, and AQUATOX include representation of mineralization, nitrification, and track levels of DO. Atmospheric diffusion (i.e., reaeration and the photosynthetic production of oxygen by algae and aquatic macrophytes) increases the concentration of DO. Respiration, sediment oxygen demand, CBOD, and nitrification all decrease concentrations of DO, which can ultimately lead to hypoxia. In-stream transformation processes represent a level of modeling detail that is not currently included in any available freshwater LCIA method. To the extent that these models provide meaningful connections between nutrient loading and DO concentrations, they provide additional insight into the LCIA cause−effect chain.

3.3. Fate and Transport in Soil and Groundwater. Soil and groundwater compartments are handled inconsistently in current LCIA methods. Several methods exclude F&T in these compartments, preferring to include them as part of the inventory phase of LCA. Table 3 summarizes key attributes of five watershed models with potential to more-fully incorporate the soil and groundwater compartments and thus provide more-consistent guidance for LCA practitioners.

ReCiPe 2008 uses the CARMEN model, which is currently the only model to provide spatially differentiated soil FFs for P. However, these FFs are specific to Europe and are being phased out with the release of ReCiPe 2016. The N soil FFs from Cosme et al.[38] are based on the NEWS 2 model and provide the only example of global soil FFs. No global, spatially differentiated FFs are available for P, and none of the current freshwater LCIA methods provide soil FFs based on detailed F&T modeling. The watershed models may yield insights into filling these gaps.

CARMEN and IMAGE-GNM represent nutrient species in the soil ecosystem as total N and total P. NEWS 2 uses aggregated nutrient categories that distinguish between dissolved organic, dissolved inorganic, and particulate forms. Both SWAT and He et al. model specific nutrient species, which facilitates representation of nutrient transformation within soil and groundwater grid cells. Both track vegetative, detrital, and humic N and P. More-detailed representation of nutrient species raises the possibility of species-specific FF development.

In CARMEN, the ratio of N transported by surface water runoff and via groundwater flow is determined by landscape factors including aquifer type, soil texture, topography, land cover, and seasonal temperature. CARMEN assumes that the exclusive transport route for agricultural P to surface freshwater is via P that is attached to eroding sediments. P losses are calculated based on loading and sediment yield. Sediment yield is a function of an empirical constant that fits factors for rainfall intensity, slope, soil texture, and land use to observed values of sediment transport.[32] In contrast to CARMEN, SPARROW employs probabilistic, statistical methods, described in the surface freshwater section, that consider variables related to

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Table 3. Comparison of Soil F&T Mechanisms for Mechanistic Watershed Models[a]

category[b]	characteristic	model name				
		CARMEN	He et al.	NEWS 2	SWAT	IMAGE-GNM
soil nutrient pools	nitrogen	TN	BN, DN, HN, NH_4, NO_3	DON, DIN, PN	NH_4, NO_3, DN, HN, PON, BN	TN
	phosphorus	TP	–	DOP, DIP, PP	DP, HP, PO_4, POP, BP, PIP	TP
transport and removal mechanisms (into and out of grid cells)	export, retention	–	N (−)	DIP, DIN, DON, DOP	–	–
	surface runoff	TN	NO_3	–	NO_3, PO_4	TN, TP
	lateral flow	TN	NO_3	–	NO_3	TN
	erosion	TP	–	PN, PP	PIP, PON	TN, TP
	deep groundwater	TN	–	–	NO_3 (−)	–
	revaporization	–	–	–	NO_3 (+)	–
	volatilization	–	NH_4 (−)	–	NH_4 (−)	TN (−)
	nitrification	–	NO_3 (−)	–	–	–
	denitrification	–	NO_3 (−)	–	NO_3 (−)	TN (−)
	vegetative cycling	TN (−), TP (−)	NH_4 (−), NO_3 (−), BN (±), DN (+)	DIN (−), DIP (−)	NO_3 (−), PO_4 (−), BN (+), BP (+), DN (+), DP (+)	TN (−), TP (−)
	groundwater use	–	–	–	NO_3 (−)	–
nutrient species transformation processes (within grid cells)	adsorption	TP (−)	–	–	PO_4 (−)	–
	weathering	–	–	DIP (+)	–	TP (+)
	mineralization	–	DN (−), HN (−), NH_4 (+)	–	PO_4 (+), DN (±), DP (±), HN (−), HP (−), NO_2/NO_3 (+)	–
	nitrification	–	NH_4 (−), NO_2/NO_3 (+)	–	NH_4 (−), NO_2/NO_3 (+)	–
	humus stabilization	–	DN (−), HN (+)	–	DN (±), DP (±), HN (±), HP (±), PIP (±)	–
	decay	–	–	–	DN (−), DP (−), HN (+), HP (+)	–
	groundwater decay	–	–	–	NO_3 (−)	–

