2.0 Nutrient Cycles

Highlights

❖ Prior to industrialization and intensive agriculture, microbial fixation was the primary mechanism for converting nitrogen gas to forms of nitrogen that could be taken up by plants. Bioavailable phosphorus was added to soil and water mainly through the weathering of phosphorus-containing rock.

❖ Human activity has increased the production of bioavailable nitrogen and phosphorus.

❖ Municipal, industrial, and agricultural effluents have drastically increased the supply of phosphorus and nitrogen to freshwater and coastal ecosystems.

❖ Fertilizer production has increased the rate at which atmospheric nitrogen is fixed as ammonia and necessitated the mining of phosphorus-containing rock.

❖ Fossil fuel combustion causes nitrogen in the air to combine with oxygen in the air and produce nitric oxide (NO) and nitrogen dioxide (NO_2) that contribute to photochemical smog and acid rain production, and nitrous oxide (N_2O) that contributes to greenhouse warming.

Nitrogen and phosphorus, along with all other chemical elements, circulate in the biosphere in characteristic paths from the abiotic environment to organisms and back to the abiotic environment. These more-or-less circular paths are known as biogeochemical cycles and they describe the chemical forms, pathways and reservoirs that exist for a particular element. Biogeochemical cycles fall into two broad categories: a gaseous-type cycle where the atmosphere is a large reservoir, and a sedimentary-type cycle where the largest reservoir is mineral-bearing rocks. Nitrogen is an example of a complex gaseous-type cycle whereas P represents a simple sedimentary-type cycle. To understand the impacts of human activity on the transport, fate and effects of N, P, or any other element, it is first necessary to examine the biogeochemical cycle prior to extensive human alteration and then evaluate the changes in pathways and reservoirs resulting from human activity.

2.1. Nitrogen Cycle

The nitrogen cycle is essentially a process by which unreactive nitrogen gas (N_2) is converted to reactive forms that can be used by biological systems until conversion back to N_2 (Figure 2.2). The N cycle is unique in that, although 80% of the Earth's atmosphere is composed of N, most of this N is in the form of nitrogen gas (N_2) that cannot be used by the vast majority of organisms.

In the atmosphere, N exists primarily as nitrogen gas, nitrogen oxides (N_2O, NO and NO_2), and ammonia (NH_3). Nitrogen gas can be produced by the dissociation of nitrous oxide (N_2O) and destroyed as a result of its conversion to nitric oxide (NO) by lightning discharges (Figure 2.2). Nitrous oxide (N_2O) can also interact with a highly reactive oxygen atom to form NO and nitrogen dioxide (NO_2). These, in turn, react with water vapour to form nitric acid (HNO_3). Nitrogen oxides (NO and NO_2) can also be formed in a reaction involving ammonia and hydroxyl (OH^-) radicals. The two common nitrogen oxides, NO and NO_2, also cycle back and forth in a complex reaction involving the conversion of an oxygen molecule and a highly reactive oxygen atom to ozone (Figure 2.2).

The soil-plant pathways of the nitrogen cycle are dependent upon the conversion of unreactive nitrogen gas in the atmosphere to reactive N. Prior to industrial development, only two processes converted unreactive nitrogen gas to reactive N: biological nitrogen fixation (i.e., microbially-mediated production of ammonia) and lightning (which results in the production of nitric oxide, NO). Biological nitrogen fixation is a process whereby N_2 in the atmosphere is reduced to ammonia and incorporated directly into living tissue. A limited number of bacteria species possess the enzyme system necessary for this task. These include some of the blue-green algae (Cyanophyta) occurring in fresh waters, some soil bacteria, and the bacterial symbionts associated with the root nodules of legumes and alders. In addition to biological fixation, NO produced by lightning discharges can be converted to nitrate. Nitrate along with ammonia is deposited on the Earth's surface in snow or rain (wet deposition) or as particles such as nitrate or ammonium salts (dry deposition).

