SEDIMENT POLLUTION (P ZHANG, SECTION EDITOR)



# Causes, Assessment, and Treatment of Nutrient (N and P) Pollution in Rivers, Estuaries, and Coastal Waters

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#### Abstract

As a consequence of industrialization, urbanization, and population growth in the past decades, high nutrient concentrations from point and non-point sources in aquatic systems have caused major problems to the water quality in rivers, estuaries, and coastal waters. Although the nutrient pollution due to land use change cannot be ignored, the combined sewer overflows and discharging sites have been important point sources of nutrient pollution. Integrated hydrodynamic, chemical, and biological models developed in recent years, which simulate the nutrient transportation from both point and non-point sources, are useful tools to assist in identifying the transport and fate of nutrients from both point and non-point sources. In this paper, water quality data from published literature were reviewed and analyzed to evaluate nutrient (N and P) pollution in aquatic systems. An integrated monitoring and management plan should be continuously developed in the future to monitor and regulate nutrient discharges from point and non-point sources.

Keywords Nutrient pollution · Nitrogen · Phosphorus · Combined sewer overflows

## Introduction

Nutrient contamination in waterbodies and waterways has been a serious environmental problem in many countries because water quality is vital to human health, ecosystems, and environment and can be affected by nutrient (N and P) concentrations due to both natural processes and anthropogenic activities [62]. Although newly urbanized land can bring economic profits and prosperity, it may also cause damage to the ecosystem [36]. Urbanization and agricultural land use can

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cause high nutrient concentrations in the water body [38]. Thus, nutrient (N and P) concentrations are highly impacted by the rapid land use change and expansion in urban coastal areas, which cause non-point source nutrient pollution. In the USA, urban development both impacts and causes environmental changes. Early studies indicated that urban or agricultural storm water runoff and wastewater discharges caused an increase in nutrient concentrations [21]. For example, the lower Passaic River and Newark Bay in the USA suffered from severe chemical, metal, and nutrient pollution for decades [53]. Most of the nutrients were from publicly owned treatment works (POTWs) and combined sewer overflows (CSOs) [16]. Both water and sediment quality data showed that the biodiversity and natural resource abundance in these areas were reduced significantly and thus resulted in water quality degradation [15]. Therefore, thousands of water quality restoration projects have been conducted in order to deal with water quality issues [51].

In coastal areas, estuaries are a transition zone between river environments and maritime environments, home to unique plant and animal communities, and vulnerable to nutrient pollution when the polluted stream water passes through these areas into coastal waters. In nitrogen cycle among atmosphere, land, sea, and sediments, atmospheric deposition of

inorganic nitrogen (NO, NO<sub>2</sub>, and NH<sub>3</sub>) is an important source to the ocean, although the input rate is still uncertain [6]. In contrast, riverine input has an insignificant impact on ocean water during the denitrification process in the coastal zone [35]. It was reported that the marine biota only contains less than 0.05% of reactive nitrogen while land biota contains 5% of the terrestrial nitrogen that is present largely in the soil [13]. However, human alterations have doubled reactive nitrogen input into the terrestrial nitrogen cycle, increased N<sub>2</sub>O emission, caused losses of soil nutrients, and greatly increased the transfer of nitrogen through rivers to estuaries and coastal oceans [66]. Anthropogenic influence, such as combustion of fossil fuels routinely used in agricultural and industrial practices, can affect nitrogen cycle and introduce a large quantity of reactive nitrogen (Nr) into water, air, and land, which causes health risks to human beings. Sediment redox condition change and iron (Fe) reduction in the waterbody can also affect the nutrient concentrations in aquatic environments [46]. Previous studies show that seasonal change with a different precipitation pattern can affect nutrient concentrations [22, 53, 61]. Due to its unique environmental settings and characteristics in different riverine and estuarine systems, water quality can be naturally different in both spatial and temporal scales to reflect local terrestrial influences [72]. Abnormal high nutrient concentrations can occur in certain circumstances, such as hurricanes that can cause sediment resuspension and accelerate the release of nutrients to the dissolved phase [33]. A study conducted in Sweden shows the impact of sediment resuspension on changes of the nutrient flux rates with a decrease in phosphate, an increase in nitrate and nitrite, and no significant change in ammonia [63]. In the Mediterranean and the Black Sea area, a study conducted by a group of researchers [39] reported that freshwater discharge in Mediterranean rivers was reduced by at least 20% between 1960 and 2000. N and P fluxes in Mediterranean rivers were strongly influenced by human activities, and riverine nutrient discharges were the major sources of nutrient pollution and a worsening local ecosystem.

