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CHAPTER 4. NUTRIENTS

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With the growth of intensive and expansive agricultural production in recent years, the use of chemical fertilizers has increased rapidly. Fertilizers are used to supplement soil fertility and to satisfy the demand for high-yielding crops by replacing soil nutrients taken by harvested crops. Agricultural nutrients come in many forms. They can be found in natural sources, such as manures, compost, biological nitrogen fixation (BNF) of legumes, and green manures. They can also be found in chemical or mined sources, such as commercial nitrogen, phosphate and potassium fertilizers. Manure and other organic fertilizers have the added benefit of providing organic matter to the soil, which may improve nutrient cycling, soil structure, aeration, soil moisture-holding capacity and water infiltration.

Nevertheless, the growing use of fertilizers can also lead to the degradation of aquatic resources such as lakes, rivers and marine water resources. The rapid expansion and intensification of livestock production has also contributed to the pollution of water resources. Water pollution from nutrients occurs when fertilizers are applied at a greater rate than they are fixed by soils or taken up by plants; when they leach into groundwater or move via surface runoff into waterways, resulting in costly environmental and health issues. When nutrients drain into rivers, lakes and streams, they can cause eutrophication and accelerate the growth of algae and aquatic plants, which, when decay, reduces the oxygen on which other aquatic life depends. An overgrowth of certain algae species can

also produce high levels of toxins and bacteria that are harmful for humans if they come into contact with contaminated water or consume tainted fish or shellfish.

This chapter focuses on nitrogen (N) and phosphorus (P) nutrient loads that result from agricultural practices, and their impacts on aquatic ecosystems. On the one hand, N and P are essential for proper crop development, high yields and associated social benefits such as income generation and livelihood provision. However, excessive nutrient use can lead to the contamination of soil and water. The next sections review the main trends in fertilizer use and the resulting effects on surface water and groundwater, followed by a discussion of the impacts of nutrient-based water pollution on human health and the environment.

4.1 Use of nutrients (N and P) in agriculture

Agriculture is the single largest user of freshwater globally. One of the root causes of degraded surface water and groundwater is excess nutrients from agricultural production. A major focus of crop breeding in recent years has been to increase yields by improving the growth response to nitrogen. In tandem, other nutrients, notably phosphorous, potassium and sometimes sulphur, have become limiting factors to yield increases, and have thus been added using inorganic products to supplement traditional methods of recycling through manuring, fallowing and crop rotation.

Plant nutrients are typically classified according to the elements that are required or plant growth and development. These include essential and other mineral elements and are typically referred to as macronutrients (e.g. C, H, O, N, P, K) and micronutrients (e.g. Fe, Zn, Mn, Cu, B, Mo) (Mengel, 1982; Frageria *et al.*; 1995). The focus of the chapter will be on P and N compounds because of their demonstrated effects on eutrophication and hypoxia in surface and coastal waters (Rabalais *et al.*, 2009) and ground water pollution by nitrates.

The world currently consumes ten times more mineral fertilizer than it did in the 1960s (FAO, 2017a), and global demand for nitrogen fertilizer is expected to increase from 110 million tonnes in 2015 to 119 million tonnes in 2020 (FAO, 2017a). In contrast, although the use of phosphorus fertilizers was in line with that of nitrogen until the 1980s, it has stalled since 1989. This global growth of fertilizers consumption masks a growing gap in access to fertilizers between developed and developing (mainly tropical) countries. Only 10 percent of the world's croplands are found in developed countries, but they account for 32 percent of the global nitrogen surplus and for 40 percent of the phosphorus surplus (Panuelas *et al.*, 2013).

Global consumption of the three main fertilizer nutrients – nitrogen (N), phosphorus (expressed as phosphate, P_2O_5), and potassium (expressed as potash, K_2O) – was estimated to have reached 186.7 million tonnes in 2016. Table 4.1 shows that consumption for N, P_2O_5, and

Table 4.1 | Global consumption of fertilizer nutrients (2015-2020) (thousand tonnes)

Year	2015	2016	2017	2018	2019	2020
Nitrogen (N)	110 027	111 575	113 607	115 376	117 116	118 763
Phosphate (P_2O_5)	41 151	41 945	43 195	44 120	45 013	45 858
Potash (K_2O)	32 838	33 149	34 048	34 894	35 978	37 042
Total (N+ P_2O_5+ K_2O)	184 017	186 668	190 850	194 390	198 107	201 663

Source: FAO, 2017a.

K_2O is forecast to grown by an average of 1.5, 2.2, and 2.4 percent, respectively, each year from 2015 to 2020, and is expected to reach 201,663 thousand tonnes by the end of 2020 (FAO, 2017b).

The overuse or misuse of mineral fertilizers and manures in agriculture severely affects the quality of water and soil resources. Beyond the farm boundary, nutrients can cause contamination and often eutrophication of water bodies through surface run off and leaching of nutrients from agricultural farmland. In excess amounts, these nutrients overstimulate the growth of weeds and algae in surface waters and can lead to serious algae blooms and oxygen depletion in rivers and lakes, which may create adverse impacts – such as fish kills – for the environment and human livelihoods. Aquaculture (particularly fed aquaculture) can also be a locally relevant source of nutrient pollution, e.g. in Bangladesh (Alam, 2001).

BOX 4.1 | Nutrient leaching and water pollution

Nutrient leaching depends on several factors, including fertilization level, type, and timing of fertilizer application; the method of application; properties of soils (i.e., pH, structure and organic matter content); types of crops and their fertilizer requirements; method of cultivation and agronomic practices; and the level of animal production. Weather conditions and catchment land use can also have a crucial impact on the intensity and quantity of nitrogen leaching.

