Chapter

Nitrogen and Phosphorus Eutrophication in Marine Ecosystems

Lucy Ngatia, Johnny M. Grace III, Daniel Moriasi and Robert Taylor

Abstract

Nitrogen (N) and phosphorus (P) eutrophication in marine ecosystems is a global problem. Marine eutrophication has a negative impact on food security, ecosystem health and economy through disruptions in tourism, fisheries and health industries. Both N and P have known point and non-point sources. Control of point sources has been easier than non-point sources particularly agricultural sources for both N and P as well as fossil fuel combustion for N, which remains a major challenge. Implementing mitigation strategies for N has been reported to be effective for P mitigation; however, the converse is not true due to mobility and volatility of N. Excessive N and P cause algae blooms, anoxic conditions, and ocean acidification with these conditions leading to dead zones, fish kill, toxin production, altered plant species diversity, food web disruption, tourism disruption and health issues. Management of N and P pollution includes reduction of leaching from farms through crop selection, timely and precise application of fertilizer and building artificial wetlands, proper management of animal waste, reduction of fossil fuel N emission, mitigating N and P from urban sources and restoration of aquatic ecosystem. Mitigation measures need to focus on dual nutrient strategy for successful N and P reduction.

Keywords: agriculture, eutrophication, marine, mitigation, nitrogen, phosphorus, pollution

1. Introduction

In the past few decades there have been massive increase in marine eutrophication globally [1]. The major drivers of marine eutrophication are nitrogen (N) and phosphorus (P) [2]. Eutrophication leads to hypoxia and anoxia, reduced water quality, alteration of food web structure, habitat degradation, loss of biodiversity and noxious and harmful algal blooms [1, 3]. In addition, coastal hypoxia contributes to ocean acidification harming the calcifying organisms for example mollusks and crustaceans [4].

Nitrogen and P are required to support aquatic plant growth and have been reported as the key limiting nutrients in most aquatic ecosystems. Further, N is needed for protein synthesis while as P is required for DNA, RNA and energy transfers [5]. Marine ecosystem heavily loaded with nutrients can display N limitation, P limitation and co-limitation [6] the limiting nutrient could change both seasonally and spatially [7].

A number of factors make N more limiting in the marine ecosystem than in fresh water ecosystem with two primary factors being (1) desorption of P bound to clay as salinity increase and (2) reduced/lack of planktonic N fixation as a result of increased salinity, resulting in flux of relatively P rich N poor marine water [4].

Increased N and P fertilizer and manure application in agricultural production have significantly improved crop yields and food security for the increasing human population, however fertilizer application on farms has led to serious problems with aquatic eutrophication (**Figure 1**) [1, 9]. As a result N and P in fertilizer and manure enter freshwater systems and are transported by streams and rivers to coastal areas resulting in eutrophication of coastal and marine ecosystems globally (**Figure 2**) [10–12]. In addition, atmospheric deposition of N from fossil fuel combustion contributes to the global budget for reactive N and is the largest single source of nitrogen pollution in some regions (**Table 1**) [1]. The chapter addresses the forms of N and P, and their sources. Consequences of eutrophication and mitigation strategies as well as some of the challenges faced during the mitigation process.

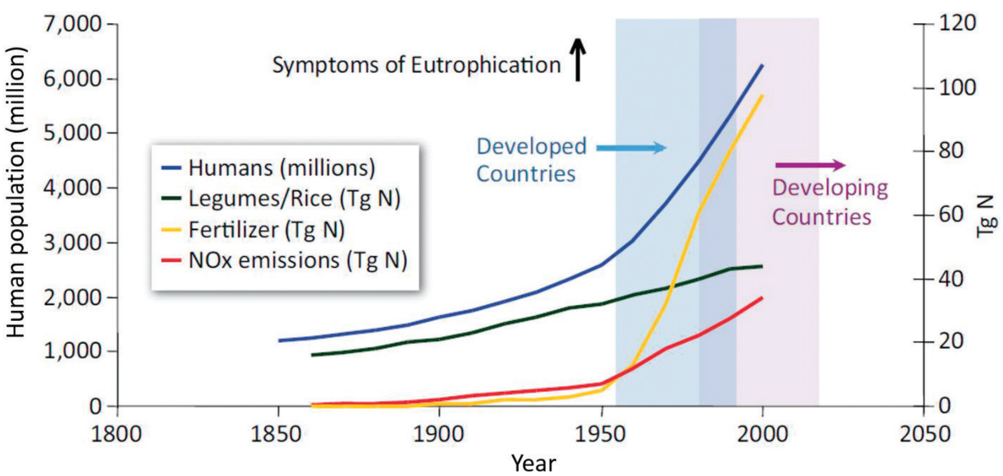

Figure 1.
Period in which the symptoms of eutrophication and hypoxia/anoxia began in developed countries and the more recent evolution of these symptoms in developing countries, modified from Schlesinger [8].