Forms of Nitrogen in the Environment

Compound Name	Symbol	Environmental Location	State
Un-ionized Ammonia	NH_3	water, soil, air	aqueous
Ionized Ammonia, Ammonium ion	NH_4^+	water, soil, air	aqueous, gas
Nitrate	NO_3^-	water, soil, air	aqueous
Nitric acid	HNO_3	air	aqueous
Nitric oxide	NO	air	gas
Nitrite	NO_2^-	water, soil, air	aqueous
Nitrogen dioxide	NO_2	air	gas
Nitrogen gas	N_2	water, soil, air	gas
Nitrogen oxides (includes NO, NO_2, N_2O)		air	gas
NO+NO_2	NO_x	air	gas
Nitrous oxide	N_2O	water, soil, air	gas

Once N is fixed, it can be converted to organic nitrogen within the fixing organism or lost from the organism as ammonium or urea. Under aerobic conditions, specialized bacteria species convert ammonium to NO_2^- and NO_3^-, a process known as nitrification. All marine, freshwater and terrestrial plants assimilate nitrogen as NH_4^+ or NO_3^-, with the exception of certain bog species that can only use NH_4^+. This assimilation process involves N uptake through the roots or other cells, assimilatory reduction of NO_3^- to NH_3, and metabolic conversion into tissue. Grazing animals ingest the organic nitrogen in plants and, in turn, are consumed by carnivores. Animals excrete nitrogenous wastes in the form of urea, uric acid or faeces, which are converted microbially back to NH_3. Organic nitrogen in dead organic material undergoes microbially-mediated decomposition (humification) in which carbon and nitrogen compounds are broken down, ultimately releasing forms of N than can be taken up by plants.

Prior to the development of agriculture and permanent settlement, the N in soils, water and plant and animal material was returned to the atmosphere largely through denitrification, the bacterially-mediated conversion of NO_3^- to N_2O and N_2 by microbes in soils and water under conditions of low oxygen (Galloway et al. 1995). Ammonia was also released by volatilization (a process by which molecules escape from a liquid phase to a gaseous phase) from vegetation, soils and animal waste, as a by-product of decomposition, and as a result of biomass burning. A comparatively smaller quantity of N

The Role of Nitrogen in Air Pollution

Urban Smog

Ground-level, or tropospheric, ozone is a major constituent of "urban smog" and is of particular concern in several of Canada's major urban areas during spring and summer. Although chemical reactions producing smog are complex, the main feature is the dissociation of nitrogen dioxide (NO_2), introduced into the air largely from automotive and industrial emissions, to yield an oxygen atom ($O^{.}$) and NO in the presence of sunlight. The resulting oxygen atom combines with an oxygen molecule (O_2) to form ozone (Figure 2.1). Ozone production cannot exceed NO availability unless an alternative means of regenerating NO_2 exists. This alternative is provided by free radicals in hydrocarbon-contaminated air. These free radicals combine with NO to regenerate NO_2, which then dissociates to form more ozone. During the day, ozone concentrations increase until the rate of ozone destruction equals the photochemical production of ozone. During the night, urban smog dissipates because dissociation of NO_2 only occurs in sunlight.
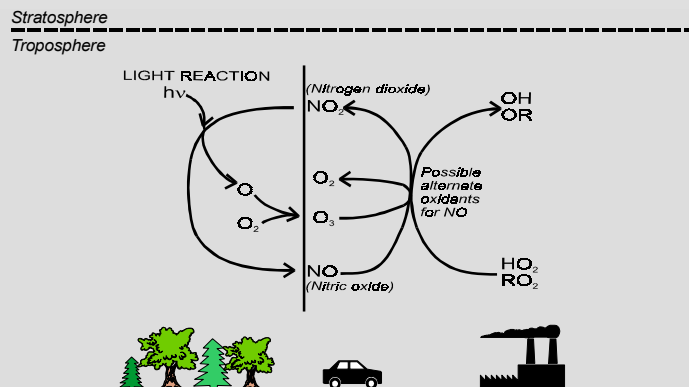

Figure 2.1. The NO_x-Ozone cycle. (hv is a photon; $HO_2^{.}$ and $RO_2^{.}$ are free radicals)

Ground-level ozone causes inflammation of the respiratory system that can persist for up to 18 hours after exposure ceases. It can also aggravate existing heart and lung conditions and may heighten the sensitivity of asthmatics to allergens.