An insufficient amount of potassium reduces nitrogen uptake by plants and thereby may increase nitrogen leaching from the soil. Insufficient availability of phosphorus leads to decreased plant biomass, even when nitrogen is in an optimal concentration compared to plant requirements. However, the relationship between these elements is not well understood in terms of nutrient leaching in agricultural areas. ➤

➤ Nitrogen, in particular the very soluble nitrate, is easily dissolved in percolating water. Phosphorus is less mobile and reaches surface water due to erosion being bound to soil particles. These different pathways complicate water quality protection, because the elimination of one source may aggravate another. For example, the reduction of fertilization level or one of the elements may not reduce the leaching of nutrients as a result of the unfavorable ratio of nutrients in the soil. A deficiency of phosphorus or potassium limits the uptake of nitrogen by plants, even when the nitrogen level is sufficient. This suggests that, at a low level of fertilization due to a shortage of potassium and phosphorus, there may occur a loss of nitrogen, which results in water and soil pollution. This could affect two-thirds of the world's agricultural land, where potassium deficiency occurs (Lawniczak *et al.*, 2015).

4.1.1 Nitrogen from croplands

In terrestrial ecosystems, nitrogen must be 'fixed' or bound into a reactive form before animals and plants can use it, because in the inert form (N_2) it is chemically unavailable to most living organisms. The reactive forms of nitrogen (Nr) (all forms of N except N_2) are actually far more important to life are (Sutton *et al.*, 2013). These include single or double-bonded nitrogenous compounds such as ammonium and nitrates. Because only a small part of the Earth's biota can convert N_2 to Nr, reactive nitrogen is the limiting nutrient in most natural ecosystems and, almost always, in agricultural systems (Erisman *et al.*, 2015).

Over 90 percent of soil N takes the form of organic N. While there are 13 major nitrogenous fertilizers in use around the world, urea is the dominant compound. Other formulations are used where conditions or crop needs require them. For example, ammonium sulphate is preferred for alkali soils as it slightly acidifies the soil and can bring the pH into a range where more trace elements are available to the plant. Microbial activity determines the transformation of organic and inorganic nitrogen in the soil, and the pathway is principally governed by redox conditions.

In addition to N loss in the form of NO_3-, N can also drain into waterways as soluble NH_4+ or NH_4+ attached to sediments. The pathway and quantity of N loss from agricultural systems can be highly variable and, because it is determined by prevailing conditions, significant changes can occur within just a few hours or days.

The global use of nitrogen fertilizer (both mineral and organic) for agriculture has been increasing in most regions in recent decades (Lu & Tian, 2013). Globally, the application of

mineral nitrogen fertilizers to croplands is currently estimated at around 115 million tonnes N per year. Moreover, the annual human-caused biological fixation of atmospheric N_2 by cultivated leguminous crops and rice is currently estimated at around 65 million tonnes N per year. Approximately 22 percent of human nitrogen inputs end up accumulating in soils and biomass, whereas 35 percent enters the oceans via atmospheric deposition (17 percent) and leaching via river runoff (18 percent) (Panuelas *et al.*, 2013).

Table 4.2 forecasts global and regional nitrogen fertilizer demand against the compound annual growth rate from 2015 to 2020. Sub-Saharan Africa and Latin America and the Caribbean are expected to have a high compound annual growth rate, accounting for 4.83% and 4.09% respectively. In contrast, West Europe and North America have the lowest annual growth, accounting for -0.99% and 0.37% respectively (FAO, 2017b).

Table 4.2 I Global and regional nitrogen fertilizer demand forecasts (thousand tonnes N) and compound annual growth rate (CAGR), 2015 to 2020

	2015	2016	2017	2018	2019	2020	CAGR (%)
WORLD	110 027	111 575	113 607	115 376	117 116	118 763	1.54
AFRICA	3 573	3 641	3 788	3 964	4 126	4 302	3.78
North Africa	*1 835*	*1 870*	*1 929*	*1 984*	*2 042*	*2 102*	*2.75*
Sub-Saharan Africa	*1 738*	*1 772*	*1 860*	*1 980*	*2 084*	*2 201*	*4.83*
AMERICAS	22 506	23 030	23 379	23 768	24 169	24 564	1.77
North America	*14 434*	*14 517*	*14 552*	*14 612*	*14 667*	*14 701*	*0.37*
Latin America & Caribbean	*8 072*	*8 513*	*8 828*	*9 157*	*9 501*	*9 863*	*4.09*
ASIA	66 294	67 082	68 446	69 493	70 525	71 476	1.52
West Asia	*2 982*	*3 048*	*3 127*	*3 213*	*3 302*	*3 395*	*2.63*
South Asia	*22 273*	*22 525*	*23 430*	*24 002*	*24 645*	*25 191*	*2.49*
East Asia	*41 039*	*41 509*	*41 888*	*42 278*	*42 578*	*42 890*	*0.89*

	2015	2016	2017	2018	2019	2020	CAGR (%)
EUROPE	15 874	16 016	16 161	16 290	16 407	16 504	0.78
Central Europe	*2 945*	*3 044*	*3 121*	*3 200*	*3 282*	*3 343*	*2.57*
West Europe	*8 448*	*8 370*	*8 315*	*8 236*	*8 139*	*8 038*	*-0.99*
East Europe & Central Asia	*4 481*	*4 602*	*4 725*	*4 854*	*4 986*	*5 123*	*2.71*
Oceania	1 779	1 806	1 833	1 861	1 888	1 917	1.50

Source: FAO, 2017b.