[a]Loading sources are excluded from the table because they are generally consistent for all models, including fertilizer, manure application, and atmospheric deposition of N. All models that span multiple media, except for CARMEN, consider biological N fixation. F&T processes that move nutrients into and out of the soil compartment are distinguished from those that transform nutrients between nutrient forms. The (+) or (−) notation refers to an increase or decrease in concentration of associated species in the soil and groundwater. [b]TP, total phosphorus; TN, total nitrogen; DON, dissolved organic nitrogen; DIP, dissolved inorganic phosphorus; DOP, dissolved organic phosphorus; PP, particulate phosphorus; PN, particulate nitrogen; NO_2, nitrite; NO_3, nitrate; NH_4, ammonium; NH_3, ammonia; PO_4, phosphate; BN, biological nitrogen; BP, biological phosphorus; DN, detrital nitrogen; DP, detrital phosphorus; HN, humic nitrogen; HP, humic phosphorus; POP, particulate organic phosphorus; PON, particulate organic nitrogen.

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sources, land (including soil permeability), and freshwater explanatory variables when estimating nutrient yield.

IMAGE-GNM tracks total N and P soil transport through overland flow and three soil and groundwater layers. The PCRaster Global Water Balance (PCR-GLOBWB) model is used to estimate runoff and simulate waterborne nutrient transport. The hydrological model considers land cover, soil texture, slope, and aquifer porosity. Additional soil and climatic factors are taken into consideration when estimating losses via specific mechanisms listed in Table 3. For example, denitrification rates are modulated by soil factors such as texture, aeration, and organic carbon content.[64]

NEWS 2 aggregates soil and groundwater F&T mechanisms for DIN and DIP into a single coefficient. DON, DOP, and an additional DIP export (for soil weathering) are calculated using a global export coefficient in combination with a runoff modulation function. The DON and DOP exports represent a combination of leaching losses associated with soil organic matter as well as a generic export from terrestrial nutrient loading. Erosion of PN and PP are addressed in a separate submodel using regression techniques that incorporate soil, groundwater, and surface-water inputs to estimate total suspended solids transport. Empirical relationships to total suspended solids are used to calculate particulate nutrient transport. The removal of N and P via crop harvest and livestock consumption is also included empirically.

SWAT and He et al. track species-specific soil nutrient pools. Both models include losses due to volatilization and denitrification. In addition, He et al. estimates gaseous N losses via nitrification. Both models include nutrient flows related to vegetation, e.g., plant uptake of inorganic nutrients, litter fall, conversion to detrital forms, and harvesting of crop biomass and removal from the watershed. He et al. does not include erosion as a transport mechanism, whereas SWAT links erosion rates to the movement of particulate inorganic P (PIP) and particulate organic N (PON). SWAT and He et al. differ in their treatment of surface runoff and leaching. He et al. uses an aggregated transport factor as a function of runoff and soil water storage whereas SWAT includes separate representation of surface runoff, lateral subsurface flow, and percolation to groundwater. Groundwater percolation in SWAT represents movement to deep groundwater, which prohibits lateral flow into surface waters. SWAT assumes that only nitrate reaches bodies of water via movement through the soil. Both DIP and nitrate are transported in surface runoff. The use of groundwater from both deep and shallow aquifers returns some nitrate to the soil surface. SWAT also considers upward movement of water, and nitrate in solution, from shallow aquifers into unsaturated soil layers to replace water lost via evapotranspiration, termed "revaporization".

Additional cycling between nutrient species and forms is represented in both SWAT and He et al. Both models include mineralization, nitrification, and stabilization and humification. SWAT divides humic N and P and PIP into active and stable pools. Stable forms must first move into the active pool before they can be mineralized. Detrital and humic N and P are mineralized to dissolved inorganic nutrient forms. SWAT assumes that mineralization increases the nitrate pool, whereas He et al. assume the increase affects the ammonia pool. (Ammonia is transformed into nitrate via nitrification.) Fresh, detrital forms of N and P are stabilized as humus in both models. SWAT differentiates the direct transformation of detritus to active humic forms, termed "decay". The active form of PIP rapidly reaches equilibrium with DIP. Stable PIP is immobilized but can rejoin the active system via transfer to active forms. SWAT includes a nitrate decay term for N entering a deep aquifer, which represents removal of nitrate via general chemical and biological processes.[50]

3.4. Fate and Transport in the Marine Ecosystem.

LCA research has traditionally ignored marine-specific impact categories due to the inherent complexity of the science.[65] Many of the common LCIA methods, including TRACI, EDIP 2003, LUCAS, and CML 2002, present eutrophication results as a single impact based on the Redfield ratio, overlooking the distinction between freshwater and marine environments. IMPACT World+ and ReCiPe 2008 treat marine and surface freshwater eutrophication separately, relying on the assumption that marine ecosystems tend to be limited by N. Both models use a simplified N F&T assumption, whereby 70% of N inputs into surface freshwater ecosystems make their way to coastal waters. None of these models include F&T processes directly within the marine compartment. Recently, Cosme et al. have developed a new set of global, spatially differentiated N FFs based on the NEWS 2-DIN model that integrate with XFs and EFs for 66 LMEs.[49,66]

The new Cosme et al.[38] model represents N F&T in the marine compartment as the sum of advective and denitrification losses (Table 4). Advective losses are determined based on an inverse function of residence time in the coastal region, with longer residence times leading to lower removal rates and increased quantities of N available to contribute to eutrophication.