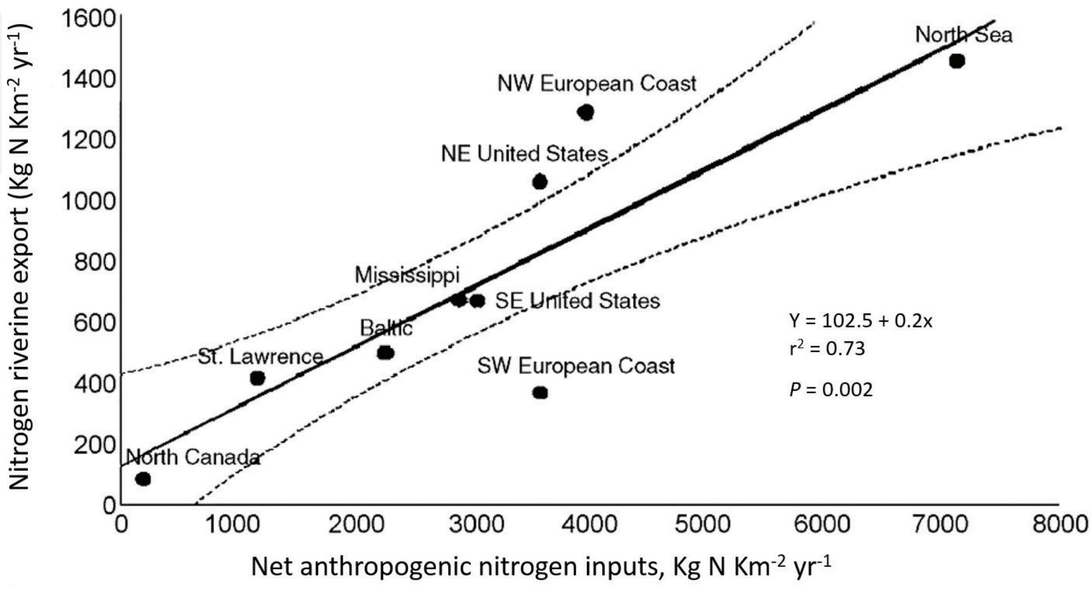

Figure 2.
Average annual nitrogen export per area of watershed from large regions around the North Atlantic Ocean to the coastal ocean as a function of net anthropogenic nitrogen inputs to the landscape per area. Modified from Howarth [1].

	1961	1997
Input		
N fixation in agricultural systems	4.9	5.9
Inorganic N fertilizer	3.1	11.2
NOx emissions from fossil fuel combustion	3.8	6.9
Total input	11.8	24.0
Exports		
Export in rivers	3.0	5.0
Atmospheric advection to oceans	0.7	1.3
Food and feed export	0.6	2.2
Total exports	4.3	8.5
Denitrification and storage	7.5	15.5
Net anthropogenic N inputs	10.5	20.5

Table 1.
Budgets indicating reactive nitrogen from human sources in United States of America (Tg N per year). Net anthropogenic N inputs indicate use of inorganic fertilizer plus N fixation in agricultural systems plus NO_x deposition from fossil fuel combustion minus the net export of N_x in food and feeds. Modified from Howarth et al. [55].

2. Forms of nitrogen and phosphorus

Most of the N on earth is molecular dinitrogen (N_2) and most of it is in the atmosphere, however, a portion of it is dissolved in the ocean [1]. Only ~0.002% of N on earth is present in living tissues and detrital organic matter [8]. Nitrogen is essential for life; however, biologically available forms such as nitrate, nitrite and ammonium are a small proportion of N on earth and as a result, N limits primary productivity in coastal marine ecosystems [13].

Soil P exists in a range of organic and inorganic compounds that differ remarkably in their biological availability in the soil environment [14]. The inorganic P compounds preferentially couple with crystalline and amorphous forms of Al, Fe, and Ca [15] the coupling is highly influenced by soil pH [16]. Organic P in most soils is dominated by a mixture of phosphate diesters (mainly nucleic acids and phospholipids) and phosphate monoesters (example; mononucleotides, inositol phosphates) with smaller amounts of phosphonates (compounds with a direct carbon–phosphorus bond) and organic polyphosphates (for example; adenosine triphosphate) [17]. Plants have the capacity to manipulate their acquisition of P from organic compounds through various mechanisms, some of which allow plants to utilize organic P as efficiently as inorganic phosphate [18]. Alkaline pH can alter the availability of P binding sites on ferric complexes as a result of competition between hydroxyl ions and bound phosphate ions [19]. Anaerobic conditions favor release of P as a result of reduction of ferric to ferrous iron [20]. While, the presence of sulfate could lead to reaction of ferric iron with sulfate and sulfide to form ferrous iron and iron sulfide leading to release of P [21]. Temperature increase can reduce adsorption of P by mineral complexes in the sediment [22]. Other physiochemical processes affecting release of P from the sediment include pH potential, redox, reservoir hydrology and environmental conditions [23]. These physiochemical processes could further be complicated by the influence of biological processes such as mineralization, leading to a complex system governing the release of P across sediment water interface [23].