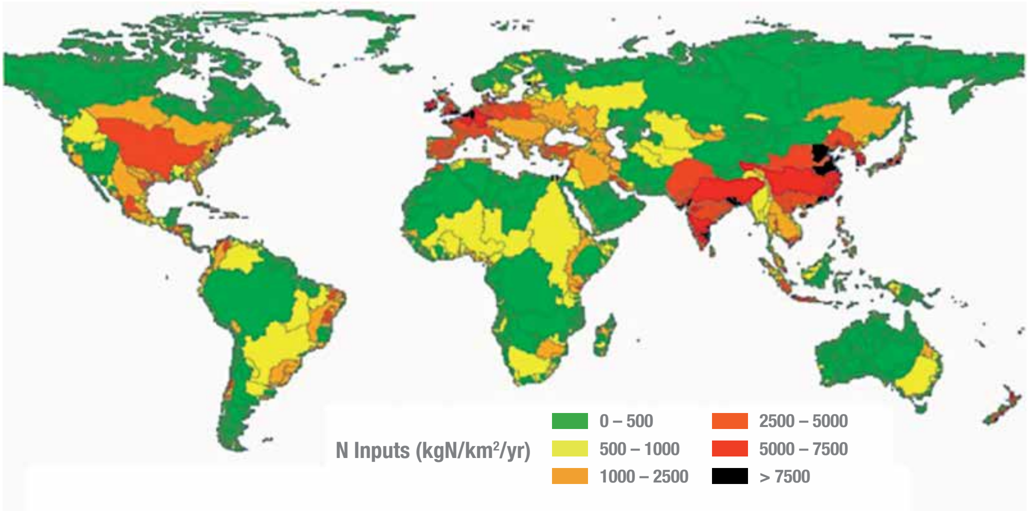
Figure 4.1 below shows the estimated net inputs of diffuse N (runoff or leached from land) in river catchments around the world, with Europe and East Asia accounting for the highest values. Watersheds where anthropogenic inputs are equal to or exceed natural inputs are calculated using data from the Global NEWS[4] database and by statistically relating the total anthropogenic inputs of reactive nitrogen to the output through the hydrosphere (see Sutton *et al.*, 2013 for supplemental material). An estimate for the continental USA in the 1990s (Howarth, 2002) indicated that returns to water were close to 20 percent of total applied agricultural nitrogen, with up to 25 percent lost in gaseous form. When returns from animal and human wastes are considered, as much as 44 percent is estimated to be leached to surface and groundwater, and subsequently transported to lakes, estuaries and the sea.

4.1.2 Phosphorus from croplands

Phosphorus is a key nutrient that stimulates the growth of aquatic organisms in water bodies, but in excessive quantities it has a fertilizing effect that affects both the ecosystem and water quality as whole (EC, 2014). Phosphorus is naturally present in surface water as a result of the mineralization of vegetable and animal residue, or due to anthropogenic pollution, e.g. diffuse sources from agriculture, untreated or insufficiently treated municipal waters and the use of polyphosphate detergents (EC, 2014).

4 Global *NEWS* is an international, interdisciplinary scientific taskforce, focused on understanding the relationship between human activity and coastal nutrient enrichment. It was formed in the spring of 2002 as a workgroup of UNESCO's Intergovernmental Oceanographic Commission (IOC), with co-sponsorship by UNEP, US-NSF, and US-NOAA. Global NEWS is a LOICZ affiliated project.

FIGURE 4.1 **Estimated net anthropogenic nitrogen inputs according to the world's main river catchments**



Source: Billen *et al.*, 2013.

The soil chemistry of phosphorous is complicated. Inorganic P is relatively immobile in the soil and adheres strongly to soil particles and organic material. Although soils often contain high levels of bound mineral P, low concentrations of plant-available P often necessitate fertilization to achieve optimum yields (Hart *et al.*, 1996). Phosphorus can be transported in runoff in the form of soluble P, often called dissolved reactive P (DRP), or attached to sediment and referred to as particulate P (PP).

Phosphorus is primarily obtained from mining finite deposits rich in phosphate. A total of 85 percent of mined phosphate is used for agriculture and only 10 percent for detergent manufacture, with the remainder used in other chemical processes and industry. A number of reports have drawn attention to the finite nature of rock phosphate reserves (see, for example, Keane, 2009; Vaccari, 2009). The majority of global supply currently comes from just a few key countries, posing a potential risk for future demand. Just three countries produce 66 percent of total rock phosphate. Many countries do not have the physical reserves or economic resources to obtain it (Sutton et al, 2013), yet in order to feed the growing world population, global phosphate fertilizer demand is expected to increase from 41 million tonnes in 2015 to 46 million tonnes in 2020. Table 4.3 below shows West Asia and South Asia with 4.4% each, Latin America and the Caribbean with 4.0% and sub-Saharan Africa with 3.6%, which have the highest expected compound annual growth rate. West Europe and North America have the lowest annual growth, accounting for -0.4% and 0.6% respectively (FAO, 2017b).