Greenhouse Warming

Water vapour, carbon dioxide, methane and nitrous oxide (N_2O) regulate the Earth's temperature by reducing the rate at which radiation escapes into space. Without this greenhouse effect, the Earth would be about 33ºC colder and inhospitable to life. Greenhouse gas concentrations have been increasing steadily since the industrial revolution, almost certainly because of human activity. In Canada, scientists predict an increase in annual mean temperatures in some regions of between 5 and 10ºC over the next 100 years. Increased incidences of extreme weather events are also predicted.

Nitrous oxide (N_2O) is a potent greenhouse gas with a warming potential over 100 years about 310 times that of CO_2. It is added to the atmosphere from fertilizers, biomass burning, fossil fuel combustion and industrial activities. In the stratosphere, it can be destroyed by photolysis or by reaction with oxygen radicals where it can catalyze the destruction of stratospheric ozone. Ozone in the upper atmosphere filters out UV radiation from the sun, so its depletion results in increased intensity of UV radiation reaching the Earth's surface.

Acid Rain

Acid rain is caused by the conversion of pollutants such as sulfur dioxide (SO_2) and NO_X (i.e., nitric oxide (NO) and nitrogen dioxide (NO_2)) into sulfuric acid and nitric acid in the atmosphere. Dilute forms of these acids fall to earth as precipitation or are deposited as acid gas or dust. A major source of both SO_2 and NO_X is combustion of fossil fuels in motor vehicles, residential and commercial furnaces, and industrial boilers and engines. Once released into the atmosphere, these pollutants can be transported long distances. For example, more than 50% of acid rain in eastern Canada comes from sources in the United States.

Acid precipitation to lakes causes loss of major elements of the food web, including crustaceans, plankton, insects and, ultimately, fish. Another effect of acidification is to increase the toxicity of heavy metals (e.g., aluminium). In forest ecosystems, acid precipitation can damage the surfaces of tree leaves and needles, reduce a tree's ability to withstand cold, and inhibit plant germination and reproduction. However, the nitrogen in acid precipitation can also stimulate forest growth (see Chapter 4.1). Ultimately, changes in soil chemistry caused by acid rain may cause a decline in soil nutrients, resulting in slower growth rates and increased death rates in trees.

was released as NO, a secondary product of nitrification (bacterially-mediated conversion of NH_4^+ to NO_3^-).

In the present world of industrialization and intensive agriculture, both fixation and emission rates of N have changed compared to pre-industrial times. Currently, three anthropogenic activities produce reactive nitrogen (in addition to two naturally-occurring activities): combustion of coal, petroleum products and natural gas, which adds NO to the atmosphere; fertilizer production, which fixes nitrogen gas as ammonia; and cultivation of legumes and other crops, which enhances biological nitrogen fixation beyond background levels. These activities have more than doubled the global rate of N fixation compared to pre-industrial times (Galloway et al. 1995; Vitousek et al. 1997).