Unlike N fertilizer, P fertilizer is not volatile, consequently very little P could be distributed from cropland to nearby terrestrial ecosystem [24]. However, excessive

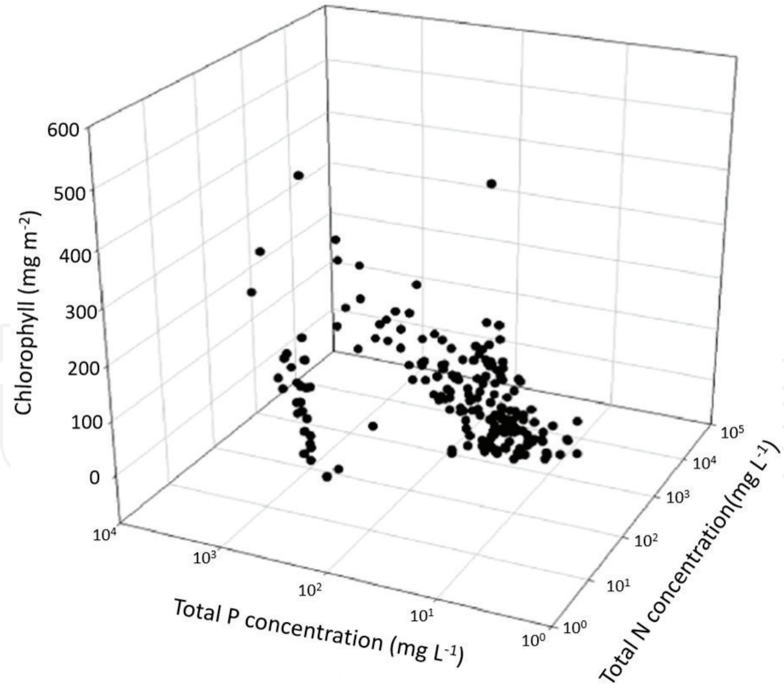

Figure 3.
Summer mean benthic chlorophyll concentrations from streams worldwide as a function of summer mean concentrations of total P and total N in the water column. Modified from Dodds and Smith [31].

P fertilizer application could result in significant transfer of P to adjacent freshwater bodies, followed by transport to coastal waters [25]. The nitrogen cycle contains diverse gaseous forms, both dissolved and particulate forms of N, while P cycle is dominated by particulate and non-gaseous forms of P [26]. This means that N pool can exchange with and escape to the atmosphere but P is trapped in receiving marine waters. The processes controlling losses of N to the atmosphere include ammonification, denitrification, nitrous and nitric oxide production and products of anaerobic ammonium oxidation (or anammox) reaction, while N fixation represents a gain from the atmosphere [27, 28]. Nitrification and denitrification are regulated by oxygen concentration and potentially can produce nitrous oxide, a climate relevant atmospheric trace gas [29]. However, there are no analogous air-water exchanges that exist in the P cycle. Therefore, while the net effect of the microbially mediated dissolved gaseous fluxes on N is loss of N to the atmosphere, P remains in the system, either as dissolved or as particulate forms [26]. While many efforts have focused on P mitigation, less attention has been given to N mitigation [30]. However, it is clear that N and P together describe eutrophication better than either can alone (**Figure 3**).

3. Sources of nitrogen and phosphorus

A century ago, the world reactive N was derived mainly through microorganisms fixation. This is the natural N fixation from the atmosphere. Currently, most of reactive N is derived from anthropogenic activities, mainly synthetic N fertilizers, manure application and fossil fuel combustion [32–36]. In addition, anthropogenic activities have accelerated biological N fixation associated with agriculture [33]. It is estimated that globally deposition of reactive N is ~25–33 Tg N per year from fossil fuel combustion, ~118 Tg N per year from fertilizer, and ~65 Tg N per year from fixation of atmospheric N_2 by cultivated leguminous crops and rice. Only ~22% of total human input on N ends up accumulating in soils and biomass, whereas ~35% enter oceans through atmospheric deposition (17%) and leaching through river runoff (18%) [25]. However, the only source of atmospheric P deposition is through mineral aerosols and the global flux is estimated at 3–4 Tg P per year [25]. Agricultural and urbanization activities are the major drivers of N pollution in the coastal waters [13]. The green revolution has led to synthetic N fertilizers, creating reactive N at a rate four times greater than fossil fuel combustion [34, 36]. Dinitrogen fixation by planktonic cyanobacteria is less likely in coastal seas compared to lakes, due to high salinity, whereby coastal planktonic N_2 fixation has not been observed at salinities higher than 8–10 and normally ocean salinity is ~35 [5].

