

The Earth Phosphate Cycle

DR. BRUNO LORAN

*Assistant Manager, Technical Operations
Western Research Application Center
University of Southern California*

ABSTRACT

The earth phosphate cycle is outlined in detail, from phosphate mining and production to phosphate disposal in lakes and oceans.

Most phosphate deposits are of marine sedimentary origin, and contain approximately 30% P_2O_5 . Large amounts of wastes—gaseous, liquid, and solid—are generated during the enrichment of the mineral and the conversion to phosphate fertilizer, phosphoric acid, or elemental phosphorus; the most difficult to control are air and water pollution by fluorides.

The major phosphate applications are for fertilizers, detergents, anti-corrosion agents, and insecticides. The excess phosphate from human and animal diet is eliminated, and becomes part of sewage or runoff waters; sewage phosphate could be recovered through tertiary sewage treatment systems. Excess phosphate addition to natural waters is a major contribution to lake eutrophication. The phosphate that reaches the ocean is precipitated and eventually forms extensive deposits located mainly along the continental coasts.

The world production and demand of phosphates have been increasing exponentially, with a doubling rate of 10-15 years. If this rate of use continues, land reserves could be exhausted in a fairly near future. Ocean deposits can supply additional amounts, but discontinuing the use of phosphate in detergents, application of correct amounts of fertilizers, and recycling of sewage phosphates would also be advisable.

Introduction

Phosphates are a component of nucleic acids, and are therefore present in all living cells; bones and many animal shells are also composed of phosphates. Among the essential plant nutrients, phosphates are one of the less abundant in most soils, and their availability is one of the most critical factors controlling plant growth [1]. Most soils in temperate climates contain enough phosphate to support crop production, but tropical soils are naturally

phosphate-deficient because of leaching. Phosphates can be added to deficient soils in the form of natural or artificial fertilizers, and for sustained crop yields they must be added to all soils. Phosphate fertilizers are used extensively in the developed countries, and their use is now increasing in the less developed ones, where lack of plant nutrients is considered one of the major factors limiting crop production.

Approximately 60% of the phosphate production is used for fertilizers, 20% for detergent builders, and 20% for corrosion prevention applications, insecticides, and other. Both production and demand of phosphates have grown exponentially. There is at present no lack of raw materials, although additional sources are needed in regions that contain no known minable deposits (such as many developing countries) because phosphates are a low-value commodity, and transportation costs may add substantially to its price.

Phosphate Mining and Production

PHOSPHATE ORES

When the earth was first formed the molten (igneous) rocks solidified into rocks containing small amounts of apatite, a calcium fluorophosphate of varying composition, with a general formula $\text{Ca}_{10}(\text{PO}_4, \text{CO}_3)_6(\text{F}, \text{Cl}, \text{OH})_2$. Exposed to the elements these rocks weathered slowly, were washed into streams, and eventually reached the ocean. There, part remained dissolved, part settled. Species of sea life used the dissolved phosphates for body and shell buildup. After their death, they contributed to the formation of thick deposits in the bottom of the ocean, especially where confluence of ocean currents or other factors accumulated them. Such deposits, raised to the surface through geological upheavals, are now the main source of phosphates.

Phosphate ores (phosphate rock) are of three main types—the marine sedimentary type, or phosphorite; the igneous apatite; and guano. Phosphorite contains approximately 30% P_2O_5 (100 g of phosphoric anhydride, P_2O_5 , contain 43.6 g of phosphorus, and correspond to 218 g of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, known in the fertilizer trade as *bone phosphate of lime*, BPL). Phosphorite deposits contributed 74% of the world P_2O_5 production in 1967. The largest deposit, containing 70% of the world's known land supply of phosphorite, is in Florida, which 10 million years ago was at the bottom of the ocean [2]. Igneous apatite deposits are more scarce. Deposits being mined at present, and containing up to 36% P_2O_5 , are in Russia (Kola Peninsula) and in Africa (Uganda, South Africa). They contributed 24% of the world production in 1967. A once major source of phosphates which is now nearly exhausted is guano, the accumulation of seafowl droppings on islands and coastal regions of South America (Peru), Africa, and Pacific Islands. The

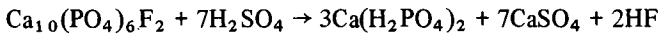
nitrogenous and other organic matter in guano undergoes decomposition, so that the material becomes enriched in phosphate (20-30% P_2O_5 , up to 39% in areas where rainfall dissolves phosphates and accumulates them in underlying rocks); 2% of the world production of P_2O_5 derived from guano in 1967 [1].

PHOSPHATE PRODUCTION

Phosphate rock is essentially a fluorapatite by the formula $Ca_{10}(PO_4)_6F_2$, mixed with silica sand. For phosphate production, the material is first ground, then beneficiated by removing most of the silica sand by flotation. After drying in kilns, it may be used directly as fertilizer (suitable only for tropical acid soils) or it may be processed to a more soluble or purer state (for most soils and for chemical uses). Three basic methods are used for this purpose: acidulation, electric furnace reduction to the elemental state, and fusion with alkali.

Depending on the kind and amount of acid used, the following products are made by acidulation:

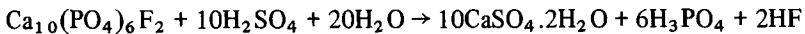
Superphosphate fertilizer (also called "normal" or "single" superphosphate), obtained by reacting phosphate rock with enough sulfuric acid to convert it into a mixture of monocalcium phosphate and calcium sulfate (gypsum), according to the reaction:



Waste sulfuric acid may be used, as long as the impurities present are not harmful to vegetable crops. Superphosphate contains approximately 20% P_2O_5 . This low phosphorus content limits its economic distribution to a 100-200 mile radius from the plant [3]; the gypsum content is beneficial for soils lacking in sulphur.

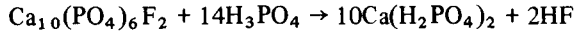
Enriched Superphosphate fertilizer, obtained by reacting phosphate rock with a mixture of sulfuric and phosphoric acids, so that the final product contains 25-30% P_2O_5 . It is used mainly in Europe.