The importance of the components of the soil-plant pathway of the nitrogen cycle has also changed from pre-agricultural to present times. In the pre-agricultural world, the breakdown of soil organic matter by soil micro-organisms supplied most of the N for plant growth. Currently, chemical fertilizers and manure are a significant source of N to agricultural crops and, in some cases, forests managed for timber harvest. In addition to enhancing fixation, human activity has liberated long-term biological storage pools through the drainage of wetlands and consequent oxidation of their organic soils. Human activity has also redistributed N between terrestrial and aquatic environments and among ecosystems as a result of municipal and industrial wastewater discharges, and runoff or leaching from land managed for urban development, forestry or agriculture. Because growth of most terrestrial vegetation increases in response to added N, the additional N supply along with its redistribution has likely increased plant growth on a global basis and thus the quantity of organic carbon stored in terrestrial ecosystems worldwide (Vitousek et al. 1997). However, for specific forested ecosystems, controversy remains as to whether productivity gains due to increased N deposition, along with a warming climate and elevated CO_2 levels in the atmosphere, have offset carbon losses caused by timber harvest, fire, and insect-induced mortality. The additional N supplied to terrestrial systems has also moved into ground and surface waters, thereby contributing to overproduction of aquatic plants (particularly in certain north-temperate coastal waters) and to exceedances of nitrate and ammonia guidelines for the protection of aquatic life (particularly near sites where human waste or manure is poorly managed).

As a result of increased fixation, liberation and redistribution of N due to human activity, the composition of atmospheric nitrogen gases has changed and this alteration has contributed to acid rain, urban smog and global warming. Ammonia emissions from fertilized fields and livestock waste, and biomass burning have become major atmospheric sources of N (Galloway et al. 1995). Likewise, fertilized soils and biomass burning have also increased NO and N_2O emissions to the atmosphere. These emissions, as well as NO emissions from fossil fuel combustion, have elevated atmospheric concentrations of nitrogen oxides. The end production of NO oxidation is nitric acid, a principal component of acid deposition (see "the Role of Nitrogen in Air Pollution" text box). As well, increased levels of nitric oxide and nitrogen dioxide react with oxygen and free radicals of hydrocarbons to produce ground-level ozone, a phenomenon responsible for urban smog. Finally, increased nitrous oxide levels contribute to global warming by absorbing infrared radiation.

