

**INDUSTRIAL METABOLISM
AND THE GRAND NUTRIENT CYCLES**

by

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**96/54/EPS
(Revised version of 92/64/EPS)**

This working paper was published in the context of INSEAD's Centre for the Management of Environmental Resources, an R&D partnership sponsored by Ciba-Geigy, Danfoss, Otto Group and Royal Dutch/Shell and Sandoz AG.

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Printed at INSEAD, Fontainebleau, France.

INDUSTRIAL METABOLISM AND THE GRAND NUTRIENT CYCLES

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October 1992
Revised September 1996

Abstract

There are four major elements that are required by the biosphere in significantly greater quantities than they are available in nature. These four are carbon (C), nitrogen (N), sulfur (S) and phosphorus (P). Natural cycles have evolved over billions of years to recycle these elements in chemically available forms. (Hydrogen and oxygen, the other two major ingredients of organic materials, are not scarce in the earth's crust). These natural cycles are driven by photosynthetic processes utilizing exergy influx from the sun. Interruption or disturbance of these natural cycles as a consequence of human industrial/economic activity would adversely affect the stability of the biosphere.

Solar Exergy: Driver of all the Cycles

Exergy inflows from the sun to the earth must be balanced by exergy outflows (i.e., IR heat radiation), exergy gains by or losses from terrestrial inventories and exergy losses from biospheric and economic processes. Stored exergy on the earth consists of biomass, fossil fuels and other potentially reactive minerals and compounds, including reduced forms of metals, reduced forms of sulfur and atmospheric oxygen and nitrogen. In a steady state condition, the difference between solar exergy inflows and IR exergy outflows is available to do work i.e. to drive terrestrial atmospheric, hydrospheric, geospheric and biospheric processes. Among these natural processes, only the biosphere extracts exergy from the solar influx and accumulates it in biomass, some of which is permanently sequestered in sediments and sedimentary. In short, whereas the physical processes merely "consume" exergy (being driven by it), the biological processes also accumulate and store some of it.

Some interesting implications follow from the exergy balance condition. For instance, consider the glacial periods, when the earth's temperature dropped 5 or 6 degrees Celsius, or about 2%, for reasons not yet fully understood. The outward efflux of exergy in the form of IR radiation — which depends on the fourth power of the earth's effective surface temperature — correspondingly decreased by around 7%. Part of this could have been due to the greenhouse effect operating in reverse. (It is known that CO₂ levels and temperature levels tracked each other rather closely). Snow cover over the glaciers must have significantly increased the earth's albedo, thus reducing the solar exergy flux absorbed in the atmosphere or at the earth's surface. If the solar exergy influx had not changed, it would follow that the exergy available for driving natural processes on the earth's surface must have *increased* quite significantly in consequence. Yet a lower surface temperature, with glaciers covering significant land areas, must have also reduced the ambient biomass and consequently the rate of photosynthesis. The only possible way of consuming excess exergy would have been to drive stronger atmospheric circulation, more violent storms and stronger ocean currents.

Now suppose industrial activities must be added to the equation. What happens when greenhouse warming increases the surface temperature? One immediate effect must be a higher exergy outflow from earth (as IR radiation). Another immediate effect is likely to be global warming, which should (other factors remaining equal) increase evapo-transpiration and the level of photosynthetic activity and the exergy consumed for plant metabolism. A third immediate effect of warming would seem to be to increase the evaporation of water from the oceans. The last two effects, taken together, would raise humidity, cloud cover and precipitation. The humidity effect would tend to increase greenhouse warming, whereas increased cloud cover would tend to increase the albedo and cause compensatory cooling. The other consequence of increased evaporation is a matching increase of precipitation. The important question: is where will it occur?

There is normally a net transport of moisture from the oceans to the land, compensated by river flows back to the oceans. Net evaporation cools the oceans, while condensation warms the land. This influences the land-water temperature gradient, which drives the onshore/offshore winds. This part of the system is self-adjusting: if the land cools too much relative to the ocean, onshore winds bring in moisture, and conversely. Unless compensated for by some other phenomenon not yet taken into account — for instance decreased high level cloud cover, and reduced albedo — the consequences of surface warming (re-radiation and increased evaporation) *must* leave less solar exergy available to drive other atmospheric and ocean processes, notably the jet streams and the ocean currents. Presumably this explains why general circulation models (GCM's) predict that global warming will affect the polar regions most drastically, in the short run, while leaving the equatorial regions relatively unaffected.