High nutrient concentrations can not only damage the aquatic ecosystem but also endanger human health. This is especially of concern for the main rivers supplying drinking water where nutrient concentrations should be controlled in a safe range [12]. Therefore, an effort to reduce nutrient input into the rivers, estuaries, and coastal waters has to be enforced globally and regionally. In the USA, the government has established a number of watermonitoring stations to monitor and ensure the water quality. Since 1987, the United States Environmental Protection Agency (USEPA) has developed total maximum daily loading (TMDL) to regulate non-point sources of nutrient input [25]. Subsequently, many TMDL models are developed by the government for different local areas. Some regional efforts have also been made, including

New York/New Jersev Harbor Estuary (NY/NJ Harbor). Delaware Estuary, Nearshore Ocean, and Shallow Coastal Bays (including Barnegat Bay) [43]. The New York-New Jersey Harbor Estuary Program (HEP) is one of the projects established to study the nutrient TMDLs throughout the NY/NJ Harbor. The program established the detailed criterion for nutrient discharge from different treatment plants and treatment processes to reduce nitrogen and phosphorus loadings. The program also categorized the total nitrogen (TN) removal levels into low (TN 10-12 mg  $L^{-1}$ ), medium (TN 6–10 mg  $L^{-1}$ ), and high (TN 4-5 mg  $L^{-1}$ ) levels according to different treatment processes [25]. The US New Jersey Department of Environmental Protection published a new nutrient requirement in 2009 for high water quality needs in our lives. For instance, total phosphorus (TP) concentration in the effluent has been changed from 1.0 to 0.1 mg  $L^{-1}$ [43].

A number of studies have shown that increased nutrient (N and P) concentrations and fluxes are strongly impacted by anthropogenic activities. Therefore, integrated management methods are in high demand for identification and control of the possible pollution sources that impact the environment [24]. Some studies suggest to use the ratio between total dissolved inorganic nitrogen and phosphate as a measure to evaluate nutrient eutrophication conditions in the waterbody [28]. In this paper, water quality data and modeling techniques from published literature were reviewed and analyzed to evaluate nutrient (N and P) pollution in aquatic systems. In the future, environmental management and ecosystem restoration should be a focal area in this regard.

## **Point and Non-point Sources of Nutrients**

Intensive urban development has caused a serious issue in habitat health as indicated by water quality. During the last few decades, anthropogenic activities contributed major nutrient contamination to the waterbody. The main contaminant sources include fertilizers, animal waste, human sewage, household products, and byproducts from petroleum production and agricultural fields. Other sources include industrial manufacturing and lawn use [5]. As shown in Table 1, inputs of nutrient contaminants are categorized into point and nonpoint sources. Land use, land cover change, and combined sewage overflow are considered as significant non-point and point sources, causing nutrient pollution. Impervious surface coverage is a quantifiable land use change indicator. The causes and corresponding treatment methods of nutrient pollution are summarized in Table 1. Strategies for landscape design should be made by administrative groups to address the environmental problems in a community [68].

Category of nutrient pollution	Causes of nutrient pollution	Treatment methods	References
Point source pollution	Combined sewage overflow (animal waste, human sewage, and household products)	Conduct a green infrastructure plan to control storm runoff, upgrade the control of combined sewer overflow outfalls, and reduce the overall amount of sewage flow; use combined hydrodynamic model to evaluate the CSO impact; establish a science-based water quality-monitoring program; construct wetlands	Reemtsma et al. [59], Amar et al. [3], Morgan et al. [47], Farnham et al. [20], Pálfy et al. [52], Masi et al. [42]
	Publicly owned treatment work	Regulation and control of discharging loading	Crawford et al. [16]
	Industrial manufacturing discharge	Regulation and control of discharging loading; reevaluate the treatment process	Crawford et al. [16], NJDEP [56]
Non-point source pollution	Land use and land cover change coupling with climate change, soil type, and sediment processes	Change physical soil to an agronomic soil practice	Adimassu et al. [1], Trang et al. [65]
	Dissolved organic matter	Plant uptake, forest vegetation	Dean et al. [17]
	Agricultural fertilizer, lawn use	Conservation practice	Garcia et al. [23], Mehdi et al. [44]