Surface freshwater FFs for Cosme et al. stem from DIN removal coefficients from the NEWS 2-DIN submodel.[39,40] The XFs translate N loading into primary production and then track the fate of the resulting biological N (BN). A fraction of BN sinks to the bottom of the euphotic zone, where it contributes to oxygen demand as it is broken down by microorganisms. EFs translate oxygen depletion into the potentially affected fraction (PAF) of species. Together these developments significantly advance marine LCIA modeling, adding in-compartment nutrient transformation processes (DIN to ON) and expanding the eutrophication cause-effect chain to include oxygen depletion.

AQUATOX includes an estuarine submodel that handles stratification, tidal amplitude, water balance, and mixing. The submodel also represents the effects of salinity on mortality and gamete loss, sinking rates of suspended particulates, and volatilization.

The remaining four models (NCOM-CGEM, FVCOM-WQS, FVCOM-GEM, and EFDC-WQM) have capabilities specific to both estuarine ecosystems and coastal ocean regions (i.e., those on the continental shelf). All four models rely on complex hydrodynamic models to estimate the circulation of water within the specified modeling region, utilizing regionally specific data sets that include information on tides, temperature, bathymetry, heat flux, wind, and precipitation. The models track speciated N and P through various organic and inorganic forms, modeling specific chemical reactions such as nitrification, denitrification, and mineralization. The rate of reaction in each of these cases is formulated as a function of temperature, salinity, and oxygen availability, as applicable. The models diverge notably in their representation of organic material, sediment layer dynamics, and biological state variables. FVCOM-GEM is the only model to not explicitly track DO concentration as a state variable.

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Table 4. Comparison of F&T Mechanisms and Nutrient Species Coverage for Marine Eutrophication Models[a]

		model name					
category[b]	characteristic	AQUATOX-Estuary	Cosme et al.	NCOM-CGEM	FVCOM-WQM	FVCOM-GEM	EFCD-WQM
freshwater nutrient pools	nitrogen	NH_3, NO_3, BN, DN, PON	DIN, BN, DN	NO_3, NH_4, BN, DN	NH_3/NH_4, NO_3, DN, BN	NH_4, NO_3, NO_2, DN	NH_3/NH_4, NO_3,-DON, DN, BN
	phosphorus	PO4, PIP, BP, DP, PON	–	PO_4, BP, DP	PO_4, BP, DP	PO_4, DP	PO_4, DP, DOP, BP, PIP
transport and removal mechanisms	advection	N, P	DIN	N, P	N, P	N, P	N, P
	diffusion	N, P	–	N, P	N, P	N, P	N, P
	biological fixation	BN (+)	–	–	–	–	–
	sediment exchange	NO_3 (±), NH_3 (±), PO_4 (±)	–	NH_4 (+), PO_4 (+)	NO_3 (±), NH_3 (±), PO_4 (±)	NO_3 (±), NH_3 (±), PO_4 (±)	NO_3 (±), NH_3 (±), PO_4 (±)
	active vertical transport	BN (±), BP (±)	BN (±)	–	BN (±), BP (±)	BN (±), BP (±)	–
	settling	BN (−), BP (−), DN (−), DP (−)	DN (−), BN (−)	DN (−), DP (−)	BN (−), BP (−), DN (−), DP (−)	BN (−), BP (−), DN (−), DP (−)	DP (−), DN (−), PIP (−), BN (−), BP (−)
	resuspension	DN (+), DP (+), PON (+), POP (+)	–	–	NH_4 (+), NO_3 (+), PO_4 (+)	NH_4 (+), NO_3 (+), PO_4 (+)	DON (+), DP (+), DN (+), PIP (+), BN (+), BP (+)
	denitrification	NO_3 (−)	DIN (−)	NO_3 (−)	NO3 (−)	NO3 (−)	NO_3 (−)
nutrient cycling processes (within grid cells)	mineralization	NH_3(+),PO_4(+),DN(−),D-P (−), BN (−), BP (−)	–	DN (−), DP (−), NH_4 (+), PO_4 (+)	NH_4 (+), PO_4 (+), DN (−), DP (−)	NH_4 (+), PO_4 (+), DN (−), DP (−)	DOP (−), PO_4 (+), DON, (−), NH_4 (+)
	nitrification	NO_3 (+), NH_3 (−), DO (−)	–	NH_4 (−), NO_3 (+), DO (−)	NO_3 (+), NH_4 (−)	NH_4 (−), NO_3 (+), DO (−)	NH_4 (−), NO_3 (+), DO (−)
	dissolution and hydrolysis	–	–	–	DN (−), DP (−)	DN (−), DP (−)	DN (−), DON (+), DP (−), DOP (+)
	decomposition, microbial	DN (−), DP (−), NH_3 (+), PO_4 (+), DO (−)	DN (−)	–	DN (−), DP (−)	DN (−), DP (−)	-
	mortality	BN (−), BP (−), DN (+), DP (+)	BN (−), DN (+)	BN (−), BP (−), DN (+), DP (+)	BN (−), BP (−), DN (+), DP (+)	BN (−), BP (−), DN (+), DP (+)	-
	biological uptake	NH_3 (−), NO_3 (−), PO_4 (−), BN (+), BP (+), DO (+)	DIN (−), BN (+)	NH_4(−),NO_3(−),P-O_4(−),BN(+),BP-(+), DO (+)	NH_4(−),PO_4(−),-NO_3(−),BN(+),-BP (+), DO (+)	NH_4(−),PO_4(−),-NO_3(−),BN(+),-BP (+)	PO_4 (−), NH_4 (−), NO_3 (−), BN (+), BP (+), DO (+)
	predation and ingestion	DN (−), DP (−), BN (±), BP (±)	BN (±)	BN (±), BP (±), DN (+), DP (+)	BN (±), BP (±), DN (+), DP (+)	BN (±), BP (±), DN (+), DP (+)	DOP (+), DP (+), PO_4 (+), DON (+), DN (+), NH_4 (+), BN (−), BP (−)
	colonization	DN (−), DP (−), NH_3 (+), PO_4 (+)	–	–	–	–	–
	adsorption	PIP (+), PO_4 (−)	–	–	–	–	PO_4 (−), PIP (+)