Phosphorus sources can be natural which includes indigenous soil P, atmospheric deposition and anthropogenic P [37]. Phosphorus sources include both point and non-point sources [38]. Excess phosphorus inputs to lakes/rivers, which are eventually translocated to the marine ecosystem, usually come from industrial discharges, construction sites, urban areas, sewage and runoff from agriculture [39]. Many countries have implemented mechanisms to control point source P, however, controlling non-point P sources especially agricultural sources remains a challenge [38, 40]. The major source of nonpoint P input to water bodies is the excessive application of fertilizer or manure on farms which cause P accumulation in soils [40]. It should be noted that crop and livestock production systems are the major cause of human alteration of the global N and P cycles [41].

4. Consequences of nitrogen and phosphorus eutrophication

Eutrophication leads to excessive plant production, blooms of harmful algae, increased frequency of anoxic events, and death of fish. These conditions lead to health implications and economic losses, including losses of fish and wildlife production and losses of recreational amenities [38, 42].

4.1 Ocean acidification

Coastal hypoxia contributes to ocean acidification harming the calcifying organisms such as mollusks and crustaceans [4]. Anoxic and hypoxic water are associated with elevated carbon dioxide which causes acidification accelerating perturbation of ocean chemistry and influencing carbon dioxide emission into the atmosphere [4].

4.2 Dead zones

Hypoxia and anoxia lead to dead zones whereby fauna is eliminated or diversity and abundance is reduced. Dead zones in the coastal area have spread significantly since 1960s (**Figure 4**) and the increases are triggered by increases in primary production as a result of increased marine eutrophication fueled by riverine runoff of fertilizers and burning of fossil fuels [44]. The increased primary production lead to the accumulation of particulate organic matter which, accelerate microbial activity and consumption of dissolved oxygen in bottom waters resulting in death of fish and other marine fauna.

4.3 Human/animal health

Ranging from United States to Japan, the Black Sea and Chinese coastal waters increased nutrient loading in marine waters has been attributed to development of biomass blooms, which lead to toxic or harmful impacts on ecosystems, human health and/or recreation [45]. Approximately 60–80 species of about 400 known phytoplankton are toxin producing and capable of producing harmful algal blooms [46]. Toxin producing algae could cause mortalities of fish, birds, and marine

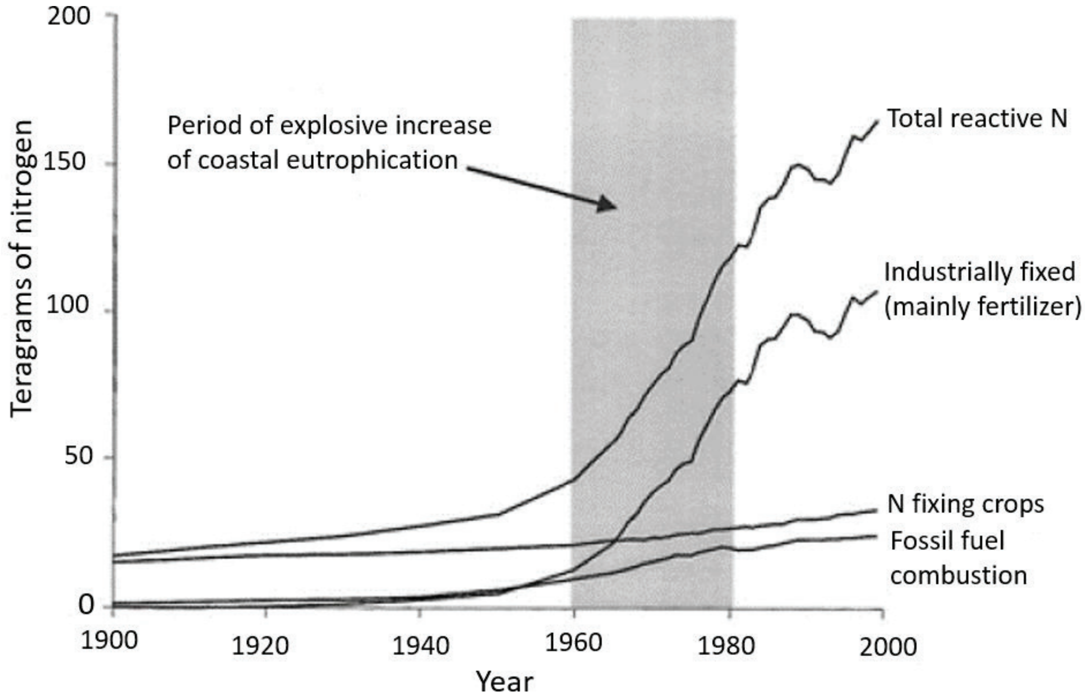

Figure 4.
Period of the explosive increase in coastal eutrophication in relation to global additions of anthropogenically fixed N from Boesch [43].