2.2.   Phosphorus Cycle

In contrast to N, phosphorus does not exist naturally in the elementary state (i.e., as P_4). Also unlike N, where the largest reservoir is the atmosphere, the largest P reservoir is rock (e.g., apatite). All P in the
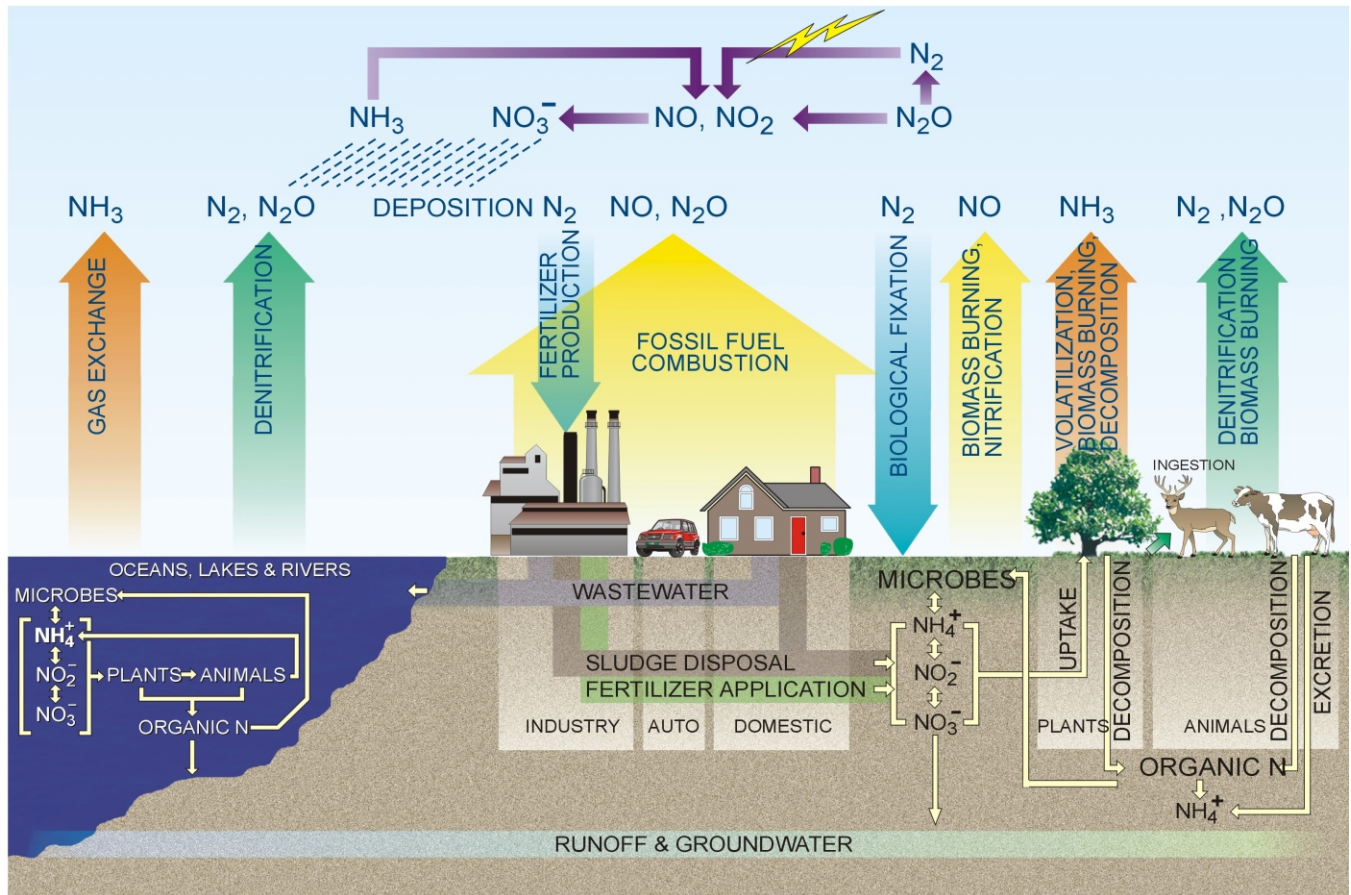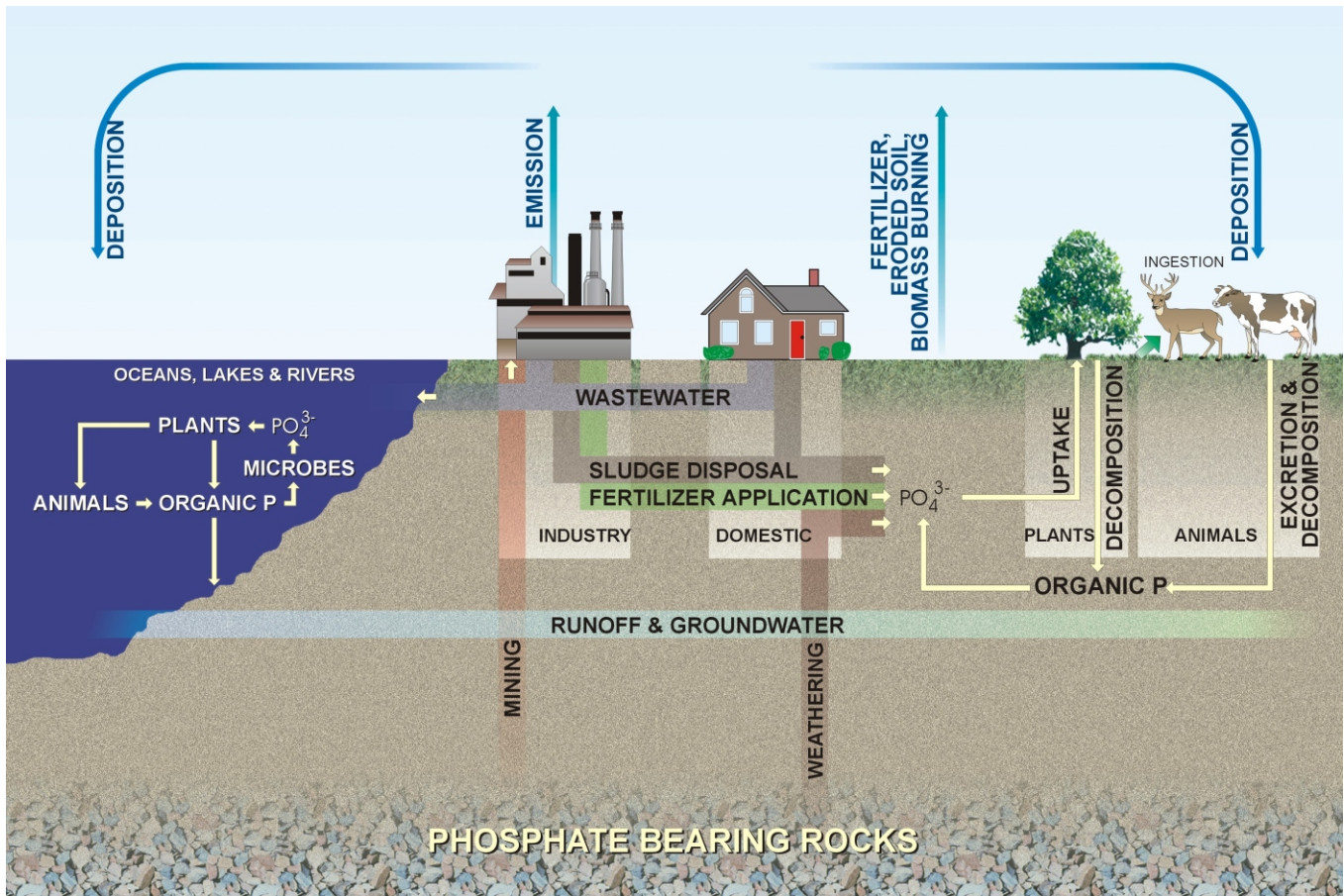
Figure 2.2. The nitrogen cycle.

