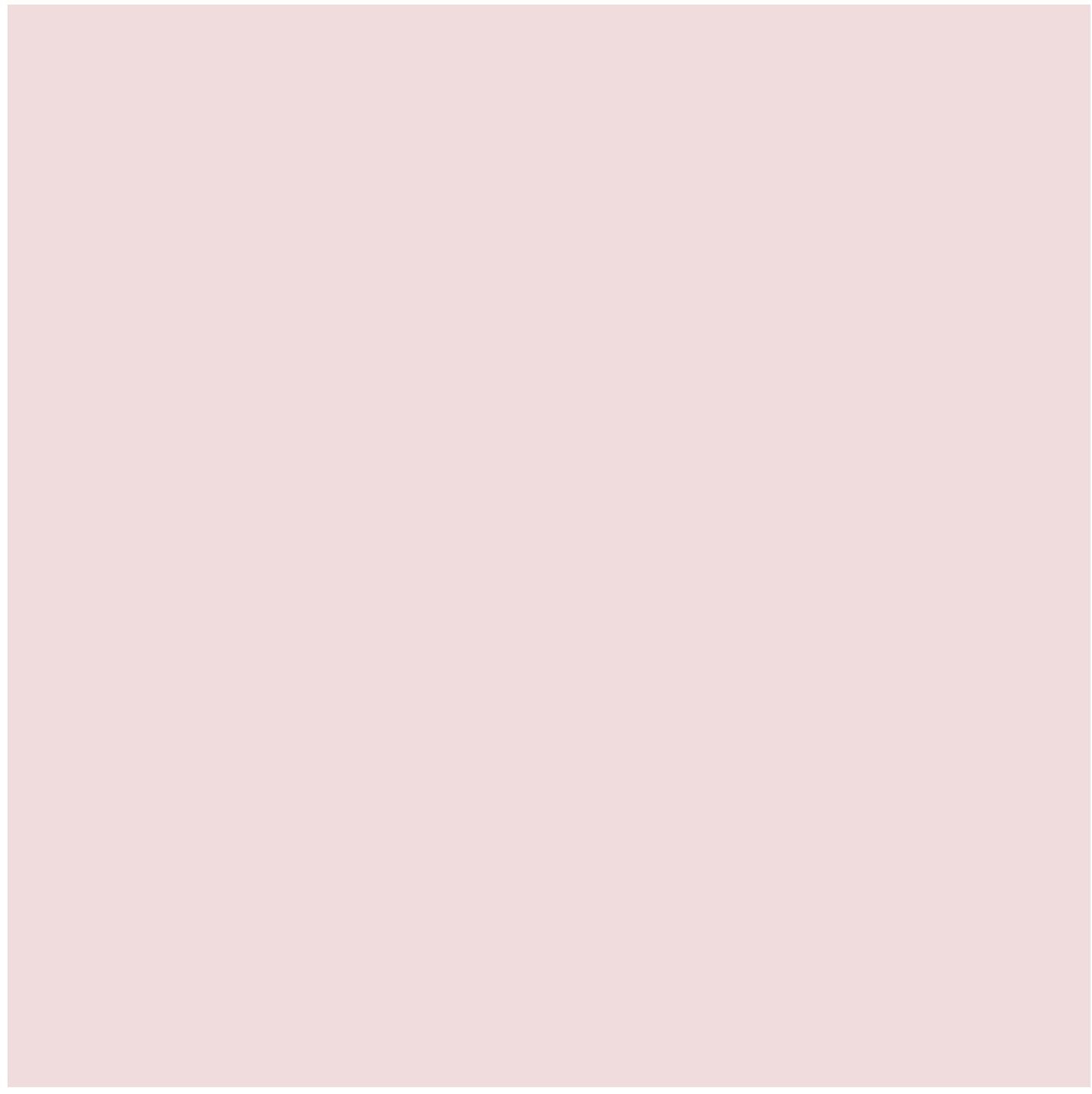


Phosphorus and eutrophication

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Without phosphorus, life is not possible. A fundamental element of life, it is essential to natural ecosystems and agricultural production. However, human activities (agriculture, wastewater, urban expansion, industry) are profoundly changing its cycle. Among the consequences, aquatic ecosystems are disrupted, algae proliferate and then decompose by consuming the oxygen needed by many species: this is called eutrophication. Moreover, phosphorus is not a renewable resource. On a global scale, estimates of future consumption predict that phosphate deposits will be depleted within one to two centuries. Controlling phosphorus flows in the environment is therefore essential to restore degraded environments and to secure human nutrition. This article presents the key mechanisms of the phosphorus cycle, restoration solutions and the medium-term management challenges of this resource.