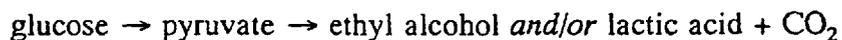
One consequence would be accelerated melting of polar ice. This would suddenly increase the influx of fresh water into the Gulf Stream as it flows through the North Atlantic. Fresh water is less dense than salt water (made saltier due to evaporation from the surface of tropical oceans). Normally when the salty — and dense — Gulf stream water reaches a sufficiently northern latitude, and cools off sufficiently, it sinks into the depths where it returns back to the southern seas. An influx of fresh water at the surface would interfere with this sinking and accelerate the warming of the polar region.

Apart from atmospheric and oceanic implications, the advent of industrial activity has altered the pre-industrial exergy balance. On the one hand, humans now dispose of a small but increasing direct share of available solar exergy "current income", mainly through agricultural use and hydrological engineering. In addition, humans are consuming exergy capital that was accumulated through past photosynthesis and sequestration. Indeed, it is the latter (mainly combustion of fossil fuels) that is the primary cause of climate warming and other environmental threats.

The Nutrient Cycles

The nutrient cycles, as they exist today, are consequences of bio-geological evolutionary processes. An observer from another galaxy might well regard these cycles as the most significant of that evolution. In fact, nutrients were *not* recycled during the earth's early evolutionary history. It should be noted that the atmosphere of the early earth certainly contained no free oxygen, and the earth's crust certainly contained no free carbon or sulfur. It is currently thought to have consisted of carbon dioxide, nitrogen and water vapor.

The earliest known forms of life, about 3.5 billion years ago, were single-celled prokaryotic organisms — essentially, protobacteria — which obtained the energy needed for their metabolic processes from a supply of simple organic molecules, like glucose. Nobody knows the origin of this primitive food supply. It may have been synthesized on earth by some unknown abiotic process. Or, it may have been created originally in cold interplanetary space. The key metabolic process of the first proto-bacteria was *fermentation*, schematically represented by the sequence:



Since there was no mechanism for replacing the original food supply, this population was not stable, or sustainable. Carbon was not recycled.

Fortunately, after the passage of half a billion years or so, the problem was solved by an evolutionary "great leap forward". This was the appearance of the first prokaryotic *photobacteria*. These were organisms capable of utilizing the energy of sunlight to create glucose from carbon dioxide. However, there was a waste product from this reaction, namely oxygen. Oxygen was highly toxic to early forms of life. However, oxygen did not accumulate in the atmosphere at first. For a long time it was removed from circulation almost as fast as it was formed. Oxygen reacted with soluble ferrous iron and/or sulfides to form insoluble ferric iron and calcium sulfates. These materials were deposited on the ocean floor as hematite (iron ore) and gypsum, respectively. We mine these ores today.

However, life on planet Earth would have self-destructed sooner or later from oxygen poisoning if another evolutionary development had not occurred. This was the appearance of first oxygen tolerant photosynthesizers. These were cyano-bacteria (2 billion years ago). The

next important evolutionary step (1.5 billion years ago) was even more radical: it was an extension of the fermentation process to oxidize the organic waste products (e.g. lactic acid) to yield carbon dioxide, plus additional metabolic energy. This new process is *aerobic respiration*. As it happens, aerobic respiration is 18 times more efficient (in energy terms) than fermentation. Thus, the respirators (eukaryotes) eventually out-competed fermenters in aerobic environments. The fermenters have been relegated to anaerobic environments, such as lake bottoms, sediments and swamps.

The advent of aerobic respiration created a route for the closure of both the oxygen and carbon cycles, for the first time. The evolutionary history of the nitrogen, sulfur and phosphorus cycles is less well-known. However, all of the grand nutrient cycles did evolve, over billions of years, to a relatively stable state. All of them can be characterized, in Prigogine's terms, as "dissipative systems" that are far from thermodynamic equilibrium [e.g. Nicolis & Prigogine 1977]. Thermodynamically they are all oxidation-reduction cycles involving a number of biologically driven steps.