"Wet process" *Phosphoric Acid*, obtained by reacting phosphate rock with enough sulfuric acid to convert all the phosphate to phosphoric acid, according to the reaction:



The phosphoric acid obtained after removal of the crystallized gypsum by filtration is impure, and is used mainly for the production of triple superphosphate.

Triple Superphosphate fertilizer (also called concentrated, double, or treble superphosphate), obtained by reacting phosphate rock with phosphoric acid according to the reaction:



which achieves complete conversion of phosphate rock to monocalcium phosphate. Triple superphosphate contains 46-47% P_2O_5 ; the high phosphorus content makes it suitable for long-distance shipping or export. In the U.S., twice as much triple superphosphate as normal superphosphate is produced yearly [4].

Electric furnace reduction produces elemental phosphorus which may be oxidized (burned), then hydrated to pure phosphoric acid suitable for use in detergents (mainly as sodium hexametaphosphate, $(\text{NaPO}_3)_6$), for anti-corrosion applications, for insecticides, and for other purposes.

Fusion with alkali (soda ash, Na_2CO_3) or magnesium silicate has been employed to a limited extent in Germany and Japan [4]. A partly defluorinated, moderately soluble slag usable directly as fertilizer is obtained.

UNIT PROCESSES AND WASTE PRODUCTS GENERATED

The preparation of the phosphate ore generates dust from the grinding and drying operations, which is generally controlled by a combination of dry cyclones and wet scrubbers. The material collected by the cyclones is recycled, and the scrubber water is discharged to waste ponds [5]. A high volume of wastewater (30,000 gal/min) is also generated in the flotation process; the water contains fine clays and colloidal slimes, as well as some tall oil from the flotators. The wastes are either stored on land areas, where slime settles, or go through mechanical clarifiers to remove sand tailings and purify the water for reuse [2, 6].

Process diagrams for the manufacture of superphosphate [3] and triple superphosphate [7] are shown in Figures 1 and 2. For both products, and for the manufacture of the phosphoric acid needed for the production of triple superphosphate, emissions of fluorine compounds as gases, in particulates, and in scrubbing water require the most difficult and expensive pollution control operations [8]. Most of the fluorine is released as gaseous silicon tetrafluoride, produced by reaction of hydrogen fluoride with silica present in the phosphate rock, in amounts of 200-500 mg/cu ft of effluent gas [5]. The reactor areas are well controlled: according to a recent EPA report [9], less than 0.1% of the fluorine input to the process is vented to the atmosphere. Spray, venturi, wet cyclone, impingement, and packed bed scrubbers are used for fluoride removal. The effluent scrubber liquors are usually treated with lime to precipitate insoluble calcium fluoride. Fluoride emissions from curing sheds, however, are much more difficult to control because of the low concentration of fluorides and the very large exhaust gas rates. There is low incentive for recovery of the fluorine compounds as salable byproducts because of the limited demand of the material. In a demonstration plant being

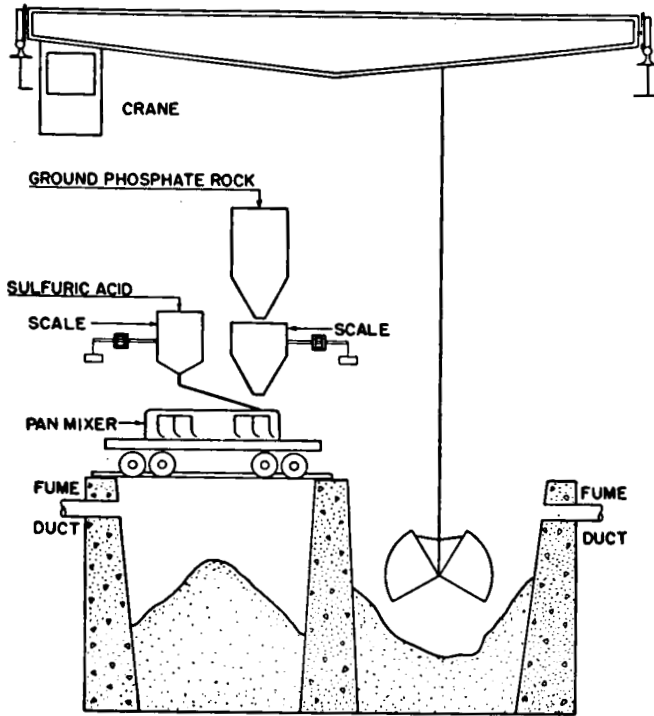


Figure 1. Batch process diagram, superphosphate manufacture (from Reference 3).

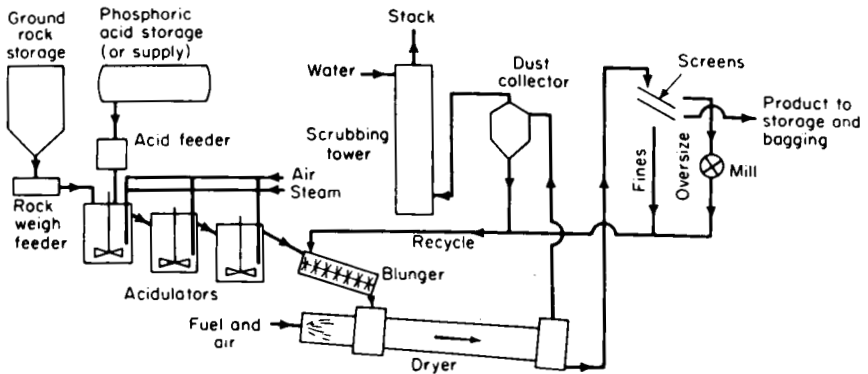


Figure 2. Continuous process diagram, triple superphosphate manufacture (from Reference 7).