Table 1 The causes and corresponding treatment methods of nutrient pollution

# Non-point Sources Due to Land Use and Land Cover Changes

Because different land use type can determine soil type, land use and land cover changes can cause changes in land geology and geomorphology. This can affect biological community, soil and sediment stability, and water runoff rate. Therefore, these are important factors affecting aquatic systems. Nutrient (N and P) concentrations in surface water are considered to be mainly controlled by water-rock interactions (i.e., weathering). A study in the Asian monsoon region shows that sediment processes have potential impacts on water quality because inorganic nutrients are mostly from storm runoff during a monsoon and can be transported to a relatively long distance [34]. When studying stream water N and P concentration, terrestrial and instream processes are important. As exemplified by a deciduous forest stream, inorganic N and P sink in upper soil horizons while the parent dolomite weathering is the major source of inorganic P into the stream [50]. In a riparian zone, when dissolved oxygen (DO) is high, inorganic P sinks. When DO is low, however, the riparian zone is a potential source of  $NH_4^+$  and  $PO_4^{3-}$  [50]. In most cases, nutrients (N and P) are good indicators of land use change impact because they are used to evaluate relationships between land use change and nutrient loading change. Specifically, land use change coupled with climate change can accelerate soil erosion and result in an increase in nutrient loading and discharge in the wet season, and a decrease in the dry season [65].

It has been reported that land use change can affect freshwater discharge and nutrient flux [18], alter nutrient biogeochemical cycle, and introduce high nutrient concentrations into the water body [38]. Thus, it can have a significant environmental impact on local ecosystems and a potential to change the biogeochemistry of aquatic systems. These include the impact on microorganisms in aquatic systems and populations of communities in an ecosystem. However, ecosystem functions, such as regulation of water flow, soil retention, habitat, and biodiversity maintenance, can better support the ecosystems and protect the environment [45]. In granite and silicate terrain landscape with low precipitation and high transpiration biomes, the uptake of N and P through vegetation has more significant influence than water-rock interaction in controlling nutrient concentrations [17]. Previous studies also indicate that forest vegetation can control sediment loads and sufficiently ensure water quality in the aquatic system, which can then ensure the conservation of the species in aquatic ecosystems [4]. In a forest ecosystem, organic matter is a major carrier of N and P. Spatial distribution and loss of N and P depend on organic matter content and its interactions with soils. Soil content is important because storm water runoff can wash out the available nutrients into streams and rivers, resulting in a high level of nutrient concentrations. Most of dissolved organic nitrogen (DON) and dissolved organic phosphate (DOP) have functional groups associated with humid, hydrophilic acid, and hydrophilic neutral fractions which have little impact on the behavior of most of dissolved organic matter (DOM). The carboxylic and phenolic functional groups of DOM are very important in governing the behavior

of nitrogen [57]. Although physical soil and water conservation practices can reduce storm water runoff, soil erosion, and nutrient depletion, they also decrease the crop yield due to the loss of cultivable area. However, if physical soil can be changed to an agronomic soil practice, then, the crop yield can be increased with a reduction in runoff and soil erosion [1]. Plant uptake of nutrients is also an important mechanism to deplete nutrients in surface water. Immobilization of inorganic N and P is found to be taken up by microbes on decomposing leaves and algae [50]. Agriculture may positively improve or negatively affect the water quality based on specific situations. For example, crop planting can help keep nutritional materials in soil and roots, but overdoses of insecticide and nutrients (e.g., phosphate and nitrogen) can result in eutrophication in the waterbody. Knowing the processes of how agricultural land use change affects the aquatic ecosystems will help to protect the water quality and implement sustainable water management [44]. Anthropogenic nutrients are mainly from agricultural fertilizer use. In order to quantify agricultural impacts on water quality, the conservation intensity is used to represent the implementation impacts of conservation practices that indicate the agricultural land use impacts on water quality. Sufficient evidence supports that conservation practice in the Upper Mississippi River Basin has a detectable larger impact on nitrogen loading than phosphate loading [23]. Another study in aquatic ecosystems indicates that the changes in land use pattern can result in changes in biological community structure and cause the diversity of the community to decline [14]. Overall, reduction of non-point agricultural source pollution is essential to improve the water quality in aquatic ecosystems.