Overview of the Grand Nutrient Cycles

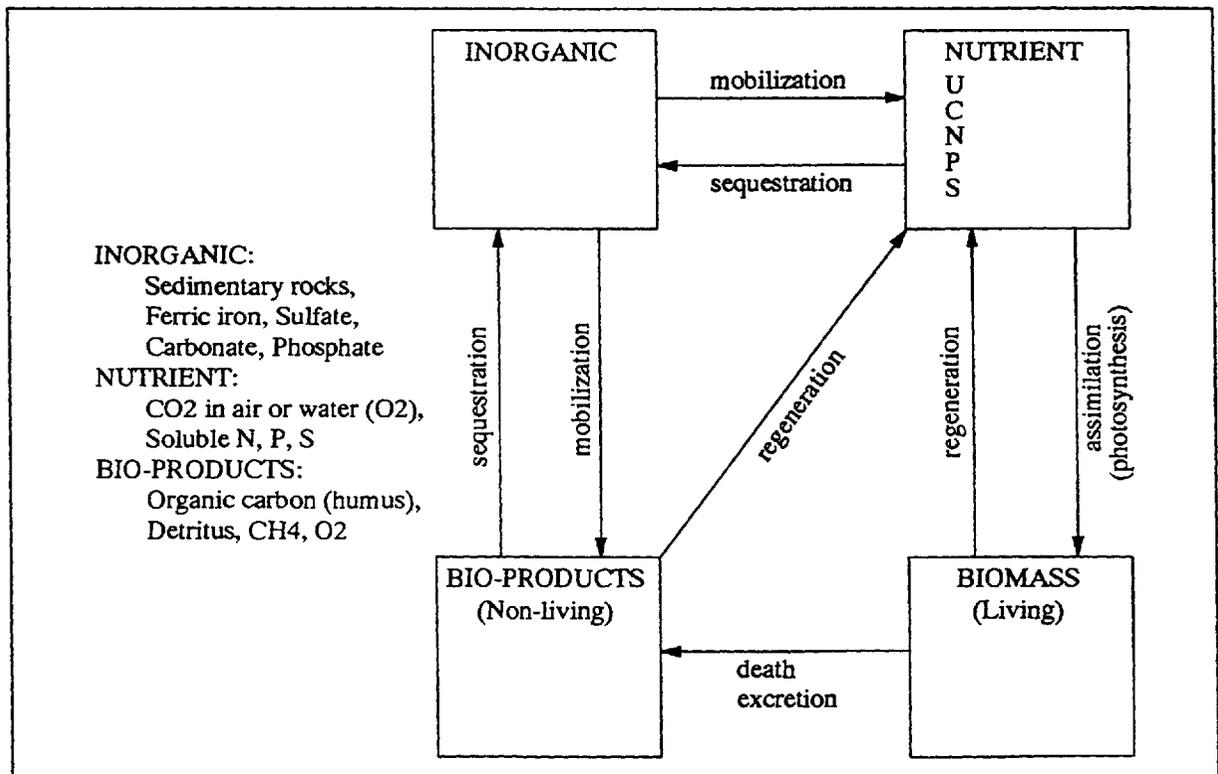


Figure 1. 4-box scheme for bio-geo-chemical cycles

It is convenient for purposes of exposition to describe the grand nutrient cycles in functional terms, as illustrated by Figure 1. The cycles differ markedly in terms of the physical and chemical form of the major inorganic reservoir, and the mechanisms for transfer from one reservoir to another. When an element passes from the bio-unavailable inorganic reservoir to the bio-available reservoir it is said to be *mobilized*. In the case of nitrogen, mobilization essentially consists of splitting the di-nitrogen N₂ molecule, which is quite stable. When a nutrient moves in the reverse direction it is *sequestered*. (In the case of carbon, the

term is also used in connection with the accumulation of carbon or carbon dioxide in a reservoir from which CO₂ cannot reach the atmosphere). A nutrient can pass from an organic reservoir (e.g. dead plant material) to an inorganic reservoir by *decomposition* or (in the case of nitrogen) bacterial *denitrification*.

There are really two sub-cycles. The first is an exchange of the nutrient element between a bio-unavailable reservoir and a bio-available reservoir. For instance, in the case of carbon, there are two bio-unavailable forms. One is the sedimentary calcium and magnesium carbonates (limestone, dolomite), and the other is reduced carbon (kerogen) also in sediments and sedimentary rocks such as shales. The bio-available (nutrient) form of carbon is the dissolved bicarbonate ion (HCO₃⁻) in water or atmospheric carbon dioxide. In the case of nitrogen, the bio-unavailable reservoir is atmospheric di-nitrogen (N₂) while the bio-available forms constituting the nutrient pool are dissolved nitrates (NO₃⁻) or ammonium (NH₄⁺) ions.