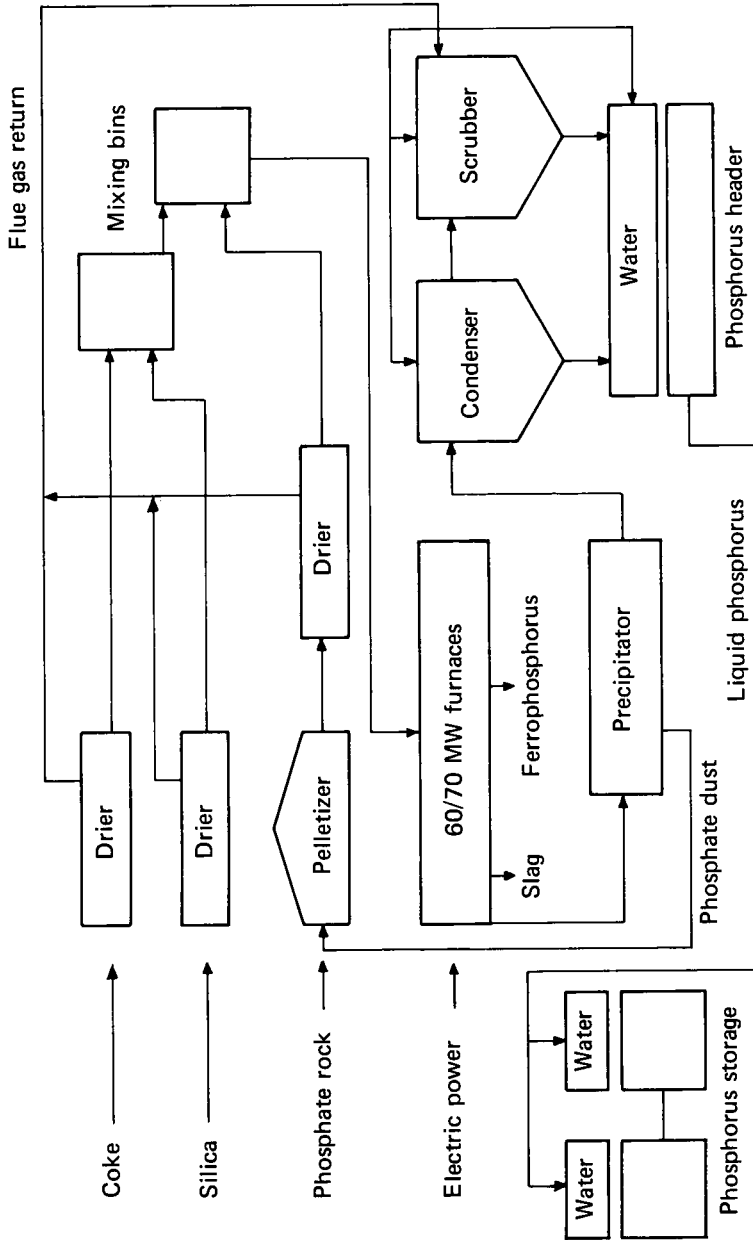


Figure 3. Process diagram for production of elemental phosphorus (from Ref. 10).

built at present under EPA sponsorship by Har-Fluor Systems, Inc., fluosilicic acid will be produced for resale.

The second most important waste product is waste gypsum, five tons of which are produced for each ton of triple superphosphate. There is no demand for this material, so that it is presently impounded in large settling basins which have to be treated with lime or limestone to prevent release of fluorides.

The process diagram for production of elemental phosphorus [10] is shown in Figure 3. In addition to the pollutants already discussed, this process releases colloidal phosphorus (400-2500 ppm) [2] with the furnace process water, called *phossey water*. A recently built (1968) plant in Newfoundland used to discharge this wastewater in the ocean, after clarification; however, this caused extensive fish kills, which damaged the major local industry. After being shut down for several months, the plant was modified to include land treatment of the wastewater with lime, producing purified water which is reused, and lime-phosphorus sludge which is recycled to the pelletizer (Figure 3).

The Utilization of Phosphate

FERTILIZERS

The substantial amounts of phosphates needed by one acre of various crops are shown in Table 1 (as lbs of elemental phosphorus per acre) [11].

When fertilizers containing a high percentage of monocalcium phosphate

Table 1. The Sulphur and Primary Nutrients Contained in Various Crops (Pounds).^a (From Reference 11.)

<i>Crop</i>	<i>Yield per acre</i>	<i>Sulphur</i>	<i>Nitrogen</i>	<i>Phosphorus</i>	<i>Potassium</i>
Corn	100 bu.	8-10	160	26	100
Cotton	1.5 bales	12-15	105	20	55
Wheat	40 bu.	9-12	70	13	41
Alfalfa	5 tons	20-24	225	21	187
Clovers	4 tons	15-20	160	18	133
Grasses	4 tons	8-10	120	18	100
Cabbage	15 tons	19-38	97	11	81
Turnips	20 tons	25-35	90	18	150
Onions	15 tons	18-20	90	18	66

^aExpressed as elemental sulphur, nitrogen, phosphorus and potassium.

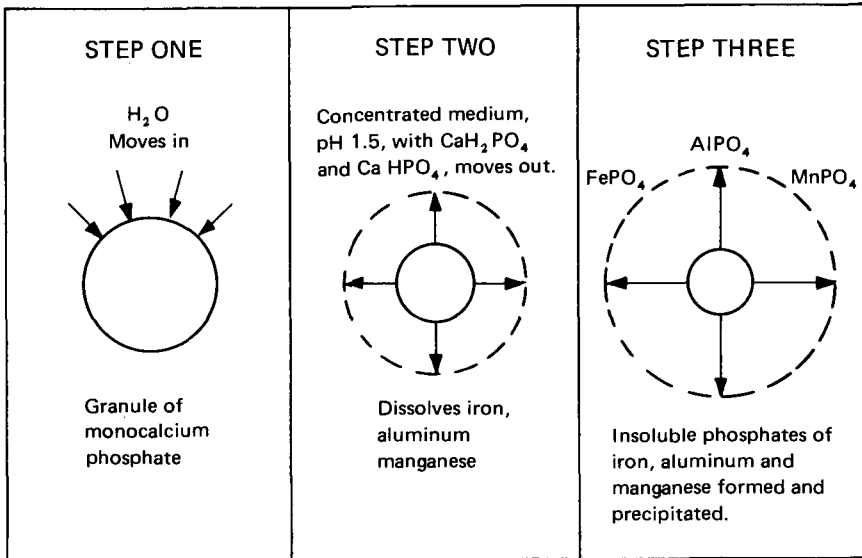


Figure 4. Behavior of phosphate in the soil (from Reference 11).

are applied to the soil, water vapor moves rapidly into each granule. A solution is formed which is saturated with monocalcium and dicalcium phosphates, and is strongly acidic (pH 1.5). The solution moves out in a front reacting with soil constituents and dissolving iron, aluminum, and manganese compounds. Eventually, the solution is neutralized and the metal phosphates precipitate (Figure 4) [11]. If the soil is calcareous, the moving phosphate front is precipitated as dicalcium phosphate on the surface of particles of calcium carbonate. In both cases, dispersion of phosphate in the soil is achieved.