1. How does the phosphorus cycle work?

Phosphorus is an essential component of living matter (DNA, cell membranes, enzymes, bone, ATP) but it is a rare element in the natural environment (< 0.1% of the mass of terrestrial rocks). It is found as calcium, iron and aluminum phosphates in volcanic and sedimentary rocks. On continental surfaces, phosphates are dissolved by the alteration (mineralogical degradation process) by dissolving the rock under the effect of the rainwater. The plants take the phosphates thus solubilized and use them to produce organic matter during the **biosynthesis** process. Phosphorus is then transferred along the food chain by plant

consumption by animals. It is again solubilized by the decomposition of dead matter by microorganisms.

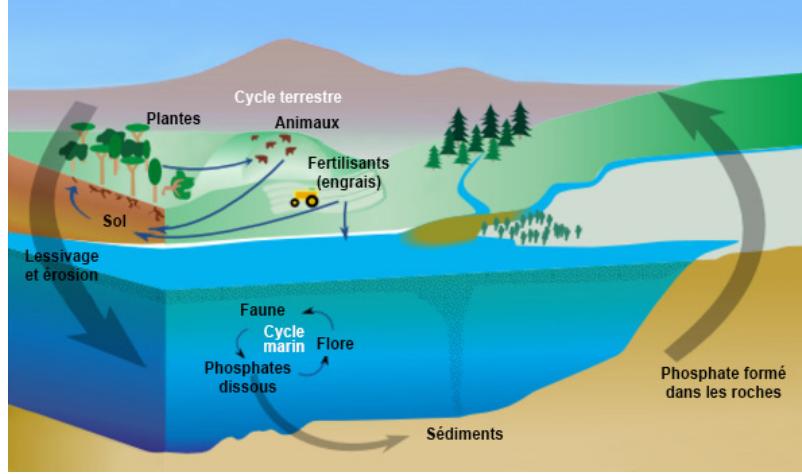


Figure 1. Global phosphorus cycle. [Source: By Bonniemf Incorporates work by NASA Earth Science Enterprise. [CC BY-SA 3.0 (<http://creativecommons.org/licenses/by-sa/3.0>)], via Wikimedia Commons (translated into French: <http://www.astrosurf.com/luxorion/eco-terre-humus.htm>)]

On a small scale (lake, river, forest, pasture), phosphorus follows a succession of **organic** (living world) and **mineral** (after decomposition of the living world) phases. On a larger scale, phosphorus introduced into ecosystems by **water erosion** and **leaching** (the process of transporting solute by rainwater from soils to groundwater and then to rivers) is carried by rivers to coastal areas where it fertilizes coastal waters. These waters are generally very productive in terms of marine **phytoplankton** (Figure 1).

Phosphorus, which does not have a gas phase, has a high affinity for soil and sediment particles (Table 1). Linked to the transport of sediments in aquatic environments, phosphorus from continents sediments the ocean floor. Its natural global cycle is therefore not completely in balance between continental losses and accumulation in the ocean floor. It is said by nature to be "open" at the scale of the biosphere. This clearly differentiates it from the natural nitrogen cycle, which runs in a real loop between the atmosphere and other compartments of the Earth. By introducing phosphates from the mining of phosphate rocks (**phosphate fertilizers** and phosphates used as **detergents** in laundry), man amplifies the **imbalance** in the natural phosphorus cycle.

Table 1. Distribution of phosphorus in large compartments of the earth.