In the case of sulfur, there are, again, two major reservoirs. The bio-unavailable reservoir consists of insoluble sulfates (e.g. gypsum) and buried metallic sulfides (e.g. pyrites). The bio-available reservoir consists of sulfur-containing organic compounds. In the case of phosphorus, the main bio-unavailable reservoir is the mineral apatite (Ca₅(PO₄)₃OH). Again, the bio-available reservoir consists mainly of organic materials.

Table I: Nutrient Reservoirs Participating in Global Cycles*

<i>Nutrient/Stable form</i>	<i>Atmo- sphere</i>	<i>Hydro- sphere</i>	<i>Lithosphere</i>	<i>Terrestrial Biosphere</i>	<i>Marine Biosphere</i>
Carbon (Pg)					
Carbonate			10 ⁷		
CO ₂	730				
Organic (CH ₂)				560	2
Fossil organic (kerogen)			10 ⁶		
Carbonates (CO ₃ ⁻ , HCO ₃ ⁻)		40,000			
Nitrogen (Tg)					
Elemental (N ₂)	3.8*10 ⁹	2*10 ⁷			
N ₂ O	1800				
Organic (amines, etc.)		} 20,000			
Fossil organic				7500	600-1000
Nitrate (NO ₃ ⁻)			} 1.4-5.7*10 ¹⁰		
Sulfur (Tg)					
SO ₂	4.8				
Sulfides (pyrite)			1.3*10 ⁷		
Sulfuric acid (H ₂ SO ₄)					
Organic		} 1.3*10 ⁹		760	7
Fossil organic					
Sulfate (SO ₄ ⁻)		0.3*10 ⁹	7.4*10 ⁹		
Phosphorus (Tg)					
Phosphate Rock			1.1*10 ⁵		
Phosphoric acid		80,000			
Organic				300-600	10-140
Sediments		0.84*10 ⁹			

* Excluding elements in igneous rock

Sources: [Smil 1991; Husar & Husar 1991; Kasting & Walker 1992]

Table I shows the (approximate) quantities of C, N, S, P in the various reservoirs. Table

II shows the ratios of C, N, P in some of the major reservoirs.

Apart from reservoirs, it is important to identify carriers. For carbon there are two main gaseous carriers: carbon dioxide (CO_2) and methane (CH_4). The water-soluble form of carbon is bicarbonate (HCO_3^-), which is also a carrier. For nitrogen the main gaseous carriers are nitrogen oxides (NO_x) and ammonia (NH_3); most ammonium compounds and nitrates are soluble in water, but the main aqueous form is nitrate (NO_3^-). In the case of sulfur, the inorganic gaseous media are hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2) and dimethylsulfide ($\text{DMS} = (\text{CH}_3)_2\text{S}$) and sulfur dioxide (SO_2); the main aqueous form is sulfate ($\text{SO}_4^{=}$), but DMS is also quite soluble in water. The only phosphorus carriers are phosphate ions PO_4^- . (The aqueous form is phosphoric acid (H_3PO_4).)

Table II: Ratios of C, N, & P in Various Reservoirs

	C	N	P
Terrestrial vegetation ^(a)	800	1×10^7	1
Marine plankton ^(b)		16	1
Soil		2	^(c) 1
Sediment		15	1
Anthropogenic ^(d)		15	1

Source: [Stumm 1977, Table 3, p. 268]

(a) [Deevey 1970]

(b) [Redfield *et al* 1963]

(c) Including insoluble P; if only soluble P is included, the C:P and N:P ratios are more than 2 orders of magnitude higher.

(d) Assuming C mobilized by FF combustion; N mobilized by industrial fixation (fertilizer) and NO_x due to combustion; P mobilized by phosphate rock mining.