Figure 2.3. The phosphorus cycle.

Forms of Phosphorus

Phosphorus occurs in the environment as inorganic phosphate and incorporated into organic compounds. The separation of phosphorus into its various forms is defined analytically; these analytical groupings have been selected so they may be used for interpretative purposes.

Total phosphorus (TP) is a measure of all forms of P in a water, soil, or air sample (Figure 2.4). Analysis for TP involves a strong digestion (in order to release P from organic matter) followed by a colourimetric determination of orthophosphate concentration ("colourimetry").

Water samples are typically analyzed for TP as well as two forms of dissolved P: total dissolved P (TDP) and soluble reactive P (SRP). When a water sample is filtered through a 0.45-μm membrane, the dissolved P forms are retained in the filtrate (Figure 2.4). TDP analysis involves a strong digestion of the filtrate followed by colourimetry whereas SRP analysis entails only colourimetry.

In soils, P is bound to soil particle surfaces. Its availability to plants for growth is assessed using a variety of extractions of differing intensity.
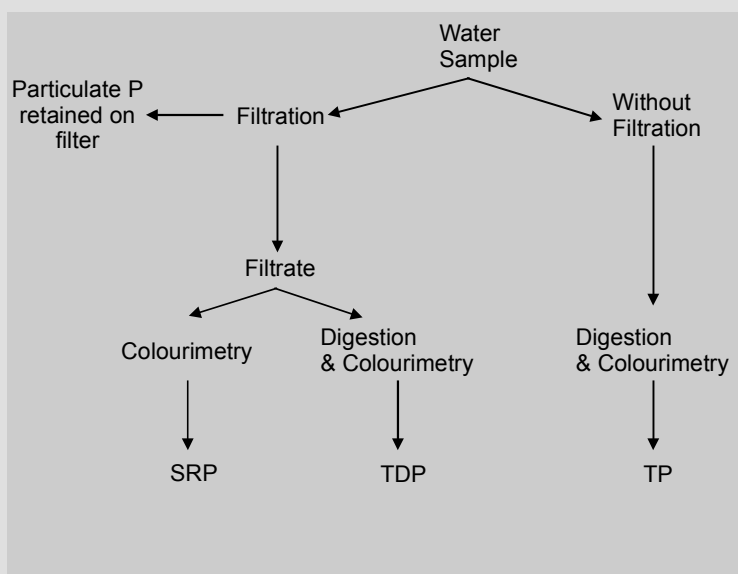
Figure 2.4. Analytical forms of phosphorus in the aquatic environment.