Phosphate is therefore bound chemically to the soil, and moves only when soil is eroded; concern for fertilizer runoff is directed more towards the more soluble nitrates than towards phosphates. Under some conditions, however, such as with frozen sloping fields or with highly organic soils, phosphate runoff may occur, according to the Illinois Pollution Control Board, which is planning to prohibit phosphate application in the first case (frozen fields with more than 5% slope) and to limit it in the second (50 lbs phosphorus/acre/year maximum for soils containing more than 20% organic matter) [12].

DETERGENTS

Phosphates (mainly sodium hexametaphosphate, (NaPO₃)₆) are used as detergent builder because they soften water (by tying up calcium ions) and help to suspend dirt particles, so that they do not precipitate and are readily rinsed away. Standard detergents contain 40% by weight of phosphate. There

is no possibility of recovering it at the place of utilization, and detergents are disposed in municipal sewers. In recognition of the possible deleterious effect of excess phosphate in natural waters, the detergent industry is planning to reduce by 25% the amount of phosphate in detergents [13]. A substitute as effective as phosphates has not yet been found. Conservationists advocate a return to common soap, used in combination with soft water (which can be obtained through household softening devices, such as ion-exchangers) [14]. Detergent phosphates could be recovered in a tertiary treatment of sewage water (see below).

OTHER USES

Phosphates are used as anti-corrosion agents in industrial water systems (mainly as polyphosphates, such as sodium hexametaphosphate) because of their complexing action which prevents the precipitation of iron and manganese oxides and the formation of calcium carbonate crystals. They also form inert coatings of calcium, magnesium, or iron phosphate, which retard the corrosion of iron [15]. Phosphate coatings are also used to prevent steel corrosion in automobiles and appliances. Recycling of phosphates from boiler water blowdown or from steel coating phosphate sludge is still at the laboratory stage. The U.S. Bureau of Mines has developed a process leading to complete phosphate recovery [16].

Phosphates are also used for agricultural insecticides which are more biodegradable than chlorinated ones, and for other lower-volume applications.

FOOD CHAIN PHOSPHATES

The phosphates used as fertilizers are utilized by plants which are consumed as food by men and animals. Part of the phosphorus is used for cell buildup, part is excreted. Dried animal manure contains up to 15% P_2O_5 [17]; runoff waters carry much of this phosphorus to natural waters, especially from high concentration areas, such as feedlots. Man consume phosphates of vegetable and animal origin, and eliminate 1.40 g P_2O_5 with urine and 0.73 g P_2O_5 with feces per capita per day [15] (a total of 940,000 lbs P_2O_5 /day in the U.S.); this phosphate reaches natural waters through the sewers.

Water-Borne Phosphate

The estimated amounts of phosphorus entering the aquatic environment nationally are reported in Table 2 (expressing the consensus of various authors; P values $\times 3 = PO_4$). Of particular interest is the amount introduced with the sewage, both because it is the largest and because it is the only one that can be controlled with relative ease.

Table 2. Phosphorus Entering the Aquatic Environment

<i>Source</i>	<i>Phosphorus (million lbs/yr)</i>
Natural (erosion, decomposition products)	250
Sewage	
detergents	350
excreta	350
Runoff	
cultivated lands	110
livestock areas	200
	1,260

CONTROL OF SEWAGE PHOSPHATE

Raw sewage contains an average of 25 ppm of phosphate (PO_4), 10 ppm of which is suspended, and originates from excreta, and 15 ppm dissolved, as orthophosphate or polyphosphate. Most of the dissolved phosphate originates from detergents [18]. Primary treatment (settling) removes the suspended phosphate; secondary treatment (biooxidation) removes part of the dissolved phosphate, so that a secondary effluent contains about 4 ppm of phosphate [19]. Much raw sewage still reaches natural waters untreated, and therefore it has been calculated [20] that an average of 15 ppm phosphate reaches natural waters from sewage.

Removal of phosphate from municipal wastewaters would require (a) primary and secondary treatment for all sewage effluents, and (b) an additional tertiary treatment for phosphate removal. It has been estimated that a 95% phosphorus removal is required for effective control of eutrophication.

Eliassen and Tchobanoglous [21] reviewed in 1968 the procedures available for removal of phosphate from sewage. Table 3 lists the procedures and their effectiveness. According to a 1970 EPA report [22], chemical precipitation is the only feasible procedure. However, since then new ion-exchange resins designed specifically for phosphate removal have been developed [23], a biological treatment using algal cultures has proved effective [24], and modified activated sludge systems have reached 97% phosphate removal [25].

EUTROPHICATION

Eutrophication is a natural aging process which involves an increase in the biological productivity of a lake (or other body of water) as a result of nutrient enrichment from natural sources. A lake acts as a settling basin, and

Table 3. Comparison of Alternative Phosphorus Removal Methods
(From Reference 21.)

<i>Process</i>	<i>Removal efficiency (%)</i>	<i>Estimated removal cost \$/mil gal</i>	<i>Type of wastes to be disposed of</i>
Conventional biological treatment	10-30	30-100	Sludge
Modified activated sludge	60-80	30-100	Sludge
Chemical precipitation	88-95	10-70	Sludge
Chemical precipitation with filtration	95-98	70-90	Liquid and Sludge
Sorption	90-98	40-70	Liquid and Solids
Ion exchange	86-98	170-300	Liquid
Electrochemical treatment	81-85	4-8 ^b	Liquid and Sludge
Electrodialysis	30-50 ^a	100-250	Liquid
Reverse osmosis	65-95	250-400	Liquid
Distillation	90-98+	400-1000	Liquid
Land application	60-90+	75-150	None

^aRemoval efficiency per single stage.