Table 4.3 | Global and regional phosphate fertilizer demand forecasts (thousand tonnes P_2O_5) and compound annual growth rate (CAGR), 2015 to 2020

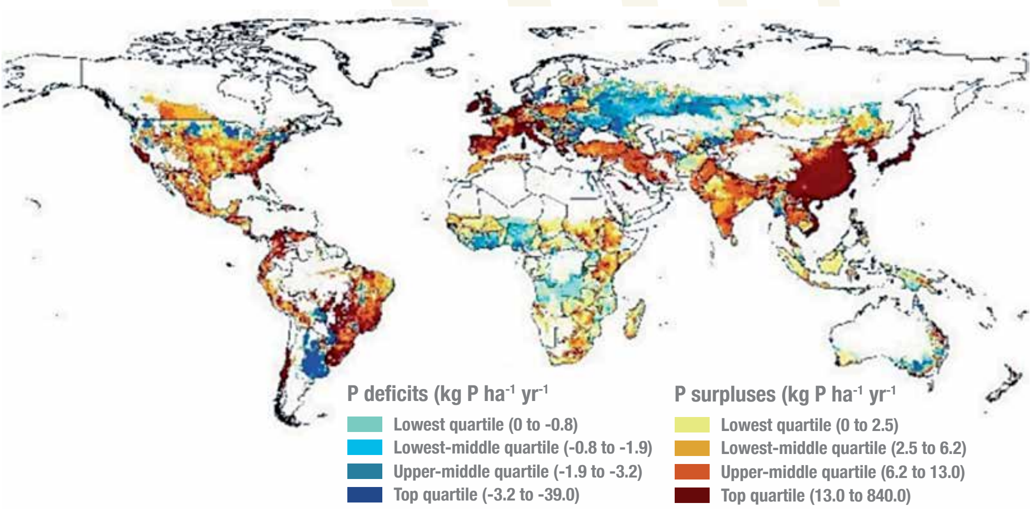
	2015	2016	2017	2018	2019	2020	CAGR (%)
WORLD	41 151	41 945	43 195	44 120	45 013	45 858	2.19
AFRICA	1 448	1 489	1 529	1 571	1 614	1 659	2.8
North Africa	*633*	*642*	*653*	*664*	*675*	*686*	*1.6*
Sub-Saharan Africa	*814*	*847*	*876*	*907*	*939*	*973*	*3.6*
AMERICAS	11 454	11 690	12 060	12 380	12 700	13 009	2.6
North America	*5 035*	*5 070*	*5 085*	*5 123*	*5 160*	*5 187*	*0.6*
Latin America & Caribbean	*6 420*	*6 620*	*6 975*	*7 257*	*7 539*	*7 822*	*4.0*
ASIA	22 918	23 312	24 056	24 544	25 005	25 432	2.1
West Asia	*351*	*367*	*383*	*400*	*417*	*436*	*4.4*
South Asia	*8 165*	*8 435*	*9 025*	*9 383*	*9 760*	*10 107*	*4.4*
East Asia	*14 401*	*14 510*	*14 648*	*14 761*	*14 827*	*14 889*	*0.7*
EUROPE	4 026	4 135	4 217	4 269	4 319	4 368	1.6
Central Europe	*756*	*780*	*807*	*835*	*864*	*889*	*3.3*
West Europe	*1 855*	*1 863*	*1 878*	*1 861*	*1 839*	*1 818*	*-0.4*
East Europe & Central Asia	*1 415*	*1 492*	*1 532*	*1 573*	*1 616*	*1 661*	*3.3*
Oceania	1 305	1 319	1 332	1 356	1 376	1 390	1.3

Source: FAO, 2017a.

The difference between P application and P withdrawal (harvested in plant matter or bound to the soil) is the P surplus. The greatest part is lost to the environment, into the atmosphere or into surface water or groundwater. A combination of data and modelling has been used to map phosphorus surplus using GIS techniques; an example is shown below. Figure 4.2 highlights the interregional variation in estimated phosphorus deficit and surplus in the world, where East Asia, Europe and parts of South America account for the highest surpluses of P. The agronomic P surpluses and deficits for the year 2000 were classified according to global quartiles (see MacDonald *et al.*, 2011 for further details). Such an exercise makes a number of assumptions about the processes, pathways and timing of nutrient application, and measures the potential pressure at source, rather than actual pressure at given points in the water system. The level of disaggregation is still somewhat coarse, but the exercise does provide a clear indication of where to prioritize efforts. Similar work at the catchment scale, mapped in greater detail and linked to more intensive modelling, can identify particular source areas in a catchment.

Phosphorus is of serious concern because it is often transported by sediment in rivers. Phosphate is not as soluble as nitrate and ammonia and tends to get adsorbed into soil particles and enter water bodies thorough soil erosion. In general, net fluxes of phosphate to surface water from soluble reactive phosphorous can be expected to be low, but where there is significant soil erosion (in surface irrigated conditions, or on soils with significant slopes that experience high rainfall), exports off-farm can be significant. The fluxes of phosphate

FIGURE 4.2 | **Estimated phosphorus deficit and surplus in the world**



Source: MacDonald *et al.*, 2011.

in rivers are generally correlated to high stream flow with increased sediment transport, but are subject to considerable variation in both temperate and tropical settings. Short duration flood flows account for the majority of phosphate movement in river systems.

Phosphate is retained in river reaches through the deposition of sediment carrying adsorbed phosphate and due to uptake of phosphate by plant matter, particularly in stiller reaches and during periods of low flow (Demars *et al.*, 2005). Sediment affects water quality physically, chemically and biologically.

4.1.3 Nutrients from livestock systems

Animal manure is a primary source of nitrogen and phosphorus flow into surface and groundwater (US EPA, 2017). Most of the water used for livestock drinking and servicing returns to the environment in the form of liquid manure, slurry, greywater and wastewater.. When livestock is concentrated, the associated production of wastes tends to go beyond the buffering capacity of surrounding ecosystems, thereby polluting surface and groundwaters. Manure is generally collected for use as organic fertilizer, which, if applied in excess, will lead to diffuse water pollution. In many cases, if manure is not stored in contained areas, it can be washed into watercourses via surface runoff during significant rainfall. Feedlots are also often located near watercourses so that (nutrient-rich) animal waste (e.g. urine) can be released directly into the water.