mammals as well as human illness through consumption of fisheries [47]. In humans, toxins arising from harmful algal blooms have mainly been reported from shellfish consumption [47] since bivalve shellfish (*Mollusca*) graze on algae and concentrate toxins effectively. In May and June 1998 the mortality of over 200 California sea lions (*Zalophus californianus*) and signs of neurological dysfunction in surviving sea lions along the central California coast was attributed to a harmful algal blooms [48].

4.4 Tourism

Coastal areas are hotspots for tourism, and are an important economic source for tourism [49]. The algal bloom resulting from N and P eutrophication have degraded the investment environment and damaged the tourism and hospitality industry (**Figure 3**) [50].

5. Management of nitrogen and phosphorus pollution and challenges faced

Generally, it has been much easier to manage point sources of both N and P however, non-point sources have been a challenge to control and are the main sources of pollution in the marine ecosystem [51, 52]. Nitrogen has higher mobility in the environment compared to P since N flows easily through both ground water and atmosphere [51]. It has been generally indicated that management practices for reducing N pollution in most cases are also effective in phosphorus control, however the converse is not true (**Table 2**) [51, 53]. Due to high N mobility and volatility, in some cases it might need different/additional mitigation strategies compared with P. In United States and Europe major progress has been made in reducing N pollution from municipal waste water sources which is a point source but very little progress has been made in reducing non-point source N and P pollution [51, 54]. The following are some technical solutions for N and P management.

	Effects on P reduction	Effects on N reduction
Agricultural systems		
Winter cover crops	Effective	Very effective
No till agriculture	Very effective	Not effective
Perennial cropping systems	Effective	Very effective
Buffer strips along streams	Effective	Effective only if groundwater flows are intercepted by rooting zone
Wastewater treatment		
Conventional septic system	Very effective	Not effective
Chemical precipitation advanced wastewater treatment plants	Very effective	Little effective
Denitrification advanced wastewater plants	Effective	Very effective

Table 2.
Relative effectiveness of some representative best management practices (for reducing nitrogen and phosphorus pollution of surface and groundwater. Modified from Howarth [51].

5.1 Leaching and runoff from agricultural fields

In United States, N inputs to agricultural fields doubled from 8 to 17 million metric tons per year between 1961 and 1997 [55]. Approximately 20% of the new N inputs to agricultural fields is leached to ground or surface water [55, 56]. Climate has an influence on N losses, whereby, losses are higher under high rainfall intensities and wetter years [57]. Significant amount of P from agricultural fields is lost through leachate and runoff to rivers, lakes and reservoirs and eventually finds its way to the marine ecosystem [38].

5.1.1 Growing perennial crops

Growing grasses or alfalfa rather than annuals such as soybeans or corn is presented here as a potentially beneficial practice to control N and P nonpoint source pollution. Perennials are known to maintain N in the rooting zone, thereby reducing losses to groundwater. Previous work has shown that fields planted with perennial alfalfa lost ~30–50 times less nitrate compared to fields planted with soybeans and corn in Iowa and Minnesota, USA [57, 58].

5.1.2 Planting winter cover crops

Winter cover crops provide a range of services that are beneficial to managing N and P pollution since these crops protect the soil during this vulnerable season with lower evapotranspiration rates and higher antecedent soil moisture conditions. Cover crops provide cover to soils vulnerable to accelerated erosion losses and reduce soil erosion, which is the primary mechanism whereby nutrients are transported to surface water systems. In particular, N and P are attached to soil particles that are transported via storm water runoff directly to receiving surface waters such as streams, rivers, lakes, wetlands, and oceans. Further, winter cover crops reduce nutrients transported such as leaching of nitrate into groundwater during winter and spring, this is the period that most leaching occurs in many climates [51] as a result of the antecedent moisture conditions due to reduced plant soil water and nutrient uptake. The previous literature reports that long term winter cover crops have the capability of reduced nitrate loss as much as 3-fold [59].