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Table 4. continued

category[b]	characteristic	model name: AQUATOX-Estuary	Cosme et al.	NCOM-CGEM	FVCOM-WQM	FVCOM-GEM	EFCD-WQM
	respiration and metabolism	NH_3 (+), PO_4 (+), BN (−), BP (−), DO (−)	DN (−)	NH_4 (+), PO_4 (+), BN (−), BP (−), DO (−)	NH_4 (+), PO_4 (+), BN (−), BP (−), DO (−)	NH_4 (+), PO_4 (+), BN (−), BP (−)	DOP (+), POP (+), PO_4 (+), DON (+), PON (+), NH_4 (+), BN(−),BP(−), DO (−)
	excretion	NH_3 (+), BN (−), BP (−), DN (+), DP (+), PO_4 (+)	BN (−), DN (+)	NH_4 (+), PO_4 (+), DN (+), DP (+)	–	–	DOP (+), POP (+), PO_4 (+), DON (+), PON (+), NH_4 (+), BN (−), BP (−)
	reaeration	DO (+)	–	DO (+)	DO (+)	–	DO (+)
	sediment demand	DO (−)	DO (−)	DO (−)	DO (−)	–	DO (−)

[a]The (+) or (−) notation refers to an increase or decrease, respectively, in the concentration of associated species in the water column. [b]P, phosphorus; N, nitrogen; DON, dissolved organic nitrogen; ON, organic nitrogen; OP, organic phosphorus; DIP, dissolved inorganic phosphorus; DOP, dissolved organic phosphorus; POP, particulate organic phosphorus; PON, particulate organic nitrogen; NO_3, nitrate; NH_4, ammonium; NH_3, ammonia; PO_4, phosphate; BN, biological nitrogen; BP, biological P; OM, organic matter; DN, detrital N; DP, detrital P; PIP, particulate inorganic phosphorus.

The advantages of the linked hydrodynamic−water-quality models lie in their mechanistic detail and their use of a sub-annual time step. Mechanistic detail provides greater model fidelity at the expense of increased effort. The sub-annual time step of these models has the potential to more closely link LCIA eutrophication with the temporal scale of real-world hypoxic events.[18]

3.5. Fate and Transport in the Atmosphere. Atmospheric transport of nutrients for use in LCIA eutrophication modeling has evolved considerably in the last three decades. Early models, such as CML,[67] provided that no spatially differentiated CFs for nutrient emissions. Potting et al. (1998) was the first to develop a set of spatially differentiated CFs.[68] TRACI estimated N deposition from NO_x releases in North America using source-receptor matrices (SRMs) that were created based on the ASTRAP model.[20] The ASTRAP model provides estimates at the geographic scale of US states and Canadian provinces. ReCiPe 2008 derives atmospheric FFs by iterating between CARMEN and EUTREND to derive deposition estimates for watersheds and coastal seas in Europe.