Compartiment	Stock en tonnes
Atmosphère	≈ 0 t
Hydrosphère	$8,6 \times 10^{15}$ t (<u>sédiments</u>)
Roches terrestres	$25,6 \times 10^{15}$ t
Matière vivante	2×10^9 t

2. What are the forms of phosphorus?

Phosphorus is found in dissolved or particulate form. Dissolved phosphorus includes inorganic forms of orthophosphate ions (mono-orthophosphate ions HPO_4^{2-} and di-orthophosphate ions $\text{H}_2\text{PO}_4^{3-}$), and organic forms in the process of mineralization (degradation process of dead organic matter by heterotrophic bacteria) of dead matter (phosphoproteins, phospholipids). Orthophosphate ions (traditionally referred to as PO) play an essential role in the functioning of ecosystems because they are the only *biologically available* form (means an element accessible to plants for collection and assimilation) for plants. They are present in the pore waters of soils and sediments and in the water column of aquatic environments. Taken by plants to produce organic matter (*biosynthesis*: the process of producing organic matter by a living being (by photosynthesis for example for plants), they are then released by **mineralization** of dead matter under the action of heterotrophic bacteria that uses dissolved oxygen from water to oxidize and mineralize dead organic matter.

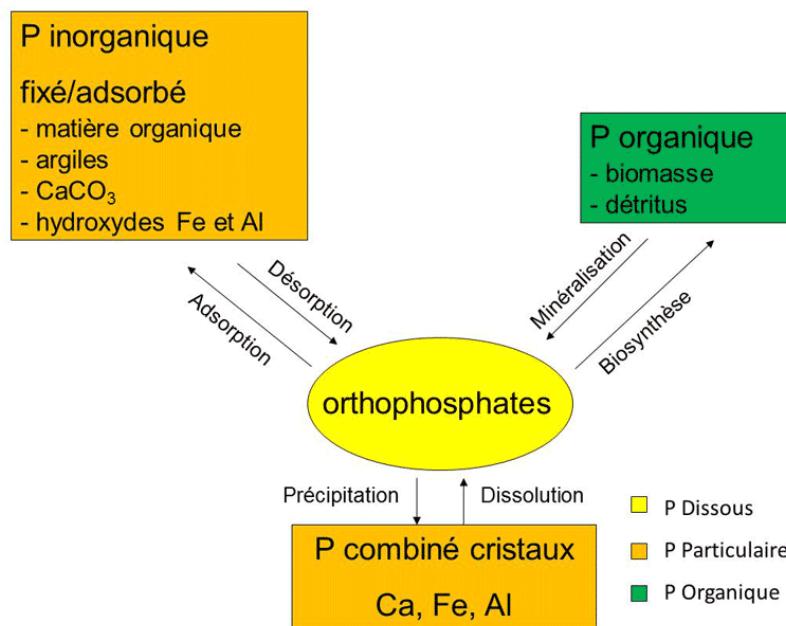


Figure 2. Phosphorus forms and their interactions.

Orthophosphate concentrations in natural environments are very low in the order of 10 µg phosphorus/litre (in the case of alpine lakes or pelagic marine waters). In environments highly disturbed by human activities, they can reach several hundred µg phosphorus/litre.

Particulate phosphorus is either organic or mineral. The **organic fraction** corresponds to all the phosphates of organic animal and vegetable matter, living or in the process of mineralization (Figure 2). It can represent a significant part of particulate phosphorus: up to 50% in river sediments in agricultural areas for example. The **inorganic fraction** can be present in two forms; crystalline phosphorus (calcium, iron or aluminium salts) which is among the least soluble forms and phosphorus fixed or adsorbed on the surface of the particles and its constituents (calcium carbonate, iron and aluminium hydroxides, clay, organic matter).

These fixed or adsorbed forms, which can be mobilized, are in permanent exchange with the dissolved forms thanks to the **adsorption** and **desorption** mechanisms. In aquatic environments, this property of ion-exchange particles strongly influences orthophosphate concentrations. Indeed, these ions are very sensitive to the **adsorption** capacities of the particles (total exchange surface, particle size). Particulate matter therefore plays a "buffer" role in orthophosphate ion concentrations.

3. What are the sources of phosphorus from human activities?

Like all living things, man needs phosphorus. Its daily food intake is about 1.5 g of phosphorus. The increase in the world population has considerably increased food needs. To feed humanity, agriculture has grown widely in the last century and has gradually intensified and industrialized. To maintain high productivity of agricultural systems in this context, soil phosphorus removed by crops must be renewed.