The second sub-cycle is an exchange between the bio-available nutrient reservoir and living organisms themselves (which constitute a secondary reservoir of the nutrient). The reverse transfer, by decomposition or mineralization, has already been mentioned. In the case of carbon the conversion of CO_2 to its primary biological form (ribose, a kind of sugar) is accomplished by photosynthetic organisms. Most of the other transfers in this subcycle are carried out by specialized bacteria or by enzymes within cells. For instance, nitrogen in living (or dead) organisms is normally in the amine group ($-\text{NH}_2$). A few free-living bacteria — notably *Rhizobium* — and some anaerobic cyanobacteria and yeasts have the ability to split the dinitrogen molecule and *fix* nitrogen in a bio-available form.

Aerobic bacteria require oxygen for metabolic purposes. The usual metabolic process is respiration, in which organic material of the general form (CH_2O) is oxidized by molecular oxygen from the atmosphere to CO_2 and H_2O . If atmospheric oxygen is not available, bacteria will obtain it from other molecular sources. In order of decreasing preference (as measured by a quantity called "redox potential"), these sources — termed "electron acceptors" — are: NO_3^- , MnO_2 , $\text{Fe}(\text{OH})_3$, and $\text{SO}_4^{=}$. Lacking any of these oxygen-containing molecules, some anaerobic bacteria can also break the CH_2O molecule directly, yielding CO_2 and methane (CH_4). Carbon dioxide and water are the main products in every case, but other by-products are generated. For instance, the process of denitrification yields N_2 or N_2O , desulfonation yields H_2S , and so on. These are the gases that transfer nutrients between marine and terrestrial reservoirs.

In principle, anaerobic bacteria could also extract oxygen from the phosphate radical PO_4 ,

yielding a gaseous compound, phosphine (PH₃). However, if phosphine is produced it would be re-oxidized very rapidly in today's atmosphere, which limits the possibilities for transport of phosphorus in gaseous form over significant distances.

If it is tempting to compare the pre-industrial nutrient "cycles" (C, N, S) with the current fluxes, on the assumption that these three cycles were, or very near, a steady-state in pre-industrial times. Steady-state, in this context, means that each of the major reservoirs remains essentially constant or fluctuates within narrow limits. Inputs and outputs of each species to each reservoir must exactly balance (on average) any chemical transformations from one species to another in a steady-state condition. By this straightforward test, as will be seen, none of the grand nutrient cycles is in steady-state now. However, it seems that the grand cycles are seldom in balance for long, if ever, thanks to geological processes such as continental drift, uplifts, episodic vulcanism and ice ages that occur over geological time scales. Thus, it can be quite misleading to compare the current state of imbalance with a hypothetical balance condition.

Brief descriptions of the main cycles follow.

The "Slow" Carbon Cycle

The major inorganic reservoir of carbon (*Table I*) is sedimentary carbonate rocks, such as limestone or calcite (CaCO₃) and dolomite (CaMg(CO₃)₂). This reservoir contains more than 10⁵ times more carbon than the atmosphere and the biosphere together. These reservoirs participate in a "slow" (inorganic) cycle, in which, carbon dioxide from the atmosphere is taken up by the weathering of silicate rocks in a reaction that can be summarized by



The calcium, magnesium and bicarbonate ions, as well as the dissolved silica, in the surface waters are carried to the oceans. There the dissolved calcium, silica, carbonate and bicarbonate are either precipitated inorganically or picked up by marine organisms and incorporated into their shells as calcium carbonate and opal¹. The calcium and carbonate part of the marine system can be summarized as:



In due course the inorganic precipitates and shells drift down to the ocean floor as sediments, eventually being converted by heat and pressure into limestone, chalk and quartz. The sum of the two reactions is



The observed rate of calcium carbonate deposition would use up all the carbon dioxide in the oceans in about 400,000 years.

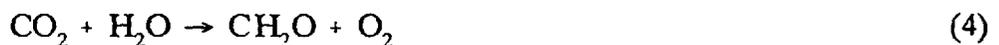
However, there is another chemical reaction that occurs at high pressures and temperatures. This reaction reverses the direction of reaction (3) and reconverts sedimentary calcium and/or magnesium carbonate rocks (mixed with quartz) into calcium or magnesium

silicate, releasing gaseous CO₂. This process occurs when carbonate sedimentary rocks are subducted into the earth's molten mantle, due to tectonic action in the earth's crust. The CO₂ is then vented through volcanic eruptions or hot springs. Weathering rates are relatively easier to measure [Holland 1978; Berner *et al* 1983] compared to outgassing rates [Berner 1990; Gerlach 1991]. But insofar as the data is available, the two rates (CO₂ uptake and emission) appear to agree within a factor of two [Kasting & Walker 1992]. The fact that agreement is not closer is an indication of the fact that much remains to be learned about the details of these bio-geochemical processes.