IMPACT World+ uses annual average atmospheric FFs developed in Roy et al. (2012).[69] Roy et al. created a new approach to calculating SRMs at a global scale based on the output of the GEOS-Chem air quality model at a 2° × 2.5° grid level. GEOS-Chem simulates NO_x, HNO_3, and NH_3 transport and deposition using meteorological data and emissions for the year 2005. The approach of Roy et al. builds on earlier work demonstrating the use of SRMs for LCA.[26,68,70,71]

The air quality models GEOS-Chem, CMAQ, and CAMx feature similar coverage of pollutants and F&T mechanisms. Each model uses emissions data as input, which in all three cases includes industrial and mobile sources, biomass burning, agricultural emissions, and dust, with the flexibility to include additional sources. Emissions data are mapped to a geographic grid using a tool such as the Sparse Matrix Operator Kernel Emissions Modeling System (SMOKE).[72] All three models include advection, diffusion, and wet- and dry-deposition processes to simulate transport between grid cells in the atmosphere.

Chemistry modules specify chemical mechanisms and reaction rates that facilitate the models' key function of projecting the concentration of chemical species resulting from specified global emissions scenarios and meteorological input data. Multiple chemistry modules are available to achieve better regional performance or chemistry representation for a species or chemical class of interest. All modules include chemistry mechanisms that cover gas-phase reactions, aqueous chemistry, organic and inorganic aerosol formation and partitioning, photolysis, and adsorption to dust. Each of the air quality models includes nitrogenous chemicals that contribute to eutrophication. Few models include atmospheric F&T of P, which is a shortcoming given the emerging opinion that windblown P can contribute to nutrient loading in surface water.[13−16,73,74]

CAMx and CMAQ are regional models that can be applied globally when linked with GEOS-Chem or other global models to provide initial boundary conditions. All models provide nested grid capability, which allows local areas of interest to be treated at a finer level of spatial and temporal resolution than surrounding regions. CAMx and CMAQ are commonly operated on 36, 12, or 4 km grids over large regions, with a finer grid resolutions of 1−2 km used in more-limited local areas. GEOS-Chem operates on a coarser grid that varies between approximately 28 and 140 km (0.25° and 1.25°) on each side. Grid size influences air pollutant concentration, particularly for

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species with short atmospheric lifespans and compact dispersal ranges, which are often under-estimated at coarse model resolutions.[75,76] Secondary particulates, some of which are nitrogenous, are thought to be less-affected by coarse grid resolutions.[77] NO_x has a relatively short atmospheric lifespan, on the order of 4 h to 1 day, indicating that accurate modeling of its atmospheric transport may require fine grid resolutions.[78,79]

Recent work at the global scale has modeled atmospheric N and P deposition. The Community Atmospheric Model (CAM) was used to estimate P deposition across the globe.[73,80] The global aerosol chemistry-climate model LMDZ-INCA coupled modeling system improves upon the prior estimates of P deposition by incorporating more information about fuel combustion sources of P.[81,82] Emissions data from LMDZ-INCA include sea salt and dust for P, primary biogenic aerosol particles, and fuel combustion for P. In contrast to N, there has historically been little focus on atmospheric P deposition. Challenges associated with measuring P deposition, combined with the presumption that other P sources drive P availability in land and water, has meant that few studies have focused on the atmospheric P source. The U.S. National Atmospheric Deposition Program does not report P in deposition. Increasing P concentrations in U.S. lakes and streams[74,83] may be linked to changing P deposition; thus, better methods are needed for monitoring and estimating this potentially important flux-affecting freshwater eutrophication.

Built-in source apportionment methods may be an alternative to SRMs for the development of atmospheric FFs. Source apportionment relates emission sources to their impact on ambient air quality. CAMx, CMAQ, and GEOS-Chem can each perform source apportionment during a model run (as a function of a source attribution algorithm), after a model run via additional processing, or as part of a sensitivity analysis. Both CAMx and CMAQ store mass throughput data for individual chemical mechanisms and time steps, which requires significant computing resources over large model extents.[84] Sensitivity analyses, in which all or part of an individual source of interest are removed from a model run, provides an opportunity to quantify the effect of the source on dependent air-quality results. These are often called zero-out simulations and constitute a "brute force" sensitivity analysis that can be applied to all air-quality models.[63]

4. DISCUSSION

The model comparisons provided in the preceding sections highlight strengths and weaknesses of the reviewed models that directly pertain to the development of improved LCIA eutrophication methods. The intention of this section is to clearly link the goals of LCIA eutrophication with the features of the reviewed models, working toward specific recommendations.