Livestock-related nutrients in water resources contribute to water pollution and can accelerate plant and algae growth, algal blooms and the reduction of oxygen in water. Structural changes

BOX 4.2 | European Union efforts to reduce nutrient loss and water pollution

In recent years, phosphorus losses to water from point sources have decreased due to improved wastewater treatment (EEA, 2005). The 7th Environment Action Programme of the European Union has also confirmed that although nitrogen and phosphorus inputs to the environment in the region have decreased considerably over the past 20 years, excessive nutrient releases continue to affect air and water quality and to have a negative impact on ecosystems, causing significant problems for human health. More attention is now being focused on reducing nutrient loss from diffuse sources, a process that has been accelerated by the Water Framework Directive (WFD, Directive 2000/60/EC), which requires improvement of the quality of surface and groundwaters (EC, 2014). However, further efforts are needed to manage the nutrient cycle in a more cost-effective, sustainable and resource-efficient way and a more holistic approach is needed to address the nutrient cycle (EC, 2014).

taking place in much of the livestock sector, such as the increasing intensity of livestock production systems, higher stocking rates on European dairy farms, and the development of industrial livestock production, are increasing animal density in some areas, and this is linked to excessive volumes of waste and greater water contamination (Carpenter *et al.*, 1998). High levels of nutrient intake by livestock and the release of high concentrations of nutrients into aquatic ecosystems can lead to eutrophication and biological contamination of water resources (e.g. bacterial and viral pathogens) that cause human health problems.

The irrigation of feed crops is one of the largest agricultural sources of water pollution. From manured agricultural lands, N losses in runoff are usually under 5 percent of the applied rate in the case of fertilizer, and P losses to watercourses are typically estimated to be in the range of 3 to 20 percent of the P applied (see Table 4.4) (Carpenter *et al.*, 1998; Hooda *et al.*, 1998 cited in FAO, 2013). Overall N export from agricultural ecosystems to water as a percentage of fertilizer input ranges from 10 percent to 40 percent from loam and clay soils, to 25 to 80 percent for sandy soils (Carpenter *et al.*, 1998). Galloway and colleagues (2004) estimate that 25 percent of the N applied escapes to contaminate water resources (FAO, 2006). Nutrient surpluses resulting from the intensive use of feeds and high rates of fertilizer on pastures and fodder crops have also increased the emissions of nitrate and phosphate to groundwater and surface waters (Bouwman *et al.*, 2013). Feed and forage production induces a loss of N to aquatic sources of some 8 to 10 million tonnes per year, if one assumes such losses to be in line with N-fertilization shares of feed and forage production (some 20-25 percent of the world total) (FAO, 2006). Intensification has mostly occurred on sandy soils, which, although low in fertility, are easy to cultivate and respond well to inorganic fertilizers.

4.2 Nitrate and phosphate concentration in surface water and groundwater

Agriculture is the largest contributor of nitrogen pollution, and excess nitrogen and phosphates can leach into surface runoff into waterways.

Nitrate is a serious threat to many global aquatic ecosystems. It is the most common chemical contaminant in the world's aquifers (Spalding and Exner, 1993; Thorburn *et al.*, 2003; Jalali, 2005; Batlle Aguilar *et al.*, 2007), Standards for nitrate limits in groundwater vary considerably across the globe, although many are more stringent than the WHO guidelines (50mg/l). Nitrate in groundwater has been reported as a major problem in Europe, the United States and South and East Asia. In Europe, even when mean concentrations of nitrate in groundwater have remain relatively stable in the last few decades, nitrate drinking water limit values have been exceeded in around one-third of the groundwater bodies for which information is currently available (Mateo-Sagasta

Table 4.4 | Estimated N and P losses to freshwater ecosystems from manured agricultural lands

Region	N from animal manure		N losses to freshwater courses	P from animal manure		P losses to freshwater courses
	Crop	Pasture		Crop	Pasture	
			(thousand tonnes)			
North America						
Canada	207.0	207.0	104.0	115.3	20.0	16.2
United States	1 583.0	1 583.0	792.0	881.7	84.0	115.9
Central America	351.0	351.0	176.0	192.4	22.0	25.7
South America	1 052.0	1 051.0	526.0	576.8	59.0	76.3
North Africa	36.0	34.0	18.0	18.5	10.0	3.4
West Asia	180.0	137.0	79.0	92.3	48.0	16.8
Western Africa	140.0	148.0	72.0	71.9	26.0	11.7
Eastern Africa	148.0	78.0	57.0	76.0	24.0	12.0
Southern Africa	79.0	3 085.0	791.0	40.6	50.0	10.9
OECD Europe	3 048.0	737.0	1 036.0	1 896.7	18.0	229.8
Eastern Europe	757.0	2 389.0	787.0	413.4	177.0	70.8
Former Soviet Union	2 392.0	167.0	640.0	1 306.2	13.0	158.3
South Asia	3 816.0	425.0	1 060.0	1 920.9	10.0	231.7
East Asia	5 150.0	1 404.0	1 639.0	3 358.3	29.0	406.5
Southeast Asia	941.0	477.0	355.0	512.0	15.0	63.2
Oceania	63.0	52.0	29.0	38.9	20.0	7.1
Japan	361.0	59.0	105.0	223.0	0.0	26.8
World	60 644.0	12 384.0	8 262.0	11 734.7	625.0	1 483.2

Source: FAO, 2006.

and Burke, 2010). Additionally, in India, hundreds of districts in 21 Indian states have reported an occurrence of nitrate in groundwater that is well beyond the national permissible limit (45 mg nitrate/l) (Central Ground Water Board, 2010).