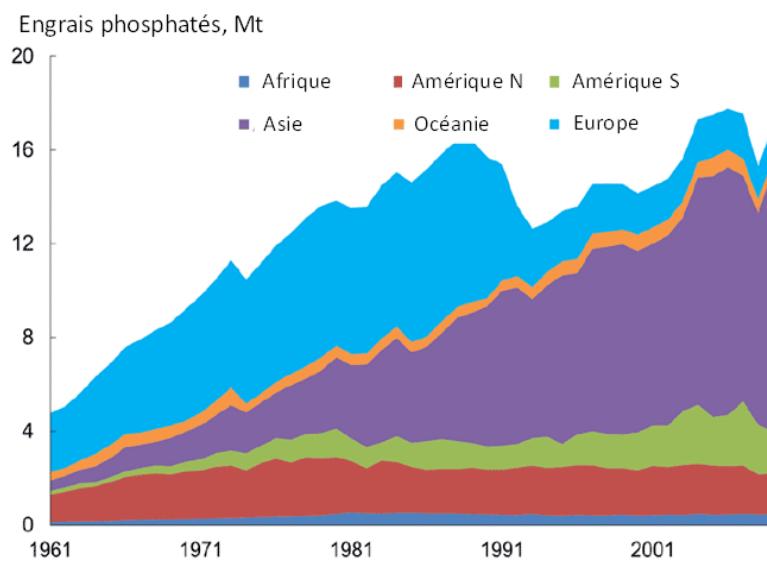


Figure 3. Trends in world consumption of phosphate fertilizers between 1961 and 2010. [Source: Van Dijk, K., Kabbe, C., Pellerin, S., Rechberger, H. & Oenema, O. (2013). Phosphorus Use in Europe. European Sustainable Phosphorus Conference. 6-7 March 2013. Brussels, Belgium. Available at: phosphorusplatform.eu/component/jifile/download/MWFjMTAzNDViYzZhZjcxYzA4YTMyZTE1OTBhYjk2OWU=/2013-eu-sustainable-p-conference.pdf]

The use of guano (fertiliser made from seabird excrement) and the discovery during the 20th century of industrial production processes for **phosphate fertilizers** from phosphorus-rich rocks led to an expansion in the use of this resource on a global scale. The use of phosphate fertilizers has spread widely in Europe and North America, with inputs well in excess of the needs of cultivated plants. In response to the collective incentive for rationalisation, Europe experienced a sharp decline in contributions in the 1990s. This reduction has not had any impact on agricultural yields and, since then, the consumption of phosphate fertilizers has remained stable. On the other hand, the emerging Asian countries with booming economies (China in the lead) have intensified their agriculture in recent decades and are now the largest consumers (Figure 3). In the near future, agricultural development in African and South American countries is likely to further increase global demand.

In addition, the reduction in production costs since the 1960s has led to the widespread use of mineral phosphate in everyday industrial products (agri-food, matches, metallurgy, detergents in the form of polyphosphates in laundry). The use of polyphosphates in laundry has led to a very large increase in the amount of phosphorus in domestic wastewater. The use of polyphosphates has been phased out in Europe since the end of the 20th century.

Recent and massive introductions of phosphorus into the environment, erosion of cultivated land (**diffuse sources**) and increased domestic wastewater (**point sources**) are contributing to the rapid increase in phosphorus concentrations in aquatic environments. Significant stocks have been built up in the environment such as overfertilized **agricultural soils** or **river sediments** that accumulate phosphorus. Understanding this new distribution of phosphorus stocks on the planet's surface is crucial for better management of this limited and non-renewable resource [11].

4. Excess phosphorus and eutrophication

The environmental pollution caused by phosphorus, particularly in aquatic environments, has increased the interest in this element for several decades. It is considered to be the main responsible for the **eutrophication** process. Etymologically, the word eutrophication means "well nourished". The term eutrophication refers to the consequence of **hyperfertilisation** of water into nutrients (**phosphorus and nitrogen**), the ultimate point of which is **dystrophication** (ecological imbalance) [2]. Eutrophication manifests itself in an increase in algal biomass and **deoxygenation** of the water column, itself caused by **heterotrophic mineralization** of the organic matter produced.