^bOn power cost only; installation costs unavailable.

the input of organic and inorganic matter eventually leads to the disappearance of the lake itself.

The discharge of excessive amounts of nutrients under man's influence can greatly accelerate the eutrophication process, creating a man-made or "cultural" eutrophication whose most evident effect is the overgrowth of algae, or "algal bloom." Algal growth requires three chief nutrients: carbon dioxide, nitrate, and phosphate. If any one of the three are missing, algal growth can be triggered by supplying it. Thus, depending on the local conditions, any of the three nutrients may be "responsible" for algal overgrowth [14]. However, carbon dioxide and nitrogen may be supplied from the atmosphere. Phosphorus can only be made available by soil erosion or artificial enrichment [26].

Surface waters in unpolluted lakes contain 0.01 ppm phosphate; highly eutrophic lakes may contain 5 ppm [27]; 0.04 ppm is sufficient for rapid algal growth. Due to the settling characteristics of lakes, most of the influent phosphate is retained. For highly eutrophic Lake Erie, it has been estimated that 174,000 lbs of phosphate per day reach the lake, while only 24,000 lbs per day leave via the Niagara River [14]. The difference is due in part to the settling of suspended phosphate, in part to the amount retained by the algal population. Most of the algae die in the winter, and also settle to the bottom. The lake sediment is therefore enriched of 55 million lbs of phosphate per year, mainly immobilized as insoluble iron(III) phosphate or calcium phosphate; however, if the oxygen in the water is depleted, iron(III) is converted to iron(II), which forms soluble salts which remobilize phosphate. Oxygen

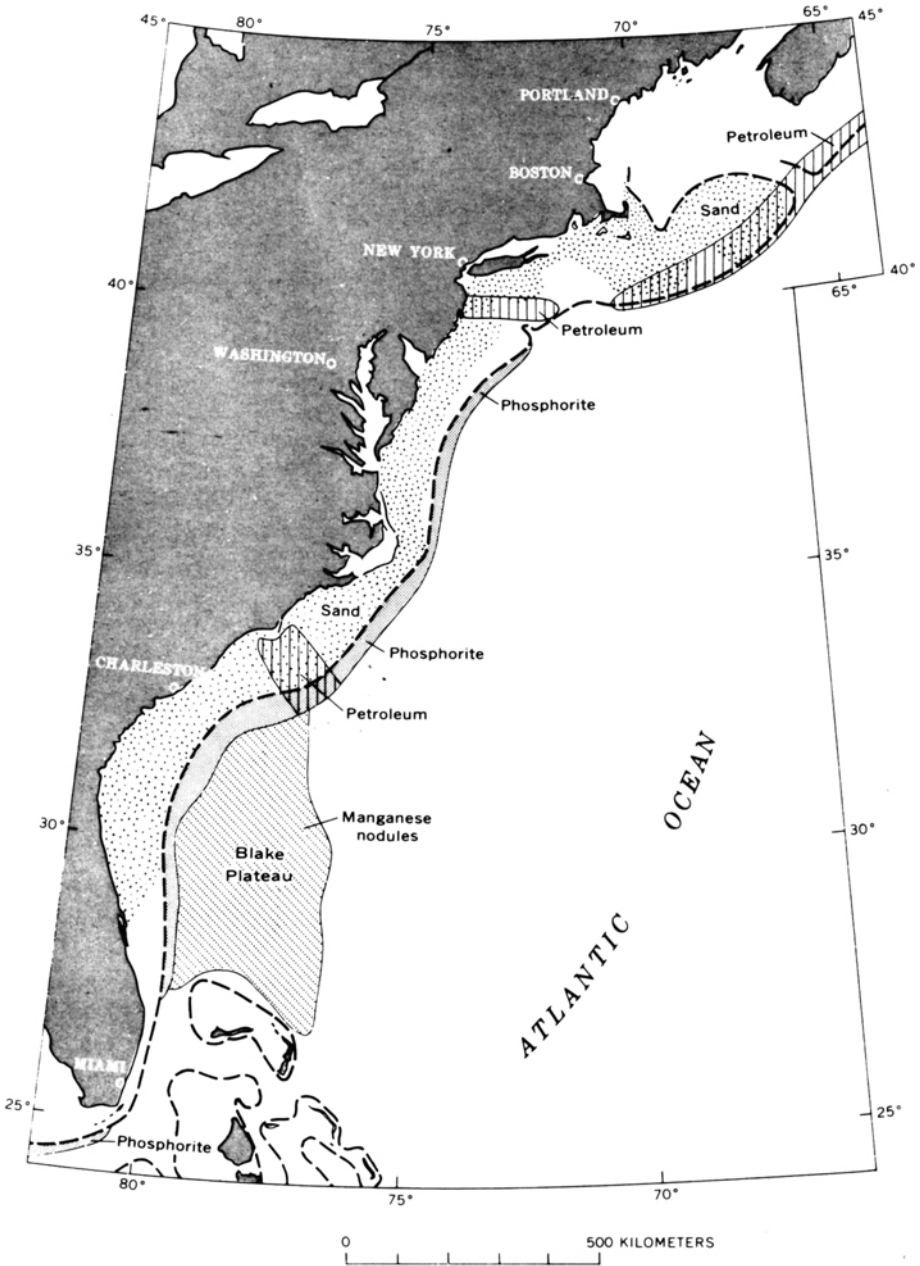


Figure 5. Phosphorite deposits along the U.S. Atlantic Coast. The heavy dashed line is the edge of the continental shelf (from Reference 30).

depletion also causes anaerobic conditions under which microbial release of soluble phosphate is known to occur [28].

OCEAN PHOSPHATE

The ocean environment differs from a lake environment because of the larger volume of water, the unavailability of sediment nutrients, and the large temperature difference between surface water and deep waters.

The ocean as a whole is nearly saturated with phosphate, and an amount equivalent to that brought by rivers is precipitated almost continuously. The phosphate distribution within the ocean is not uniform—deep cold waters contain 0.3 ppm phosphate (PO_4), but warm surface waters contain only 0.01 ppm, or less. Precipitation occurs by inorganic processes such as direct formation of calcium salts or replacement of carbonate by phosphate in calcite (which is converted to apatite). It can also occur by biological process, through formation of organic skeletons or shells which settle to the bottom on death of the organisms.