Nitrate levels in groundwater remain above prescribed limits in many OECD countries, on average in roughly 10-15 percent of these cases. Due to the EU Nitrate Directive and national measures, nitrogen pollution from agriculture has been reduced in some areas over the last ten to fifteen years (see Table 4.5) (EEA, 2015). Nitrate Vulnerable Zones, areas designated as being at risk from agricultural nitrate pollution, must be specified to comply with the Nitrate Directive. However, the methodologies for defining at-risk zones vary from country to country and are not governed by regulations in some cases. They are commonly based on an assessment of whether the risk of N leaching to groundwater is high in order to identify areas where reduced fertilizer applications are necessary. Such assessments require modelling or simple assumptions about the partitioning of nutrient balances to determine the proportion of applied nitrogen that is transported to the aquifer.

At the European level, there was a slight increase in average annual mean nitrate concentration in European groundwater from 1992 to 1998. Since 2005, concentrations have declined again and, in 2011, the mean concentration had almost returned to the 1992 level. River nitrate concentrations also declined steadily over the period from 1992 to 2012, when average nitrate concentration in European rivers declined by 0.03 milligrams per liter of nitrogen (mg N/l) (0.8 percent) per year. For example, water body monitoring in Bulgaria, over the periods 2004-2007 and 2008-2011 shows a generally slight and stable improvement of water quality and reduced nitrate concentration. However, this does not mean the problem has been resolved. The status of water bodies in vulnerable areas, mainly in the Danube and East Aegean basins, is dire. The most recent data from 2013 show higher nitrate concentration in the surface waters than in 2012 levels. Similarly, groundwater concentration

Table 4.5 I Average annual mean Nitrate and Phosphate concentration in freshwater in the European Union (1992-2012)

Year	1992	1997	2002	2007	2012
GW nitrate (mg NO_3/l)	17.4	18.8	17.7	18.8	17.6
Rivers nitrate (mg NO_3/l)	2.66	2.49	2.25	2.30	2.10
Rivers phosphate (mg P/l)	0.133	0.120	0.092	0.083	0.055
Lakes phosphorus (mg P/l)	0.039	0.033	0.033	0.026	0.027

Source: EEA, 2015.

remains steadily above 50 mg/l. In some places in the Danube Basin, concentrations are up to 140 mg/l, while in unconfined aquifers in the East Aegean Basin, they reach as high as 230 mg/l. Nitrate concentrations in the lower layers of groundwater are even worse, reaching up to 120 mg/l. These aquifers are the only sources of drinking water and, due to the hazardous situation, emergency measures need to be taken to improve the situation (EC, 2014).

In other hand, during the past few decades, there has been a gradual reduction in phosphorus concentrations in many European lakes. Average lake phosphorus concentration decreased over the period from 1992 to 2012 by 0.0004 mg P/l, or 0.8 percent per year. Phosphorus pollution from point sources is gradually becoming less significant. The treatment of urban wastewater has improved, phosphorus in detergents has been reduced and many wastewater outlets have been diverted away from lakes. However, diffuse runoff from agricultural land continues to be an important source of phosphorus in many European lakes. Moreover, phosphorus stored in sediment can keep lake concentrations high and prevent improvement of water quality despite a reduction in inputs (EEA, 2015).

The average orthophosphate[5] concentration in European rivers decreased markedly over the period from 1992 to 2002 (by 0.003 milligrams per liter of phosphorous [mg P/l], or 2.1 percent per year). In many rivers, this reduction started in the 1980s, but the marked decline is also evident for the time period from 2000 to 2012. Average concentrations are somewhat higher where more river stations are included. The decrease in river orthophosphate can be linked to measures introduced by national and European legislation, in particular the Urban Waste Water Treatment Directive, which calls for the removal of nutrients. Moreover, the switch to phosphate-free detergents has contributed to lower phosphorus concentrations.

4.2.1 Concentration of nutrients resulting in eutrophic lakes, reservoirs and coastal waters

The global distribution of reactive nitrogen is far from uniform, and N pollution in coastal waters is greatest where agricultural activity and urbanization are the highest (Howarth, 2006). The 1970s saw an explosive increase in coastal eutrophication in many parts of the world, which correlates with the increased production of reactive N for agriculture and industry during that period. In some regions, such as the North Sea and the Yellow Sea, human activity probably has increased N fluxes to the coast by 10- to 15- times or more (Howarth, 2006). On average, human activity has likely increased N fluxes to the coast of the USA six-fold.

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5 Phosphates are very important in fertilizer production. Orthophosphates are normal phosphates that are composed of one phosphate unit per molecule. The main difference between phosphate and orthophosphate is that phosphate is any compound composed of phosphate units whereas orthophosphate is composed of one phosphate unit.

Coastal zones and estuaries receive nutrient loads from the open ocean as well as from upstream sources, whereas inland lakes only receive nutrient loads from upstream. Despite the knowledge that N is the key factor in the development of hypoxia, there is considerable variation in the susceptibility of coastal zone across a range of N loadings. Oceanic N:P ratios are well below the threshold value for eutrophication (the Redfield Ratio), as denitrification occurs along the continental shelf. Nitrogen, while clearly very significant, is not the only element of concern for coastal systems, even for those in the temperate zone. Phosphorus is probably limiting in some estuaries, (Howarth 1998), for example, the Apalachicola estuary on the Gulf Coast of Florida and in several estuaries on the coast of the Netherlands in the North Sea. Seasonal switching of nutrient limitation has also been observed in the Chesapeake Bay and the hypoxic zone of the Gulf of Mexico.