# Point Sources Associated with Combined Sewer Overflow

With development of water treatment technology, wastewater treatment systems have been used to improve water quality by decreasing the nutrient discharge into aquatic systems [16]. However, combined sewer overflows (CSOs) and industrial waste discharge are still the major sources of nutrient pollution. The combined sewer overflows are used to assemble water from point and non-point pollution sources together and then discharge nutrients as a point source into rivers, streams, estuaries, and coastal waters. Studies in the late 1990s showed that major mass loading of nutrient pollution was from publicly owned treatment works and combined sewer overflows (D. W. [16]). According to laboratory and field analyses, water samples from combined sewer overflows exhibit higher nutrient concentrations (e.g., N,  $24 \pm 10$  mg L<sup>-1</sup>; and P,  $1.8 \pm$  $0.5 \text{ mg L}^{-1}$ ) than from publicly owned treatment works [59]. Thus, water discharged from CSOs causes relatively high nutrient concentrations [59], which makes combined sewer overflows an important point source of nutrient pollution to aquatic systems. In other words, discharge of untreated nutrients and other chemicals from combined sewer overflows can place high risks on aquatic environments and human health. In order to evaluate the combined sewer overflows in a less expensive way, subjective assessment criteria are proposed by some studies [47]. Knowing the dynamics and toxicity of nutrients discharged from combined sewer overflows can enhance the management of CSO accidents. Based on the evaluation and characterization of sediment and downstream water quality and flow dynamic information, recommendations can be made to optimize management methods [8].

Since the combined sewer overflows can have a significant impact on water quality, evaluation of combined sewer overflows is of great importance to ensure a better quality ecosystem. In order to improve water quality, the government at different levels has made a concerted effort to enact new regulations, manage the combined sewer overflow events, and evaluate the cost of nutrient reduction in each area [56], which has challenged the treatment process of facilities located upstream of lakes, ponds, or reservoirs. To address storm flooding and associated combined sewer overflows, both the New York Department of Environmental Conservation and the New Jersey Department of Environmental Protection in the USA have proposed several solutions such as conducting a green infrastructure plan to control storm water runoff, upgrading the control of combined sewer overflow outfalls, and reducing the overall amount of sewage flow [3]. Management of combined sewer overflows is conducted by several methods including but not limited to model evaluation, wetland construction, and multiple management methods. In the meantime, it is necessary to construct a large database to evaluate the impacts of combined sewer overflows. In the USA, New York City is seeking a citizen science-based water quality-monitoring program coupled with efficiency and cost analysis, which is focused on establishing a more efficient, time, and cost-saving system to monitor combined sewer overflow impacts [20]. So far, diverse methods have been developed to treat combined sewer overflows. One of the methods is to construct wetlands. A case study in Italy demonstrated the monitoring of combined sewer overflows' quality and quantity at different sites [42]. The results show that wetland treatment can reduce nitrogen concentration by 93%, which implies a significant success [42].

## Modeling Approach in Nutrient Study

In order to better estimate the relationship between land use change and nutrient concentration, modeling approaches have been applied to estimate the total nitrogen and phosphate loading from different sources [32]. Various modeling approaches have been developed to evaluate the sources of nutrient pollution and further the fate and mass transfer of nutrients [10, 30]. This is now a commonly used method to predict the impacts of land use changes on water quality over decades. The results can help management teams to evaluate water pollution and make strategies to control nutrient input [32]. For example, a research group in Kenya used modeling approaches to find relationships between land use and nutrient cycling in applicable areas [29]. Their results indicate that different types of land use can impact the nitrate concentrations in streams with seasonal alteration between wet and dry seasons [29].