Oceanic circulation brings phosphate-rich water to the surface in several locations, and phosphate precipitates as the temperature and the pH increase. These nutrient-rich waters support abundant plant and animal life, including large colonies of fish-eating seafowl. The ocean circulation also leads to the formation of extensive phosphorite deposits, especially near the coasts where prevailing winds or currents move surface water away from the coast and create a convective upwelling of deep waters [1]. Large phosphate deposits exist near the Lower California Coast and the Atlantic Coast (Figure 5) [29, 30].

Phosphate as a Global Resource

A diagram of the present phosphate utilization and disposal is shown in Figure 6. The earth's crust contains an average of 0.25% P_2O_5 , concentrated in phosphorite and igneous apatite deposits (phosphate rock). World reserves of phosphate rock were estimated in 1953 to be of the order of 45 billion tons [30]. Since then large deposits have been discovered, and advances in processing technology have made possible to include lower grade deposits in the overall total which is now believed to be in the range of hundreds of billions of tons [1].

The world production totaled 98 million tons in 1966; a geographic breakdown is shown in Table 4 [31]. Of the total amount, about 60% was used for fertilizers, 20% for detergents, and 20% for other uses. As mentioned previously, the present trend is towards lower amounts of phosphate in detergents. If suitable substitutes are found, this application may be discontinued entirely.

The world consumption of fertilizers (phosphate expressed as P_2O_5 ;

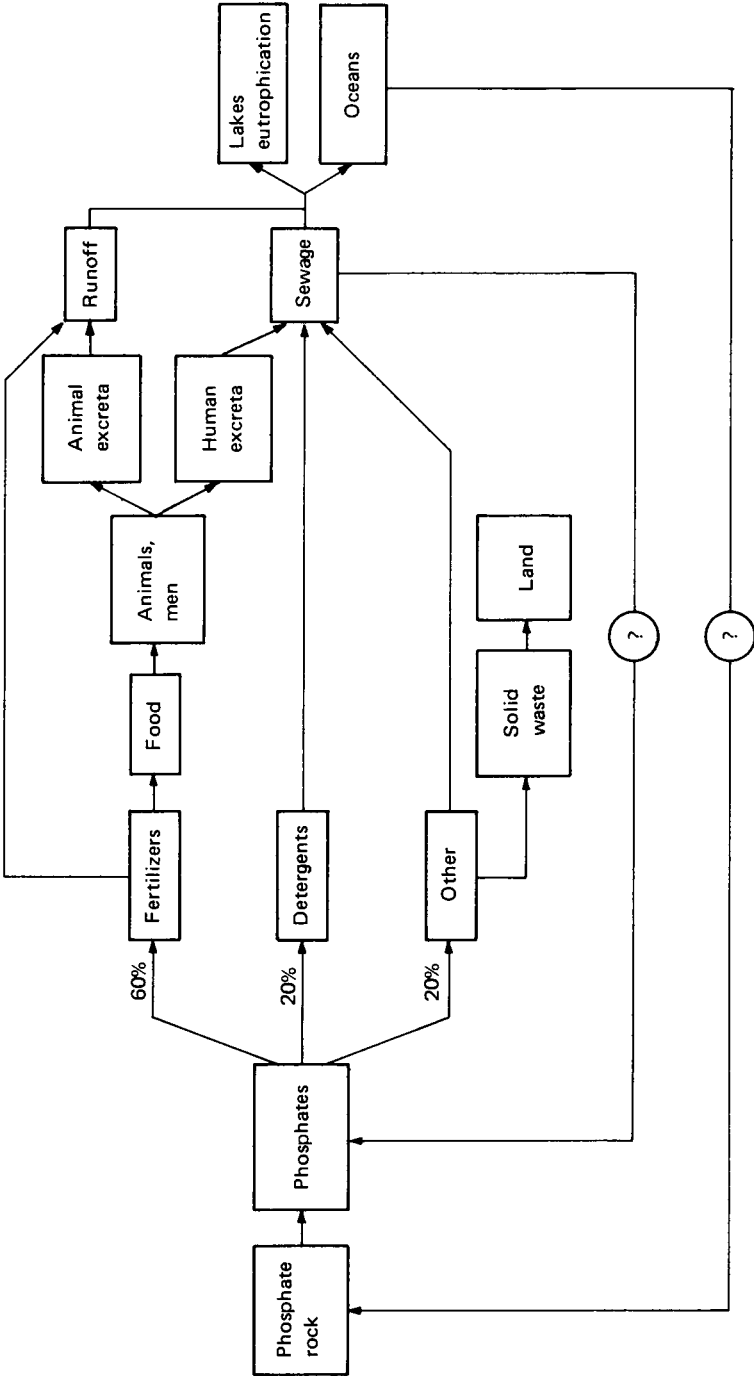


Figure 6. Phosphate utilization and disposal.

Table 4. World Phosphate Rock Production (1964) and Capacity (1970)
(From Reference 31.)

<i>Countries</i>	<i>Unit: thousand tons of material</i>		
	<i>Production 1964</i>	<i>Anticipated capacity by 1970</i>	<i>Possible additional capacity</i>
North America			
United States	23,000	38,000	—
Eastern Europe			
USSR	13,000	25,000	—
Latin America			
Brazil	127	100	—
Curacao	102	100	—
Mexico	33	35	—
Peru	—	—	400
Asia			
Jordan	565	2,000	—
Israel	221	1,700	—
Africa			
Algeria	73	1,000	—
Tunisia	2,700	4,500	—
Morocco	10,095	16,000	—
Senegal	667	1,000	—
Togo	778	1,000	—
UAR	613	3,500	—
South Africa	344	600	—
Spanish Sahara	—	—	10,000
Oceania			
Ocean/Nauru/Makatea	2,560	2,350	—
Christmas	861	800	—
World Total ^a	56,195	97,500	10,400
Mainland China, North Vietnam, North Korea	1,900	2,500	—

^aExcluding Mainland China, North Vietnam, North Korea.