Eutrophication affects rivers, lakes and coastal areas. In addition, eutrophication can lead to a disruption of the structure of planktonic stands. For example, the proliferation of **unwanted algae** such as Dinophyceae and Cyanobacteria, some species of which can produce toxins. Deoxygenation can promote the release of sediment-associated pollutants (metals, micropollutants). Not to mention the economic impacts on bathing areas (toxic algae) and drinking water production (obstruction of pumping filters, establishment of parasitic fauna in networks, development of tastes and odours incompatible with the notion of consumption, etc.).

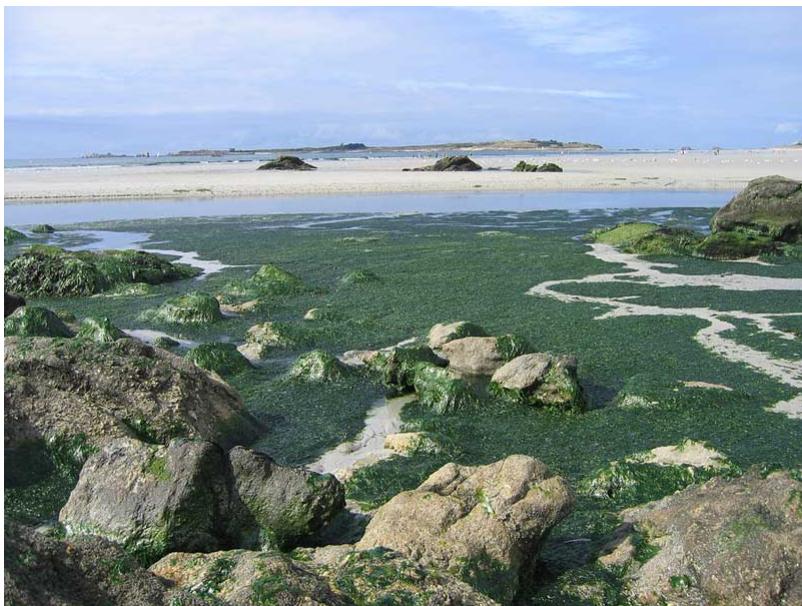


Figure 4. Green algae blooms on a Breton beach. [Source: By Thesupermat (Own work)/GFDL (<http://www.gnu.org/copyleft/fdl.html>) or CC BY-SA 2.5.]

During the biosynthesis process, algae need carbon (C), nitrogen (N) and phosphorus (P). Algae growth is conditioned by the ratio in which they remove nutrients (**Redfield ratio** C: N: P = 106:16:1). This ratio refers to the molar elemental composition of carbon, nitrogen and phosphorus in an algal cell. If these elements are present in these ratios in the aquatic environment there is no growth limitation. If one of these elements is missing, it is called an algal growth **limiting factor** (nitrogen or phosphorus limitation for example). In this report, phosphorus is often referred to as the main **limiting factor** in algal growth. Its responsibility is clearly demonstrated in freshwater aquatic environments where nitrogen is largely in excess. In contrast, for coastal marine environments, nitrogen (in the form of nitrates; see [Nitrates in the Environment](#)) is often referred to as the main factor in eutrophication. This is the case, for example, in Brittany, where nitrates of agricultural origin are responsible for the spectacular proliferation of green algae on beaches (Figure 4).

As early as the 1960s, many cases of eutrophication were reported worldwide. First, the studies were conducted on lake environments (lakes and reservoir dams) where disturbances are most severe, such as the large North American lakes or, closer to home, the large alpine lakes (Lake Geneva, Bourget and Annecy). This extensive work leads to a classification of disturbance intensity based on the main indicators of trophic status of water bodies (Table 2).

Table 2. Threshold values for classifying the trophic status of water bodies

Statut trophique	Phosphore total (µg/L)	Chlorophylle a (µg/L)	Transparence (m)
Ultra-oligotrophe	< 5	< 2,5	> 6
Oligotrophe	5-10	< 8	> 3
Mésotrophe	10-30	8-25	3-1,5
Eutrophe	30-100	25-75	1,5-0,7
Hypereutrophe	> 100	> 75	< 0,7

Chlorophyll a: refers to a photosynthetic pigment in plants that allows photosynthesis through light. Chlorophyll a is used as an indicator of the plant biomass of an ecosystem: indicator of the intensity of algal development in waters. **Transparency:** limit of light penetration.