The five LCIA models reviewed (including Cosme et al.) vary considerably in approach and level of detail by which they quantify eutrophication midpoint impacts. Midpoint eutrophication impacts are expressed in three ways depending on the method selected:

(1) The Redfield ratio describes a generic elemental composition of algae. The ratio is used to develop an equivalency between elements and nutrient forms based on stoichiometric relationships, calculating biomass growth as a function of nutrient loading.
(2) The residence time of nutrients in freshwater or marine environments is calculated as a function of nutrient loading, retention, and removal and approximates the availability of nutrients to contribute to eutrophication. Given an emission rate, these residence times also indicate steady-state mass in each compartment.
(3) Oxygen depletion expresses midpoint impacts as kg O_2 depleted per kg of N influent to the marine ecosystem. The XF calculation is based on a simple ecological response model.[40]

The three midpoint indicators represent a progression of LCIA modeling detail (from 1 to 3) and associated expansion of the LCIA cause−effect chain. Early LCIA eutrophication models, such as CML, did not model nutrient F&T and instead assumed that increased nutrient emissions would yield increased impacts regardless of environmental compartment or location. More recent modeling efforts identify the importance of capturing F&T spatial variability in eutrophication impacts and recommend the use of F&T models when information is available to LCA practitioners on the location of a nutrient release. Consideration of F&T mechanisms facilitated the development of a midpoint indicator based on residence time, which considers not only presence but also the duration of a nutrient load. The consideration of nutrient transformation processes and their interaction with DO concentration from Cosme et al. leverages additional F&T processes to more-directly link nutrient emissions to environmental effects.

These developments clearly demonstrate the role and importance of F&T modeling within LCIA eutrophication characterization. The next step is to move toward the use of F&T models that most-accurately reflect the real-world processes they represent. The challenge is to do so without placing undue burden on developers and practitioners.

TRACI uses advection as a proxy indicator of N F&T, providing a novel, simplified approach that was well-suited to historical data availability and LCA tools. More-sophisticated approaches to nutrient F&T estimation are now available that simulate nutrient retention, water use, and denitrification.[21,49,66] While ReCiPe 2008 is limited to the European geographic scope, it remains the only freshwater LCIA method that incorporates P soil and groundwater F&T modeling when calculating midpoint CFs, a feature that is lost in the ReCiPe 2016 update and in the proposed IMPACT World+ method. ReCiPe 2016 and IMPACT World+ do, however, improve upon the simplified approach to nutrient F&T in surface freshwater used by ReCiPe 2008 via the cumulative FFs of Helmes et al.[21] while expanding to a global geographic scope. No significant advancements are made to the marine eutrophication impact category in IMPACT World+, and ReCiPe 2016 excludes this impact category altogether.

Cosme et al. advanced LCA's ability to assess marine eutrophication impacts by providing the first set of global, regionally differentiated fate, effect, and damage factors for 66 LMEs.[39,40] Cosme et al. also introduce new soil and freshwater FFs for N emissions across 5772 global river basins.[38]

The LCIA methods currently available provide limited guidance to practitioners on estimating F&T in the soil compartment. While Helmes and Cosme et al. rectify this problem for the freshwater and marine compartments, respectively, the question of model fidelity remains. Additionally, Cosme et al. notes that the use of an annual time-step and LME size restrict the ability to reflect the temporal and spatial reality of real-world hypoxic events.[18]

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Of the six watershed models, NEWS 2, SWAT, and IMAGE-GNM provide the best opportunity to yield further improvements in LCIA eutrophication. He et al. does not provide a comprehensive option because it lacks representation of F&T pathways for P releases, which is essential to the estimation of freshwater eutrophication impacts. SPARROW is limited by the need for high-quality global monitoring data and by challenging model calibration when the model simulates large spatial extents.

NEWS 2 has demonstrated its usefulness in developing soil and surface freshwater FFs but is currently limited to the spatial scale of basins as defined in the STN-30p river network. Still, basin-level resolution may be sufficient for LCA studies when the exact location of emissions is unknown. Additionally, NEWS 2 FFs are based only on DIN export; there is potential for further development based on transport of DON or PN, as estimated by other NEWS 2 submodels.

SWAT estimates the yield of ON, OP, nitrate, and DIP to each stream reach within a watershed and could be used to calculate speciated and spatially differentiated CFs at the resolution of user-defined hydrologic response units (HRUs).[85] Feasibility of applying SWAT in an LCA context is limited by the fact that SWAT is run at the basin scale, though studies have demonstrated that wide geographic coverage across multiple basin scales can be achieved.[86]

IMAGE-GNM provides the most-comprehensive option to develop global, spatially differentiated soil and freshwater FFs for both N and P at the 0.5° × 0.5° grid scale, as was observed by Cosme et al.[18] The model calculates discharge to surface-water grid cells, N and P soil budgets, ammonia emissions from soil, and wastewater discharge to surface freshwater. IMAGE-GNM also estimates nutrient concentration in surface freshwater bodies facilitating validation with monitoring data and estimation of annual export fractions for use in the development of FFs using an annual average or marginal approach.

The surface-freshwater models WASP and AQUATOX provide detailed mechanistic representation of nutrient F&T, transformation processes, and biological interactions that link nutrient-loading information to organic matter growth and subsequent ecological effects, often as functions of dual-nutrient limitation, light availability, and temperature. AQUATOX stands out among the reviewed models in that it estimates endpoint impacts in the form of ammonia toxicity and lethal and nonlethal effects of low oxygen. These considerations are largely absent from current LCIA methods and the reviewed watershed models. However, the data collection burden and limited geographic coverage of WASP and AQUATOX limit their potential to directly generate FFs or EFs with global applicability.