5.1.3 Effective N and P application

Nitrogen and P fertilizer application timing is critical to managing nonpoint source pollution in cropping systems. Fertilizer application as close as possible to the time of crop need during the growing season is presented as a viable control for pollution challenges related to N and P. In particular, fall fertilizer application is often not the most agronomically, economically, or environmentally efficient or sustainable practice since much of this amendment would be either have direct connectivity to receiving surface waters through storm water runoff during the dormant season or eventually leach to ground waters since plant uptake is limited to negligible amounts because, with the exception of fall or winter cash crops, growth begins in the spring. The previous literature has found that fall application of fertilizer can result in as much as 30–40% leaching of the fertilizer [57].

5.1.4 Optimal fertilizer application rates

Application of the right quantity of the fertilizer is critical to responsible nutrient management in most all ecosystems. Prudent nutrient management and sound economics requires that fertilizer amendment to the point of optimal yield without excess application that results in increased nutrient export via surface runoff or leaching. Incremental application rates above the point where more fertilizer application increases crop yield and N and P are no longer limiting has no effect on production [60] and can actually have negative return on yields as well as the excessive fertilizer is susceptible to surface storm water runoff and leaching to groundwater (**Figure 5**).

5.1.5 Effective buffer strips and/or forest buffers

Buffers in the form of grass hedges, stiff grass hedges, field buffers, riparian forests, forest buffers, and wetland forests are commonly applied to minimize the effects of agricultural and urban land uses. Forested conditions are optimal for control of nonpoint source pollutions due to a range of characteristics that minimize the storm runoff and subsequent soil and nutrient transport that can result [61]. These characteristics include increased infiltration rates, increased vegetative cover, a thick organic layer, increased surface roughness, and higher evapotranspiration rates among other attributes. Each of these characteristics singularly reduces the quantity of surface water available to transport nutrients as well as nutrients

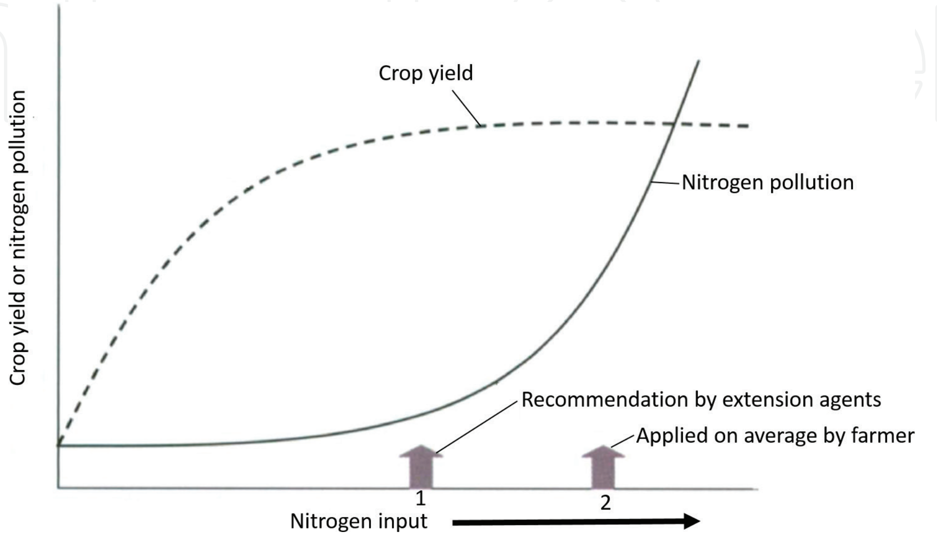

Figure 5.
Schematic representation of crop yield and reactive nitrogen export to surface and groundwater as a function of reactive nitrogen inputs to agricultural field. Arrows indicate level of fertilization recommended by extension agents (1) and actual levels applied on average by farmers (2). Modified from Howarth et al. [55].

available to leach to groundwater. Uptake of grass and/or tree species can remove excess nutrients as a means of production of a component crop whether it come in the form of biomass, wildlife habitat, timber, or hay among other economic benefits.

5.1.6 Artificial wetlands/constructed wetlands

Artificial or constructed wetlands can receive storm water runoff with increased nutrient concentrations and/or intercept tile drainage on farms by serving as a N and P sink. These wetlands reduce flux of nitrate and phosphate to receiving surface waters [62].

5.2 Animal production and concentrated animal feeding operations

Animal waste is a major contributor of N and P to coastal waters [51]. In the United States waste from animals in feedlots tends to be spread on the farm through land application, held in lagoons, or recently it is being composited [51, 53].

5.2.1 Manure application

Manure has been considered as fertilizer; however, applying manure at a rate appropriate to crop needs is a challenge as a result of uncertainty in time of nutrient release and difficulty in uniform distribution of manure (**Figure 6**) [53].

5.2.2 Lagoons hold animal waste

Lagoons can be used for holding animal waste as a retention area to prevent unacceptable pulse of nutrient loads to receiving waters. Lagoons retain nutrients until a time when they can strategically and effectively utilized, however diligence is required due to there could be significant leakage on N to groundwater and volatilization of N as ammonia to the atmosphere. The volatilized N contributes to the flux of N to marine system [53].