Previous studies on hydrodynamic models have shown their importance in evaluating the sources of nutrients. For example, the Everglades Wetland Hydrodynamic Model (EWHM) was originally designated to be used in wetlands [49]. Then, it was turned into a nutrient removal model with the proper calibration. The model prediction results showed a significant correlation to the observed data [49]. Another three-dimensional hydrodynamic model based on a 4-year data calibration was developed to estimate the amount of net nutrient inflow from the Baltic proper [27]. The dynamic balance of mass loading calculation was used in the model and indicated the importance of background nutrient loading from Balti proper [27]. Hydrodynamic models have been developed over time from one-dimensional to three-dimensional models which are commonly used to evaluate nutrient transportation in rivers and estuaries [64]. In a sense, hydrodynamic modeling is a combination of computer simulations with a consideration of physical and biological processes in surface water systems. Nutrient cycle, water flow, oxygen demand, and other chemical and biological indices can be the components in the one-dimensional models. With the information compiled from different nutrient concentrations, organic matter content, and biological components, the models can be adjusted to any kind of lakes and reservoirs [48]. In order to further evaluate the water quality in different aquatic environments, integrated models are also used in the nutrient study. Table 2 shows some examples of different models for nutrient study. For example, a model used by the Chicago Area Waterway System (CAWS) in the USA can capture the fate and transport of combined sewer overflow discharges [58]. The hydrodynamic model simulates the transportation of combined sewer overflows. The results indicate that due to large water dilution impact, there is no significant combined sewer overflow impact in water quality within the system boundaries [58].

Because water quality is a major global issue today, the water quality model development has been attracting significant attention. Since a one-dimensional model has its drawbacks in determination of the hydrodynamic and ecological response, a three-dimensional model has been introduced into lacustrine ecosystems. For example, ELMO (an ecological model) is a three-dimensional water quality model for nutrient study, which can show a quick ecosystem response to hydrodynamic influences [9]. Chemical parameters are often used in the water quality model. In a study assessing phosphorus control in the James River estuary in Virginia, USA, parameters that can reflect the water quality, such as carbonaceous biochemical oxygen demand (CBOD), dissolved oxygen, nitrate, nitrite, and other chemical parameters, are used for model simulation of chemical reaction kinetic processes [40]. The modeling results suggest that the wastewater treatment plant can reduce a massive phosphorus loading and control phytoplankton biomass to a reasonable level [40]. The same modeling process is also used for nitrogen estimation [41]. The results show that phosphorus control in the upper estuary can provide the lower estuary with more nitrogen, but the additional nitrogen has no significant impact on algae growth [41]. Other than just using a simple hydrodynamic model, an integrated hydrodynamic model with water quality components is more practically useful. For example, a combined physical-biological model was used as a tool in a study to estimate the impact of the nutrient cycling on zebra mussels in a lake system [37]. Algal blooming is also an important indicator of eutrophication of water body. In a nutrient study conducted in the Daoxiang Lake, Beijing, China, a biological model named EFDC (Environmental Fluid Dynamics Code) was used to predict algal blooming [69]. The results from this model showed that the simulation matched the observed results reasonably well with an accuracy of 63.4% for algal bloom prediction [69]. To ensure the efficiency of a wetland construction, various models have been developed to simulate the performance of the treatment. For example, a biokinetic model evaluates transformation and degradation processes of combined sewer overflows with or without constructed wetlands with pollution loading and transportation estimates [52]. Ammonia nitrogen and COD are a good fit for this model [52].

Usually, a model for nutrient studies has to be modified before it can be applied to different local areas, in order to ensure its applicability and the accuracy of the application [69]. For example, due to limited biological data in a 2-year simulation study, a three-dimensional hydrodynamic model (ELCOM) coupling with a one-dimensional aquatic ecosystem dynamic model (CAEDYM) was used to improve the accuracy of biogeochemical simulation in two different reservoirs [60, 67]. In a study on the North West European Shelf, a threedimensional ecosystem model was applied to estimate nutrient fluxes and budgets based on a seasonal cycle [55]. The United States Environmental Protection Agency developed a threedimensional hydrodynamic-eutrophication model (HEM-3D), which was tested in Korea, as a tool to estimate total maximum daily load (TMDL) [54]. The results showed that organic wastes degraded the water quality along Korea coastal areas especially in Kwang-Yang Bay [54]. In construction of a biological model, it is usually difficult to quantify the biotransformations of nutrients. Because of the complexity in different water zones, ecological models have to be applied differently for each purpose. In order to overcome this problem, a two-dimensional hydrodynamic model coupled with the biogeochemical MIRO model was developed to quantify the biogeochemical transformations and fluxes of nutrients in coastal