The silicate weathering rate is directly dependent on climate conditions. A buildup of CO₂ in the atmosphere would lead to greenhouse warming. This increases the rate of evaporation (and precipitation) of water, thus accelerating the weathering process, which removes CO₂ from the atmosphere. This would eventually halt the temperature rise. In principle, then, there is a somewhat crude geological mechanism that would tend to keep the silicate weathering rate roughly equal to the volcanic outgassing rate, over very long time periods. If the atmospheric CO₂ level rises, due to abnormal volcanic activity, there will be an increase in the rate of weathering and CO₂ uptake. Conversely, if the CO₂ level is dropping, so will the temperature and the weathering rate.² In fact, it is asserted by some geologists that the inorganic carbon cycle is sufficient to explain the major features of paleoclimatic history [Holland 1978].

The "Fast" Carbon Cycle

The geochemical response mechanisms described above are much too slow to account for the strong observed correlation between climate and atmospheric CO₂ levels over much shorter periods. These are part of the "fast" carbon cycle, which is biologically controlled. The observed seasonal cycle of atmospheric CO₂ is an obvious short-term effect of the biosphere. Photosynthetic activity in the spring and summer in the northern hemisphere brings about a measurable reduction in the atmospheric CO₂ concentration. Actually, CO₂ is biologically transformed by photosynthesis into sugars and cellulose, with the generic formula CH₂O, viz.



Aerobic respiration is the reverse of carbon fixation. On a longer time-scale, CO₂ fertilization of terrestrial vegetation is a factor (along with temperature) tending to maintain atmospheric CO₂ at a constant level. Rising atmospheric carbon dioxide directly enhances the rate of photosynthesis, other factors being equal.³ It also causes climate warming, and increased rainfall, both of which further enhance the rate of plant growth, subject to the availability of other nutrients, water, etc.

However, the organic carbon cycle cannot be understood in terms of the biochemistry of photosynthesis alone. Nor is all sedimentary carbon in the form of carbonates. There is a significant reservoir of reduced organic carbon (kerogen), buried in sediments, some of which has been aggregated by geological processes and transformed by heat or biological activity to form coal, petroleum and (possibly) natural gas.⁴ Of course, it is the geologically concentrated sedimentary hydrocarbons that constitute our fossil fuel resources and which are currently being re-converted to CO₂ by combustion.

The Methane Sub-Cycle

Methane (CH₄) has its own sub-cycle. In any anaerobic environment⁵ — including the guts of cellulose-ingesting animals such as ungulates and termites — organic carbon is broken down by bacteria. The methane is generated according to the reaction:



In sediments, these anaerobic bacteria produce "swamp gas" (while the organic nitrogen and sulfur are reduced to ammonia and hydrogen sulfide). In the stomachs and intestines of grazing animals such as cattle and sheep, or termites, the methane is excreted by belching. At least half of all buried organic carbon is recycled to the atmosphere by one or the other of these mechanisms. The methane in the atmosphere is gradually oxidized, via many steps, to CO₂. It is not recycled biologically, as such. However methane is a very potent greenhouse gas, much more so than CO₂. Thus, any mechanism that increases that rate of methane production by anaerobic bacteria will have a pronounced impact on climate, *ceteris paribus*. For instance, the expansion of wet rice cultivation in the orient, together with the spread of cattle and sheep husbandry worldwide, constitute a significant anthropogenic interference in the methane cycle.

The Carbon-Cycle as a Whole

The carbon cycle as a whole is summarized in *Figures 2 and 3*. The carbon cycle is not now in balance. (Whether it was truly balanced in pre-industrial times is debatable [e.g. Sundquist 1993]). In any case, the carbon dioxide level of the atmosphere has been rising sharply for over a century. Anthropogenic extraction and combustion of carbonaceous fuels, together with deforestation to clear land for agriculture, have contributed significantly to altering the atmospheric CO₂ balance. About 5% of total CO₂ emissions from the land to the atmosphere are anthropogenic [Bolin 1986]. The CO₂ concentration is now approaching 360 ppm, more than 25% above the pre-industrial level (estimated to be 280 ppm). The rate of increase is about 0.4% per year. As of 1990 approximately 5.4 Pg/yr of carbon was being converted to CO₂ by combustion processes and transferred from underground reservoirs of reduced carbon to the atmosphere. A further 1.6 Pg/yr is attributed to tropical deforestation, for a total of 7 Pg/yr [Stern *et al* 1992, Table 3.2].