atmosphere is derived from sources on Earth (e.g., from erosion, fertilizer drift, industrial emission, etc.). Finally, unlike N, P exists in only one environmentally reactive form, orthophosphate (PO_4^{3-}).

Prior to industrialization and intensive agriculture, P was added to soil as the orthophosphate ion (PO_4^{3-}) only through the weathering of parent material (Figure 2.3). Phosphorus is taken up from the soil mainly as orthophosphate through plant root systems or other cells. Plants are grazed and animals excrete excess P as phosphorus salts in urine and faeces. This P is then either taken up directly or converted from organic phosphorus to phosphate ion by a wide range of bacteria and fungi (Ricklefs 1990). The decomposition of organic matter also returns inorganic phosphorus to the soil. Phosphate is extremely reactive and binds with many cations (i.e., iron, aluminum, and calcium) to form relatively insoluble compounds. This binding results in the storage of phosphate in poorly labile forms in both terrestrial and aquatic ecosystems.

In the modern world of industrialization and intensive agriculture, mining of phosphorus-containing rock to produce fertilizer has increased the supply of P to soils. These fertilizers are applied in locations where the rock is naturally lower in P and at rates that far exceed weathering. In addition, municipal and industrial sources contribute P to water (wastewater discharges), air (stack emissions) and soil (landfills, sludge application). Runoff from land managed for urban development, forestry or agriculture is also a major P source for aquatic vegetation. The result is that P is distributed around the globe as P-bearing rock, fertilizer, livestock feed and agricultural produce, and as waste emissions to water and the atmosphere. Because plant growth in most freshwater ecosystems is constrained by a shortage of P, the addition of P, albeit dilute, can cause significant increases in the productivity of lakes and rivers.

2.3.   Conclusions

Human activity has increased the supply of bioavailable forms of both N and P. In the case of N, atmospheric nitrogen is converted to fertilizer and applied to agricultural fields to grow crops, which are then transported to urban areas. Urban sewage, which is high in N, is discharged to surface waters because it may be contaminated or too costly (because of long transport distances) to apply to agricultural land. Fossil fuel combustion (by industries, in automobiles, and for household heating) enhances nitrogen oxide production as the high temperatures associated with fossil fuel combustion cause N in the air to combine with oxygen in the air. As a result, the amount of available N has more than doubled since the 1940s, with human activities contributing 210 million tonnes per year to the global supply of N compared to only 140 million tonnes generated per year during pre-industrial times (Vitousek et al. 1997). Human alterations to N cycling have increased concentrations of the potent greenhouse gas N_2O globally; increased concentrations of nitrogen oxides driving the formation of photochemical smog in large regions of the Earth; increased the supply of N to vegetation; increased transfer of N to freshwater and coastal ecosystems; and enhanced surface water acidity through the addition of nitrate (Vitousek et al. 1997).

Similar changes have occurred in the phosphorus cycle. Weathering of phosphate-bearing rocks as a source of P is now overshadowed by mining activities, with approximately 17 million tonnes of P now mined each year. Manufactured fertilizer is transported to agricultural fields far from the rock source. Agricultural crops, in turn, are transported as feed to areas with high livestock concentrations and to urban areas. Urban sewage is discharged to surface waters because it may be too contaminated or too costly to apply to agricultural land. The environmental consequences of human alterations to P and N cycling are serious and long term.