The hydrodynamic models NCOM, FVCOM, and EFDC could resolve the issues of spatial and temporal mismatch noted by Cosme et al.; however, the level of effort required to achieve global coverage makes implementation more challenging. The structure of these models allows for simplifications that could reduce the modeling effort to a reasonable level, as is demonstrated by current efforts to develop an FVCOM model of the entire Atlantic Ocean basin.[87] When linked with water quality modules, these models operate at a time-step (in minutes) that can capture the temporal scale of real-world eutrophication events, with the potential to open new lines of inquiry within the scope of LCA. To take advantage of FFs with subannual resolution, LCA practitioners would need to provide inventory data with similar temporal scope, which is not currently common practice.

Within the atmospheric compartment, the approach of Roy et al.[69] exemplifies the use of a complex, global F&T model to develop FFs using the SRM approach. These FFs represent the 2005 data year, which is believed to be representative of average conditions for the preceding period, but patterns of NO_x emissions are shifting rapidly,[88−90] necessitating frequent updating. Despite this caveat, the implementation of atmospheric N F&T modeling in LCIA eutrophication closely aligns with the goals of being global, spatially differentiated, and representative of the most recent science.

Whereas CAMx and CMAQ offer increased spatial resolution and better source apportionment methods compared to GEOS-Chem, these benefits can only be realized in a single, regional model run. Targeted validation of simulated deposition would be beneficial in justifying the level of effort needed to pursue developments using these models.

5. RECOMMENDATIONS

Table 5 summarizes our recommendations for improving LCIA modeling for eutrophication. The purpose of these recommendations is to (1) fill gaps in existing characterization models, (2) provide greater spatial differentiation of FFs, and (3) add F&T mechanisms as needed to improve the environmental relevance and scientific robustness of LCIA eutrophication methods.

5.1. Separation of Freshwater and Marine Eutrophication Methods. First and foremost, we propose separating freshwater and marine LCIA eutrophication methods. This is in line with recent method updates, e.g., ReCiPe 2016 and IMPACT World+, and with the findings of the 2013 LC-IMPACT report.[22] The simplifying assumptions that P and N are limiting in surface freshwater and marine waters, respectively; the improved availability of FFs, XFs, and EFs; and the differences in oxygen depletion mechanisms affecting biomass growth, hypoxia, and endpoint effects all support this recommendation.

5.2. Freshwater FF Availability. For freshwater eutrophication, we recognize Helmes et al. 2012 as the best available source of freshwater FFs. Factor values are provided at a 0.5° × 0.5° grid scale, allowing the aggregation of FFs with state, province, watershed, or country boundaries. Both ReCiPe 2016 and IMPACT World+ aggregate FFs at the country level. We recommend a re-aggregation of FFs for the United States at the state scale in addition to the currently available watershed factors. Further performance validation of the Helmes et al. F&T model will ensure appropriate, regionalized characterization. Comparison with the results of NEWS 2 and SPARROW should also be feasible based on annual nutrient export fractions. The outcome of this model comparison can guide future model developments.

5.3. Freshwater Characterization Expansion. An opportunity exists to expand characterization of the freshwater cause-effect chain by adapting the oxygen depletion midpoint indicator of Cosme et al. for freshwater systems. This indicator would reduce the distance between the midpoint indicator and ecological effects without introducing the uncertainty associated with estimates of species-response. This is listed as being priority 2 in Table 5; however, if stopping at the same point on the cause−effect chain is considered to be a high priority to the model developer, it could be considered priority 1. Gaps in characterization would persist, such as the inability to estimate HAB occurrence.

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Table 5. Recommendations for the Improvement of Freshwater and Marine LCIA Eutrophication Methods[a]

LCIA method	environmental compartment	priority	level of effort	recommendation
freshwater and marine	all compartments	1	E	Separate freshwater and marine eutrophication LCIA methods.
	soil and freshwater	2	D	Use IMAGE-GNM[b] to develop subwatershed-level, spatially differentiated terrestrial and freshwater FFs.
freshwater eutrophication	freshwater	1	E	Adopt freshwater FFs from Helmes et al., providing state or watershed aggregated fate factors for the United States.
		2	M	Adapt the O_2 depletion midpoint indicator approach developed in ref 18 for freshwater systems.
		2	M	Validate the performance of Helmes et al. retention rates and resulting FFs against other models and monitoring data to assess long-term needs for method improvement.
	soil	1	E	Apply standard emission fractions to terrestrial nutrient loads, as in the ReCiPe approach (e.g., 10% land-applied P to freshwater).
		1	M	Provide spatially differentiated guidance on emission fractions based on landscape characteristics.
marine eutrophication	freshwater and marine	1	E	Adopt soil, freshwater, and marine FFs, and marine XFs and EFs from ref 18, reaggregating to the state level for the United States.
	marine	2	D	Refine residence time values that serve as the basis of Cosme et al. marine fate and transport factors[b].
		3	D	Use hydrodynamic water quality models to develop marine FFs and XFs, increasing spatial resolution beyond 66 LMEs.
	air	2	M	Adapt the research of Roy et al. to develop global marine eutrophication FFs for atmospheric N emissions. Consider updating FFs based on more recent inventory data.
		3	D	Run a series of nested CMAQ or CAMx model runs at a regional scale using GEOS-Chem at a coarser grid resolution to provide boundary conditions. Explore options to apply the SRM approach of Roy et al. or internal source apportionment functions.