Estuaries generally have a lower N:P ratio than lakes, therefore nitrogen can often be the limiting factor for eutrophication. Furthermore, conditions for eutrophication are affected by the chemical makeup of sediments (e.g. acidity, carbon contents changes and C:P:N ratios related to sulphate), levels of salinity and water conditions that control the zooplankton-grazing phytoplankton and, therefore affect the equilibrium of trophic webs (Howarth, 1998). At the same time, the reservoir of accumulated P in estuarine sediments is large, tending to increase P concentrations in seawater as compared to those in lakes. The factors controlling increased desorption of P in estuaries are perhaps not yet fully understood. It is thought that the higher sulphate concentrations in estuarine sediments reduce storage and accelerate desorption by sequestering more iron as iron sulphide. However, there is also variation in the response of estuaries to N loading, with some estuaries being far more sensitive to eutrophication than others (NRC, 1993).

The global anthropogenic P load to freshwater systems from both diffuse and point sources is estimated at 1.5 Tg/yr. Asia accounts for more than half of this total load, followed by Europe (19%) and Latin America and the Caribbean (13%). Overall, the domestic sector contributes 54 percent of the total, agriculture 38 percent and industry 8 percent. In agriculture, cereals production makes the largest contribution to the P load (31 percent) followed by fruits, vegetables and oil crops, each of which contributes 15 percent (Mekonnen and Hoekstra, 2017).

4.3 Impacts on health and environment

4.3.1 Human health impacts

Nutrient pollution and harmful algal blooms create toxins and compounds that are dangerous to human health. There are several ways that people, livestock (and pets) can

be exposed to these compounds, including contact with polluted water or consumption of contaminated water or foods (US EPA, 2017). Nitrate poses significant health hazards. It is highly soluble in water and can seep into groundwater from septic tanks, animal waste, fertilizers (manufactured and compost) and sewage sludge. Stormwater runoff also carries nutrients directly into rivers, lakes and reservoirs, which provide drinking water for many people. When disinfectants used to treat drinking water react with toxic algae, harmful chemicals called dioxins can be created. These byproducts have been linked to reproductive and developmental health risks and even cancer (US EPA, 2017).

Nitrate pollution in drinking water is a serious health concern in many developing countries. Nitrate poses a serious threat to the health of infants under six months of age, pregnant women and people with low stomach acid (Hypochlorhydria). The World Health Organization (WHO) thus recommends limiting nitrate-nitrogen in drinking water to 10 mg/l. Infants under six months of age who drink water too high in nitrates can develop methemoglobinemia, the so-called 'blue-baby' syndrome. Infants have bacteria in their stomach that converts nitrate to nitrite. The nitrite enters the baby's bloodstream and reacts with hemoglobin to form methemoglobin, which interferes with the blood's ability to carry oxygen (Wedin and Sorensen, 2013). Infants may show signs of suffocation and blue-tinted skin and can become seriously ill and even die. Although there are no reliable estimates on the current levels of methaemoglobinaemia, according to WHO (2017) the most common cause is a high level of nitrates in drinking water from the use of manures and fertilizers on land.

Direct exposure to toxic algae is another major problem arising from agricultural nutrients and water pollution. Elevated levels of phosphorous can promote the unwanted growth of algae in freshwater, leading to reduced water quality and low levels of oxygen in the water, which can cause fish kills and pose a risk to human health. Species of algae that are common in algal blooms produce neurotoxins (which affect the nervous system) and hepatoxins (which affect the liver). Most algae are generally harmless, but some produce hazardous toxins, which are extremely dangerous when touched or consumed. Drinking, accidentally swallowing or swimming in contaminated water affected by a harmful algal bloom can cause serious health problems including rashes, stomach or liver illness, respiratory problems and neurological affects (US EPA, 2017).

4.3.2 Environmental impacts: eutrophication and hypoxic water

The livestock sector is probably the largest sectoral source of water pollution, contributing to eutrophication, 'dead zones' in coastal areas, degradation of coral reefs, human health problems, emergence of antibiotic resistance and many others. Generally, as the load (or

concentration) of N and P in a lake or river increases, the probability of algae growth also increases. A sudden 'population explosion' of naturally-occurring microscopic algae is known as an algal bloom. Algal blooms can be caused by many factors, such as seasonal changes in temperature, abundance of sunlight and/or high nutrient concentration in the water. When the algal species produce toxic organic compounds, they can be harmful or even deadly for humans and biodiversity. After being consumed by small fish and shellfish, these toxins move up the food chain and harm larger animals like sea lions, turtles, dolphins, birds, manatees and fish (US EPA, 2017).

Not all algal blooms produce toxic compounds. But even when they are not toxic, algal biomass and the organic matter they produce can accumulate in dense concentrations near or below the water surface, which can lead to an explosive increase of bacteria present in the water through the degradation of this organic material. Algal blooms can hurt aquatic life by blocking out sunlight, clogging fish gills and causing a sudden drop in dissolved oxygen concentration in the water. This can reduce the ability of fish and other aquatic life to find food and can cause entire populations to leave an area or even die out (Villacorte *et al.*, 2015).

When surface waters become enriched with plant nutrients, eutrophication can also result. The use of fertilizers is associated with eutrophication, which is generally the result of complex interactions between temperature, nutrient loading, flow rate and other biological and geochemical factors. The OECD (2012) defines eutrophication as "the increase in the rate of production and accumulation of organic carbon in excess of what an ecosystem is normally capable of processing". Similarly, eutrophication is defined by the European Commission as the "accelerated growth of algae and higher forms of vegetation caused by the enrichment of water by nutrients, particularly compounds of nitrogen and/or phosphorus, inducing an undesirable disturbance of the ecological balance in the reservoirs (EC, 2014)."