Source: International Superphosphate Manufacturers Association; Council of Scientific Advisers to President Johnson.

phosphate rock contains approximately 30% P_2O_5) in the period 1909-1966 is shown in Table 5 [31]. It is seen that the consumption increased exponentially, with a doubling time of 15 years up to 1960, of 10 years in the 1960-1970 period. The exponential increase is expected to be lower in the seventies [32], with a worldwide demand increasing from 19.8 million metric tons of P_2O_5 in 1971 to 29.3 million metric tons in 1980 [32]. In the last 10 years the U.S. phosphate consumption for fertilizers increased less than that of the world, probably due to the already high consumption in 1960. This is shown in Table 6 [33].

Table 5. World Consumption of Fertilizers 1909-1966
(From Reference 31.)

<i>Years</i>	<i>N</i>	<i>P₂O₅</i>	<i>K₂O</i>	<i>Total</i>
1909-10	568	1,562	785	2,915
1914-15	641	1,654	809	3,104
1919-20	757	1,729	1,070	3,556
1924-25	1,124	2,636	1,641	5,401
1928-29	1,802	3,519	2,374	7,695
1929-30	1,797	3,538	2,384	7,719
1930-31	1,499	2,986	1,959	6,444
1931-32	1,237	2,403	1,508	5,148
1932-33	1,205	2,467	1,549	5,221
1933-34	1,267	2,780	1,956	6,083
1934-35	1,592	2,974	2,281	6,847
1935-36	1,969	3,104	2,432	7,505
1936-37	2,147	3,399	2,707	8,253
1937-38	2,485	3,678	2,960	9,123
1938-39	2,670	3,637	2,904	9,211
1945-46	2,075	3,375	2,100	7,550
1946-47	2,618	4,368	2,677	9,663
1947-48	3,201	5,017	3,104	11,322
1948-49	3,422	5,497	3,540	12,459
1949-50	3,734	5,864	3,994	13,592
1950-51	4,265	6,208	4,514	14,987
1951-52	4,634	6,273	5,006	15,913
1952-53	5,359	6,639	5,392	17,390
1953-54	6,025	7,192	6,053	19,270
1954-55	6,790	7,540	6,260	20,590
1955-56	7,145	7,980	6,780	21,905
1956-57	7,680	8,280	7,170	23,130
1957-58	8,380	8,530	7,420	24,330
1958-59	9,355	9,050	7,915	26,320
1959-60	9,830	9,630	8,225	27,685
1960-61	10,970	9,970	8,500	29,440
1961-62	11,605	10,440	8,670	30,715
1962-63	13,360	11,130	9,280	33,700
1963-64	15,060	12,260	10,060	37,380
1964-65	16,630	14,000	11,100	41,730
1965-66	19,225	14,900	12,200	46,325

Sources: FAO, *Annual Review of Fertilizer Production, Consumption, and Trade*; FAO, *Monthly Bulletin of Agricultural Economics and Statistics*, February 1962; FAO, *Monthly Bulletin of Agricultural Economics and Statistics*, No. 3, Volume 16, March 1967.

Table 6. U.S. Fertilizer Consumption (From Reference 33.)

<i>Thousands of tons</i>	<i>Consumption</i>				<i>Annual Change</i>	
	<i>1971^a</i>	<i>1970</i>	<i>1969</i>	<i>1961</i>	<i>1970-71</i>	<i>1961-71</i>
Nitrogen (N)	7,925	7,459	6,833	3,004	6%	10%
Phosphate (P ₂ O ₅)	4,785	4,574	4,595	2,597	5	6
Potash (K ₂ O)	4,176	4,036	3,866	2,165	4	7
Total	16,887	16,069	15,293	7,766	5%	8%

^aYears ending June 30. Source: Department of Agriculture

Assuming a world reserve of 200 billion tons of phosphate rock, a present world demand of 0.1 billion tons/year, and a demand doubling time of 15 years (approximately 5% exponential growth), the world reserve of phosphate rock would be exhausted in 100 years. A world reserve of 400 billion tons would be sufficient only for 12 more years of supply. According to some sources [34], the exponential growth of fertilizer demand is 7% (10 year doubling time); at this rate, the land reserves of phosphate rock would be exhausted in 75 years. The fertilizer or phosphate experts whose work has been reviewed apparently are not familiar with the nature of exponential growth. They all believe that the land reserves of phosphate will last "for many years to come." The only dissonant voice so far has come from the Inter-American Institute of Ecology [35]; according to their calculations, phosphate reserves will be exhausted in 60 years.

A factor to be considered is that there is a limit to the use of fertilizer—namely, the area of arable land. The extreme case would involve application of fertilizer to the whole world land area (32 billion acres) at a rate suggested by agricultural experts. According to the Sulphur Institute [36], the 1.1 billion acres presently farmed in the U.S. should be fertilized with 10 million tons of P₂O₅ per year (twice the present rate). Using this rate of application, approximately 300 million tons of P₂O₅ per year would be required worldwide, or 1 billion tons of phosphate rock. If fertilizers would still use up only 60% of the phosphate production, this worldwide demand would be 1.66 billion tons of phosphate rock per year. With a 7% exponential increase in demand, this rate would be reached in 45 years. Assuming a constant demand for phosphate fertilizers after that date, the worldwide reserve of 200 billion tons would last a further 45 years.

It is doubtful that the entire world land area will ever be cultivated, but the figures show that the results obtained using exponential increases are not out of place.

What are the alternatives? Clearly the first action should be to discontinue

the use of phosphate in detergents as soon as possible. This would free additional phosphate for fertilizer use, greatly reduce eutrophication, and save the electric energy required for the phosphorus furnace reduction process. The rates of application of phosphate fertilizer should also be reviewed, and the minimum amounts required for high crop yields should be applied.

It is also imperative to chart and plan to develop the underwater ocean phosphate deposits. The ocean reserves of phosphate have been estimated at 240 billion tons of P_2O_5 , increasing by 28 million tons every year [27]. Extensive phosphorite deposits have been discovered, for example, in the area offshore San Diego. Their development has not materialized because costs were not competitive with land-based phosphate deposits.