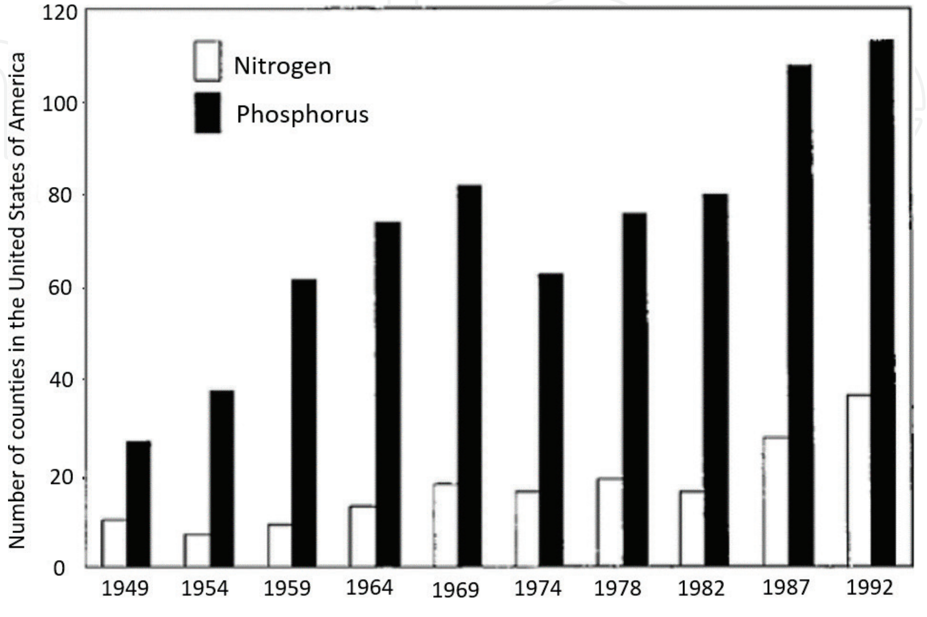

Figure 6.
Graphical representation of number of counties where manure nutrients exceed the potential plant uptake and removal, including pastureland application, modified from Howarth et al. [55].

5.2.3 Composting of animal waste

After animal waste is composited, it becomes easier to use it as effective fertilizers. However, during composting ammonia volatilization takes place, which contributes to the flux of N to marine system. In addition N volatilization lowers the quality of compost as fertilizer [53].

5.3 Fossil fuel sources of nitrogen

Fossil fuel combustion emits oxidized forms of N (NO_x) to the atmosphere [51]. In United States fossil fuel combustion emits ~6.9 million metric tons of N per year to the environment (**Figure 7**). This is ~60% of the rate of N fertilizer use in the country [55]. Most of the N emitted from fossil fuel is deposited back on the landscape in rain and dry deposition with a significant contribution to nutrient pollution in coastal water [51]. Approximately half of the fossil fuel N emission comes from mobile sources, which includes automobiles, busses, trucks and off road vehicles [51]. Electric power generation produced ~42% of reactive N [63]. Reduction of N emission from fossil fuel combustion could be achieved through; encouraging less driving and more energy efficient vehicles and remove NO_x from exhaust using catalytic converters [51]. Stricter emission standards should be applied to sports utility vehicles, trucks and off road vehicles [51]. Promote generation of electric power using fuel cells rather than traditional combustion would mitigate NO_x emissions [35]. In addition, electric power plants built for example in the United States before Clear Air Act could be modified to modern standards [63].

5.4 Urban and suburban sources

Approximately 29% of population of the United States is served by septic tanks instead of sewers [61]. In some coastal areas, septic tanks are the primary sources of N to coastal water [64]. Reduction of N leakage from septic tanks in coastal areas could be accomplished through replacing septic system with sewers and nutrient removal sewage treatment [51].