[a]The priority of each recommendation is assessed on a scale of 1−3 as follows: (1) an immediate need, (2) beneficial in the medium-term, or (3) requires validation to justify the effort. The level of effort associated with each recommendation is assessed as easy (E), medium (M), or difficult (D). Easy recommendations represent adoption of the best, currently available methods. Recommendations assessed as medium difficulty represent extensions of existing approaches. Difficult recommendations require novel modeling techniques or applications. [b]This possibility was suggested in ref 18.

5.4. Best Available Marine LCIA Method. For marine eutrophication, we recognize the work of Cosme et al. as the best-available LCIA method because it fills previously existing gaps in the characterization model and cause−effect chain. Integrating the Cosme et al. method with the atmospheric FFs from Roy et al. would close additional gaps in the model.

5.5. Linked Hydrodynamic Water Quality F&T. The use of linked hydrodynamic water quality F&T models could increase spatial and temporal resolution of the resulting mid-point and endpoint CFs. These models could refine residence time estimates in coastal waters for LMEs (or a smaller spatial unit) and could help refine the Cosme et al. marine eutrophication method. They could likely also help generate marine FFs and XFs. Feasibility of implementation could be assessed via a case study for a region where detailed coastal modeling is already available, e.g., the Louisiana Coastal Shelf.[53]

5.6. Terrestrial F&T of Land-Applied Nutrients. The terrestrial F&T of land-applied nutrients requires further research because terrestrial eutrophication modeling is largely absent from LCIA despite its importance to agricultural and other land use sectors.[22] The assumption by ReCiPe 2016 that 10% of land-applied P reaches surface waters is currently the best available approach without overburdening the user with data collection requirements. More-specific guidance needs to be developed for landscape characteristics such as soil type, climate, and proximity to freshwater (as given in EDIP 2003) to better-estimate terrestrial export fractions associated with land-applied nutrients. Cosme et al. provide the best currently available soil and freshwater FFs for N based on the NEWS 2 model, spatially differentiated at the 30 min (STN-30p) river basin scale.

5.7. Development of New Soil and Freshwater FFs. Finally, we recommend the development of new soil and freshwater FFs based on IMAGE-GNM, given the global availability of data at the 0.5° × 0.5° grid scale. The potential of this option was earlier recognized by Cosme et al.[18] This approach would improve upon the general soil F&T guidance of ReCiPe 2016, increase spatial resolution compared with N FFs from the NEWS 2 model, and provide a consistent framework for dealing with N and P F&T in soil and surface freshwater. IMAGE-GNM runs using an annual time-step. No feasible means of achieving sub-annual (seasonal) temporal resolution has been identified that conforms with the preferred global scope of LCIA modeling.

6. CONCLUSIONS AND OUTLOOK

The goals of this work were to (1) document the current state of eutrophication methods in LCIA, (2) review and compare selected nutrient F&T models that could inform existing and future LCIA eutrophication methods, (3) discuss potential linkages between these methods and models, and (4) offer recommendations for how to improve eutrophication impact categories in LCIA and LCA going forward.

We reviewed 5 LCIA eutrophication methods and 15 nutrient F&T models. Based on the outcomes of the review, we offered several recommendations for the next steps in freshwater and marine eutrophication modeling in LCIA. In particular, our first-order recommendations are to (1) represent freshwater and marine categories in LCIA eutrophication modeling separately; (2) to apply published (e.g., Helmes et al. 2012) state- or watershed-aggregated freshwater fate factors for the United States; and (3) to adopt marine fate, exposure, and effect factors from Cosme et al., reaggregating to the state level for the United States. Wherever possible, the trend for eutrophication modeling in LCIA should be to move toward greater site specificity.

Part of this work involved translating modeling principles between F&T and LCA communities. As each community

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becomes more aware of the ongoing work and emerging issues of the other, together we gain a more holistic perspective of the knowledge gaps and technical needs of the science and better recognize where opportunities for collaboration may exist. The scientific advancements here have focused on freshwater and marine eutrophication. This critical review process could be replicated for other LCIA impact categories such as acidification or smog formation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00967.

Tables showing acronyms, model descriptions, a comparison of surface freshwater F&T mechanisms, and a model rubric. (XLSX)

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Notes

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