Eutrophication symptoms may include the following:

- excessive phytoplankton and macroalgal growth at the water surface, which may reduce light penetration and cause the decline of submerged aquatic vegetation;
- an imbalance in nutrient ratios that can lead to a shift in the composition of phytoplankton species, creating favourable conditions for toxic algal blooms;
- changes in the composition of benthic species, leading to reduced diversity and negative impacts on the food web;

- reduction of dissolved oxygen and formation of hypoxic waters (dead zones) in coastal and marine settings.

Despite some data gaps, 415 coastal areas have been identified worldwide as experiencing some form of eutrophication, of which 169 are hypoxic (see the section below), 233 are areas of concern and 13 are systems in recovery (WRI, 2008).

Hypoxic waters (dead zones)
Anthropogenic eutrophication (nutrient over-enrichment) is the main driver behind the expansion, intensity and duration of coastal hypoxic conditions (Rabalais *et al.*, 2009). Hypoxic areas are 'dead zones' where there is insufficient oxygen to support normal marine flora and fauna. The threshold oxygen concentration for hypoxia is not well defined, but a value of 2 mg/l is generally used, based on the observed behavior of a range of marine organisms. This is equivalent to 1.4 ml/L, 63 μmol/L or 30 percent of oxygen saturation (Rabalais *et al.*, 2009). Since it is hard to detect oxygen accurately at such low levels, the exact oxygen threshold for hypoxia is difficult to identify; however, an effective indicator of hypoxia is nitrite content, which is an intermediate of denitrification.

Hypoxia affects an area of 240 000 km^2 globally, comprising 70 000 km^2 of inland waters and 170 000 km^2 of coastal areas. Municipal wastewater is often the main driver, although agricultural nitrogen is also a major factor in some areas, such as the Bay of Mexico. The spatial scales of hypoxic systems range from inshore estuaries to coastal shelves and open ocean areas and span depths of 1-2 m up to 600-700 m. Large areas in the open sea naturally have low oxygen content. These are known as Oxygen Minimum Zones (OMZs) and are the largest hypoxic areas in the world, covering 30 000,000 km^2, which is roughly 8 percent of the total ocean surface area. Methane often builds up in anoxic conditions in seawater and, more notably, in freshwater. Recent studies demonstrate that fluxes of methane (CH_4), a potent greenhouse gas, to the atmosphere from the expanding coastal hypoxic zones are probably insignificant, but coastal upwelling areas with shallow OMZ generate significant quantities of nitrous oxide (N_2O).

Coastal hypoxia kills or impairs fish and other marine life populations, and reduces fisheries catches. Pelagic fishes that are vulnerable to hypoxia and large populations of hypoxia- tolerant gobies now dominate the trophic structure of upwelling areas. Larger mobile predator species are the first to be affected by hypoxic areas. For example, the habitats of Atlantic blue and white marlin and sailfish are reduced and appear to have declined with the shoaling of the OMZ in the Pacific Ocean. They tend to be replaced by

non-pelagic species, such as gelatinous plankton and squid, as observed in the Benguela and California upwelling regions, but exact changes in community composition are difficult to estimate.

However, it is the recent emergence of coastal hypoxia that has put the spotlight on the consequences of intensified agricultural production systems. Until recently, hypoxic areas were found mainly on the coasts and in estuaries of developed countries, but the largest future increases in the number of hypoxic systems are expected in southern and eastern Asia. The best-known examples of hypoxic zones are found in the Baltic Sea, Gulf of Mexico, Black Sea, Mediterranean, Benguela, West Indian Ocean, Sea of Japan, Yellow Sea and South China Sea. The Baltic Sea is the largest hypoxic zone in the world, followed by the Gulf of Mexico. Over the past three decades, oxygen concentrations in both have been declining faster within 30 km of the coast with between 0 and 300 m water depth than in the open ocean.

BOX 4.3 | Nutrient impact in the Baltic Sea

The Baltic Sea is the largest single marine area in the world where hypoxia and anoxia are the result of human activity. Hypoxia has occurred intermittently and naturally over the past 8 000 years of its existence, since it is a 'close'" sea with limited water exchange with the North Sea.

The annual total nitrogen (N) input into the Baltic Sea is estimated to be around one million tons complemented by around 50 000 tonnes of phosphorus (P). The main sources of N within the Baltic Sea catchment are agriculture, municipalities, industry, power plants and traffic (HELCOM, 2002). Although nutrients are mainly carried into the Baltic Sea by rivers, about one quarter the N load is estimated to be airborne, resulting from the burning of fossil fuels. The contribution via groundwater and direct discharges cannot be neglected, but is not well quantified. Denitrification removes about 470 000 tonnes of N per year, and a further 130 000 tonnes/year are fixed in biomass and substrate, resulting in a net export of 150 000 tonnes of N and zero net flux of P to the North Sea.

The surrounding land mass naturally exports high nutrient loads; these have been magnified by agricultural development, which saw a four-fold increase in nitrogen and an eight-fold increase in phosphorous loads during the 20th century. Fish catches rose from a stable level of 0.5 m tonnes per year to 1 m tonnes in 1984, in parallel with increasing nutrient content, then subsequently declined to 0.6m tonnes in part due to overfishing of cod. Baltic cod is particularly sensitive to low oxygen concentrations at early stages of growth and hypoxia has resulted in habitat loss over vast areas, the eradication of benthic fauna, and the severe disruption of the food web.

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