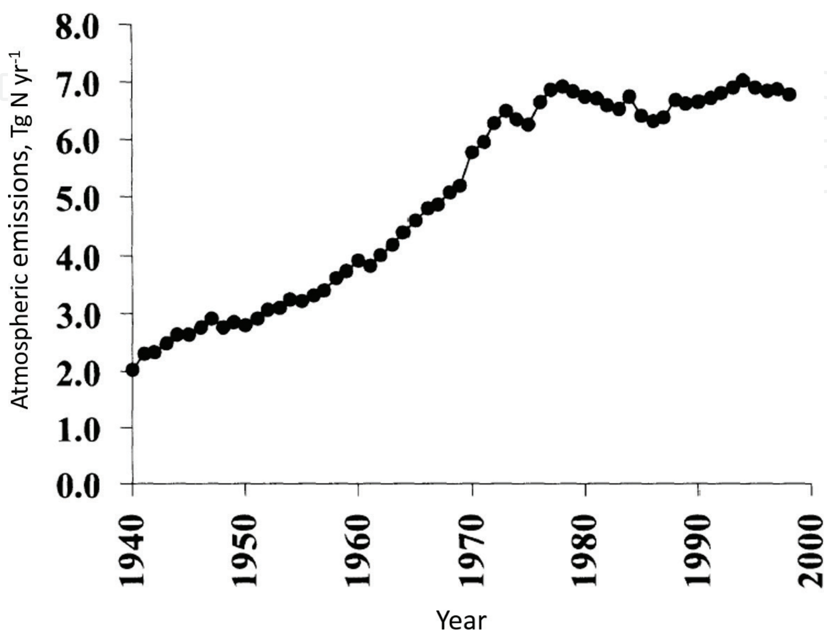

Figure 7.
Atmospheric NO_x emissions in the United States of America from 1940 to 2000, modified from Howarth et al. [55].

5.5 Aquatic ecosystem restoration

5.5.1 Wetlands as nitrogen and phosphorus interceptors: enhancing sinks

Wetlands, riparian zones and ponds can act as N and P traps, they can sediment out particulate N and P and convert reactive N into harmless N_2 through the process of denitrification [51–53]. Wetlands play a key role in P removal as a result of processes that include uptake by microbes and vegetation, peat accretion (sorption and burial in soil and sediments), and precipitation by iron and aluminum [65–67].

5.5.2 Riparian area restoration

Both N and P have been reported to contaminate groundwater [68], but s there is no clear evidence of the location and the source of the contaminant. Therefore, measures to decrease groundwater and surface water derived P and N call for the need to implement measures in the riparian area eliminate groundwater N and P directly before it enters the water bodies, this will avoid translocation of the pollutants to the marine ecosystem.

5.5.3 River/lake maintenance and restoration

River and lake rehabilitation and restoration improves their capacity to retain nutrients [69] and buffer nutrient fluxes to reduce N and P concentration in surface water reaching marine ecosystems.

6. Conclusion

Eutrophication is a major problem in the marine ecosystems that is driven primarily by N and P loading. Nitrogen and P pollution are contributed from both point and non-point sources. Many countries have been successful at controlling point sources for both N and P, however non-point sources remains a major problem. Phosphorus input into freshwater and subsequently marine systems are a result of anthropogenic activities that result in excess P with agricultural fertilizers serving as the leading cause of excess P. Historically, reactive N was contributed primarily by microorganisms and microbial activity. In recent years, reactive N is contributed by a myriad of anthropogenic activities which are led by fertilizer and manure application and fossil fuel inputs. While P is transported to the marine ecosystem in particulate and dissolved form, N is translocated as particulate, dissolved and gaseous form. The volatility and mobility of N makes it difficult to control and manage. In marine ecosystem, the salinity condition favors availability of P while limiting planktonic N fixation. This indicates that translocated N has greater effect on marine ecosystem than onsite fixed N. The consequence of N and P loading in freshwater and marine systems is multifaceted with eutrophication perhaps having the greatest impact. Eutrophication can result in increased incidence and significance of algae bloom, anoxic conditions, ocean acidification, and altered plant species diversity. The effects of eutrophication are production of toxins that affect human and animal health, fish kills that negatively impact the food security, food web disruption, and dead zones that disrupt ecosystem functioning. Further, the disruptions in ecosystem functions translate to negative impacts to the tourism industry with economic consequences. Therefore, eutrophication mitigation is essential in order to prevent excessive N and P loading to lotic and lentic systems from upslope anthropogenic activities and subsequently reaches marine ecosystems. The previous literature and investigations indicate that mitigation strategies should focus on both N and P loading reduction to ensure sustainability. Mitigation strategies to reduce the impact of N & P loading include reduction of leaching from agricultural activities, growing perennial plants, prudent application of fertilizers, and planting winter cover crops to reduce nutrient leaching via increased plant uptake. Strategies include policy and/or industry standard modifications that are likely more controversial yet likely the key to sustainable practices. These strategies include reduction of fossil fuel N emissions through transportation demand reductions, vehicle efficiency advancements, enhanced removal of NO_x from exhaust, and stricter emission standards for the transportation system. Further, terrestrial and aquatic ecosystem restoration in terms of flora and fauna are critical to ensure greater quantities N and P are effectively trapped or tied up prior to reaching marine ecosystems. Overall, measures to control eutrophication need to focus on dual nutrient reduction, instead of focusing on N or P alone in order to ensure sustainability, unless there is evidence that focusing on only one nutrient is justifiable for a given ecosystem.

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