	Model type	Parameters	Suitable estimation area	References
Hydrodynamic and water quality model	One-dimensional hydrodynamic model	Nutrient concentration, organic matter component, biological environment	Lakes and reservoirs	Hamilton and Schladow [26]
	Two-dimensional hydrodynamic model	Nutrient concentration, organic matter component	Stream, water quality	Xu et al. [70]
	Three-dimensional hydrodynamic model, Everglades Wetland Hydrodynamic Model, ELMO	Bathymetry, rainfall, humidity, solar radiation, wind velocity inflow, and outflow, water surface elevation, horizontal velocities, and temperature	Estuaries and coastal area; tide flow	Jin et al. [31]
Physical and biological model	Three-dimensional ELCOM	Biological data, rainfall, humidity, solar radiation, wind velocity inflow, and so on	Lake; nutrient cycle, fate, and transport of nutrients	León et al. [37]
	Three-dimensional numerical model	Navier–Stokes equations and mass transfer with nonlinear reactions in the biofilm	Porous, heterogeneous system	Eberl et al. [19]
	CE-QUAL-ICM model	Multiple forms of algae, carbon, nitrogen, phosphorus, and silica, and dissolved oxygen	Time-variable, eutrophication process, nutrient runoff	Cerco and Cole [11]
	EFDC model	Algae blooming	Swamp	Wu and Xu [69]; Zou et al. [73]
	CAEDYM + ELCOM	Flow and adjective transport	Reservoir	Romero et al. [60]
	HEM-3D	Total maximum daily load	Bay	Park et al. [54]
	Two dimensional + MIRO	Nutrients	Coastal	Arndt et al. [7]
	Two dimensional + CONTRASTE	Nutrients	Estuary	Arndt et al. [7]

 Table 2
 Examples of selected one-, two-, and three-dimensional models and their associated parameters, categories, and functionalities in nutrient studies

zones [7]. In the meantime, another biogeochemical model (CONTRASTE), which was combined with a hydrodynamic model, was used to evaluate nutrient concentrations in estuarine water [7]. The results indicate that both nutrient input and physical constraints are important factors that control phytoplankton blooms in coastal zone. The interface between estuary and coastal zone plays a central role in the continuum of water body [7]. Since marine and coastal systems are so complicated, hydrodynamic-ecosystem models should have error quantification by using analytical methods to ensure the model performance and prediction accuracy, which include correlations, model bias, and efficiency [2]. Overall, the integrated one-dimensional, two-dimensional, and three-dimensional models, which include hydrodynamic model, biological model, and water quality parameters, can be used to identify the major factors controlling the nutrient loading from rivers and streams into estuaries and coastal waters and estimate the nutrient budgets in the aquatic systems. Besides combining hydrodynamic and biological models together with water quality models to evaluate combined sewer overflow impact, an approach with a geographical information system (GIS) model as a supplementary method is also cost-effective in the evaluation of both chemical and ecological factors [47].

## Conclusion

In summary, combined sewer overflows (CSOs) are still the major point sources of nutrient pollution in rivers, estuaries, and coastal waters. However, wetland construction and CSO management methods are effective methods to reduce the CSO impacts on the aquatic environment. On the other hand, land use and land cover changes are the major non-point sources of nutrient pollution. Although modeling methods can correlate landscape use change to water quality, non-point source pollution such as storm water runoff from agricultural and urban areas is still difficult to quantify and identify. It is relatively feasible to identify and control the point source pollution when the discharge locations are given. As nutrients are important indicators of water quality that is vital to human life and aquatic ecosystems, multiple management strategies should be enforced to improve water quality. From economic aspects, in the meantime, a cost-benefit analysis should also be conducted in the future. It was reported that a mixed-integer management method could achieve more than 13% in cost savings [71]. In the future, an integrated hydrodynamic, chemical, and biological model should be further developed to assist in identifying the transport and fate of nutrients from both point and non-point sources.

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#### **Compliance with Ethical Standards**

**Conflict of Interest** The authors declare no competing financial interests.

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