These threshold values make it possible to prioritize water bodies. **Oligotrophic** refers to a nutrient-poor environment with reference to its phosphorus concentration. A **hypereutrophic** environment is, on the contrary, the ultimate stage of degradation. The term mesotrophic refers to a transitional environment between ultra-oligotrophic and hypereutrophic. In rivers, attention to eutrophication problems is more recent. Rivers are considered as **self-purifying** systems, capable of digesting and discharging far downstream disturbances at a given point in the hydrographic network. However, the problem is very real in large rivers, with the proliferation of microalgae (phytoplankton refers to plant plankton in aquatic environments (microalgae), as in smaller rivers, where aquatic plants (macrophytes refer to aquatic plants rooted in sediments or floating on the water surface). In addition, significant nutrient inputs to **rivers** inevitably affect receiving coastal environments, lagoons, fjords and estuaries, which are themselves subject to serious eutrophication problems on a global scale.

5. How to restore eutrophic environments?

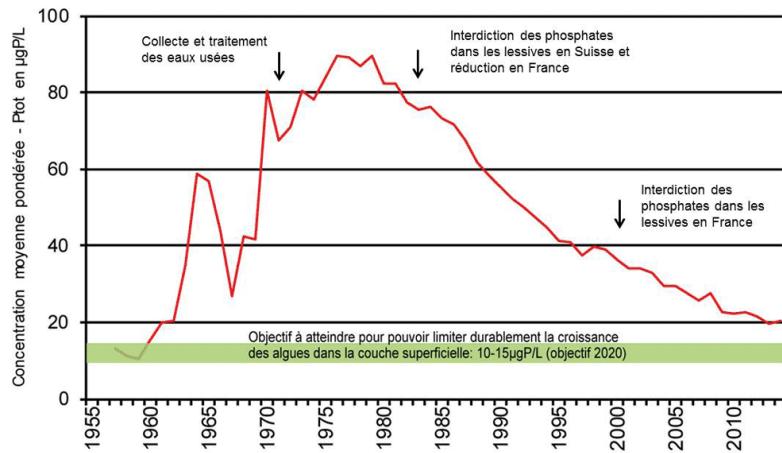


Figure 5. Total phosphorus curve in the waters of Lake Geneva. [Source: CIPEL illustration (International Commission for the Protection of Lake Geneva Waters) www.cipel.org/themes/phosphore].

The first work to combat eutrophication first focused on **reducing point phosphorus inputs**. In many industrialized countries in Europe and North America, the collection of domestic wastewater, the reduction of polyphosphates in laundry and the treatment of phosphorus in wastewater treatment plants have significantly reduced phosphorus inputs to aquatic environments.

This management policy, which was very effectively applied from the 1980s onwards to restore the waters of **Lake Geneva** on the French-Swiss border, has made it possible, for example, to gradually reduce phosphorus concentrations in the lake's waters (Figure 5). To achieve the objective of reducing eutrophication set by the CIPEL (International Commission for the Protection of Lake Geneva Waters), efforts have also focused on the management of **diffuse sources** from the *watersheds* refers to the geographical area drained by a river and its tributaries. Its surface is delimited by the topography. The drained water converges towards an agricultural outlet{end-tooltip}.

With the accumulation of phosphorus in agricultural soils, and despite measures to limit *erosion* the process of detachment and transport of soil particles due to precipitation and *water runoff* (grass strips) and reduction of phosphate fertilizer inputs, the problem of **diffuse sources** of agricultural origin remains relevant [3]. Mechanisms for transferring phosphorus from agricultural sources are still being studied to identify the role of hydrology on transport modes. It is noted that the restoration process is very long (several decades) from diagnosis, decision making and action to visible results.

How far should we go in reducing phosphorus inputs to aquatic environments? Aren't we going to radically change the way aquatic environments work? The issue of reducing phosphorus inputs has recently entered the public debate in Europe. This is reflected in the demands of professional fishermen on Lake Geneva who have been observing a decline in fish stocks for several years and are asking for more phosphorus in the lake to increase the productivity of the ecosystem [4].

While eutrophication is declining in Europe, the situation is critical in some emerging global regions where extremely rapid urban growth and agricultural development are still not taking environmental quality into account.

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