Phosphates can also be recycled from sewage sludge. The sludge may be applied directly to the fields or decomposed by composting with solid waste. If tertiary sewage treatments for phosphate removal were installed, the extracted phosphate would be present in a concentrated form and could be recovered. A process using a combination of mild heating and vacuum to cause precipitation of ammonium phosphate (which can be used directly as fertilizer) has been tested at the pilot plant level by the W. R. Grace Co. [37]. A more radical procedure would be the replacement of water-flushed toilets with chemical toilets containing dilute sulfuric acid. The acid would solubilize organic phosphates and destroy the bacteria.

REFERENCES

1. V. E. McKelvey, "Phosphate Deposits", U.S. Geol. Survey Bull. 1252-D, 1967.
2. N. L. Nemerow, "*Liquid Waste of Industry*", Addison-Wesley Publ., Reading, Mass., 1971.
3. H. B. Siems, in "Fertilizer Technology and Resources", K. D. Jacobs, editor, Academic Press, New York, 1953.
4. Agricultural Research Depts., U.S.D.A., T.V.A., "Superphosphate", U.S. Government Printing Office, Washington, D.C., 1964.
5. H. F. Lund, "*Industrial Pollution Control Handbook*", McGraw-Hill Publ., New York, 1971.
6. Battelle Memorial Inst., "Inorganic Fertilizer and Phosphate Mining Industries—Water Pollution and Control", Nat. Tech. Inf. Center (NTIS) Report number PB-206 154, U.S. Government Printing Office, Washington, D.C., 1971.
7. J. R. Van Wazer, "*Phosphorus and Its Compounds*", Vol. II. Interscience Publ., New York, 1961.
8. Nat. Ind. Polln. Control Council, "Fertilizers and Agricultural Chemicals", U.S. Government Printing Office, Washington, D.C., 1971.
9. Nat. Air Polln. Control Adm., "Atmospheric Emissions from Wet-Process Phosphoric Acid Manufacture", Report # AP-57, U.S. Government Printing Office, Washington, D.C., 1970.

10. Anon., "Waste Control in a Fragile Environment", *Env. Sci. and Technol.*, 6, 980-2, 1972.
11. S. L. Tisdale and D. L. Rucker, "Crop Response to Various Phosphates", The Sulphur Institute, Washington, D.C., 1964.
12. Anon., "Controversy Builds over Fertilizer Runoff", *Chem. and Eng. News*, p. 17-8, Jan. 10, 1972.
13. Nat. Ind. Polln. Control Council, "Detergents", NTIS Report # COM-71-50244, Springfield, Va., 1970.
14. B. Commoner, "*The Closing Circle*", A. A. Knopf Publ., New York, 1971.
15. T. R. Camp, "*Water and Its Impurities*", Reinhold Book Co., New York, 1963.
16. R. F. Waters et al., "Recovery of Phosphates and Metals from Waste Phosphate Sludge by Reduction-Sinter Process", NTIS Report number PB-201 891, Springfield, Va., 1971.
17. K. M. Mackentun, Nitrogen and Phosphorus in Water, an Annotated Bibliography", U.S. Government Printing Office, Washington, D.C., 1965.
18. F. A. Ferguson, "A Nonmyopic Approach to the Problem of Excessive Algal Growths", *Env. Sci. and Technol.*, 2, 188-93, 1968.
19. R. D. Grundy, "Strategies for Control of Man-made Eutrophication", *Env. Sci. and Technol.*, 5, 1184-8, 1971.
20. J. J. Morgan, "Equilibrium Calculations and Preliminary Observations for Metal Ions in Wastewater Effluents", Seminar presented at the University of Southern California, Los Angeles, Dec. 14, 1972.
21. R. Eliassen and G. Tchobanoglous, "Removal of Nitrogen and Phosphorus," Twenty-third Purdue Ind. Waste Conf. Proceedings, p. 35, 1968.
22. J. J. Convery, "Treatment Techniques for Removing Phosphorus from Municipal Wastewaters", U.S. Government Printing Office, Washington, D.C., 1970.
23. B. I. Loran et al., "Investigation of a New Phosphate Removal Process", U.S. Government Printing Office, Washington, D.C., 1970.
24. D. E. Greer and C. D. Ziebell, "Biological Removal of Phosphate from Water", *J. Wat. Polln. Control Fed.*, 44, 2342-8, 1972.
25. Anon., "Phosphate Removal", *Chem. and Eng. News*, p. 27, Nov. 1, 1972.
26. G. F. Lee, "Eutrophication", NTIS Report # PB-197 697, Springfield, Va., 1970.
27. W. Stumm and J. J. Morgan, "*Aquatic Chemistry*", Wiley-Interscience Publ., New York, 1970.
28. C. W. Randall et al., "Microbial Release of Soluble Phosphate in an Activated Sludge Environment", NTIS Report # PB-202 583, Springfield, Va., 1971.
29. P. Cloud, Ed., "*Resources and Man*," W. H. Freeman and Co., San Francisco, Ca., 1969.
30. K. O. Emery, "Some Potential Mineral Resources of the Atlantic Continental Margin", U.S. Geol. Survey Prof. Paper 525-C, Washington, D.C., 1965.
31. Anon., "Supply and Demand Prospects for Fertilizers in Developing

- Countries”, Org. for Economic Cooperation and Development (OECD), Paris, France, 1968.
32. Anon., “World Fertilizer Use to Grow Less Rapidly”, *Chem. and Eng. News*, p. 10, Sep. 18, 1972.
 33. Anon., “U.S. Fertilizer Consumption Up 5% in 1971”, *Chem. and Eng. News*, p. 14, June 5, 1972.
 34. D. L. Meadows et al., “*The Limits to Growth*”, Universe Books, New York 1972.
 35. Anon., “Ecology: Getting Out of Hand”, *Chem. and Eng. News*, p. 9, Oct. 11, 1971.
 36. J. D. Beaton and S. L. Tisdale, “Potential Plant Nutrient Consumption in North America”, The Sulphur Institute, Washington, D.C., 1969.
 37. M. G. Dunseth et al., “Ultimate Disposal of Phosphate from Wastewater by Recovery as Fertilizer”, (NTIS Report number PB-196 739), U.S. Government Printing Office, Washington, D.C., 1970.