Roughly half of this excess anthropogenic flux, or 3.5 Pg/yr, is known to be accumulating in the atmosphere. At first glance, it would appear that the remainder must be accumulating either in the oceans or in terrestrial biomass. Although it has been assumed until recently that the ocean must be the ultimate sink [e.g. Peng *et al* 1983], there is increasing evidence that the known atmosphere-ocean transfer mechanisms cannot account for all the "missing" carbon [Tans *et al* 1990; Schlesinger 1991; Sundquist 1993]. Some oceanographers have suggested that the estimates of carbon lost from land may be too high or that the rate of photosynthesis by the remaining vegetation — especially northern forests — may be stimulated by higher atmospheric CO₂ concentrations, climatic warming and/or nitrogen fertilization (from NO_x emissions and deposition of nitrates).

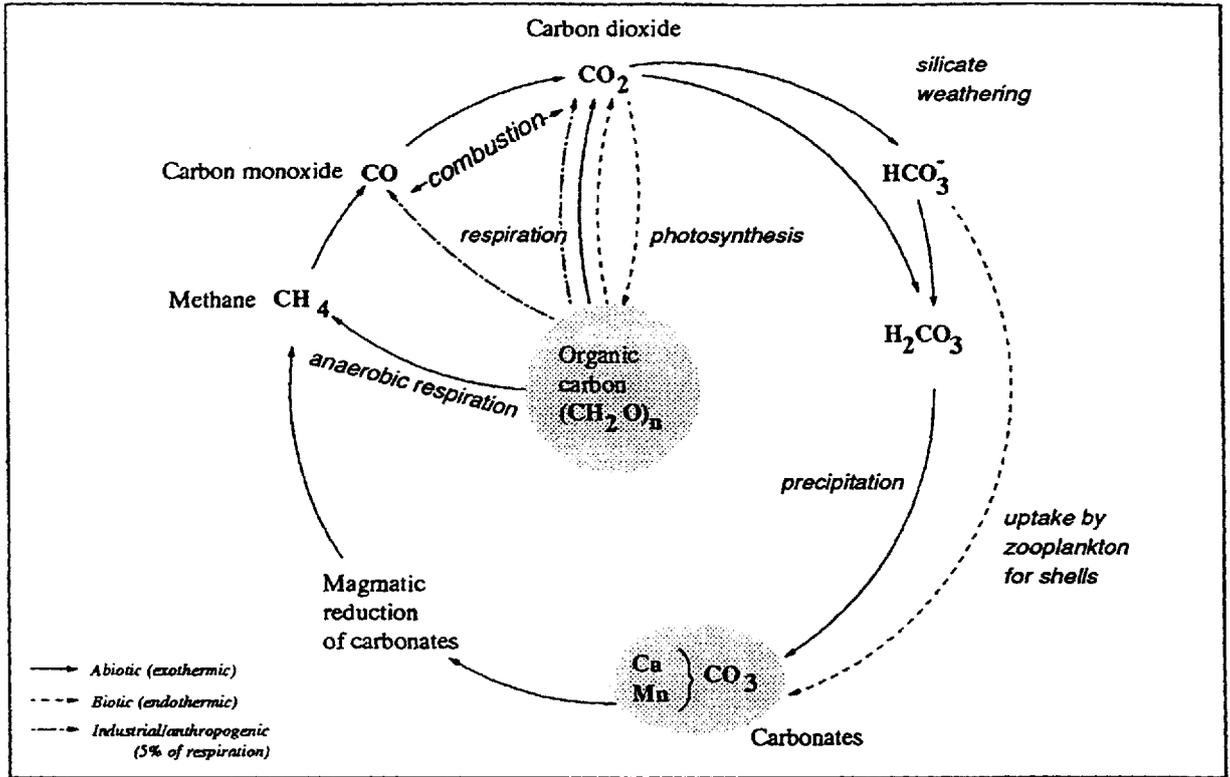


Figure 2. Carbon cycle: chemical transformations

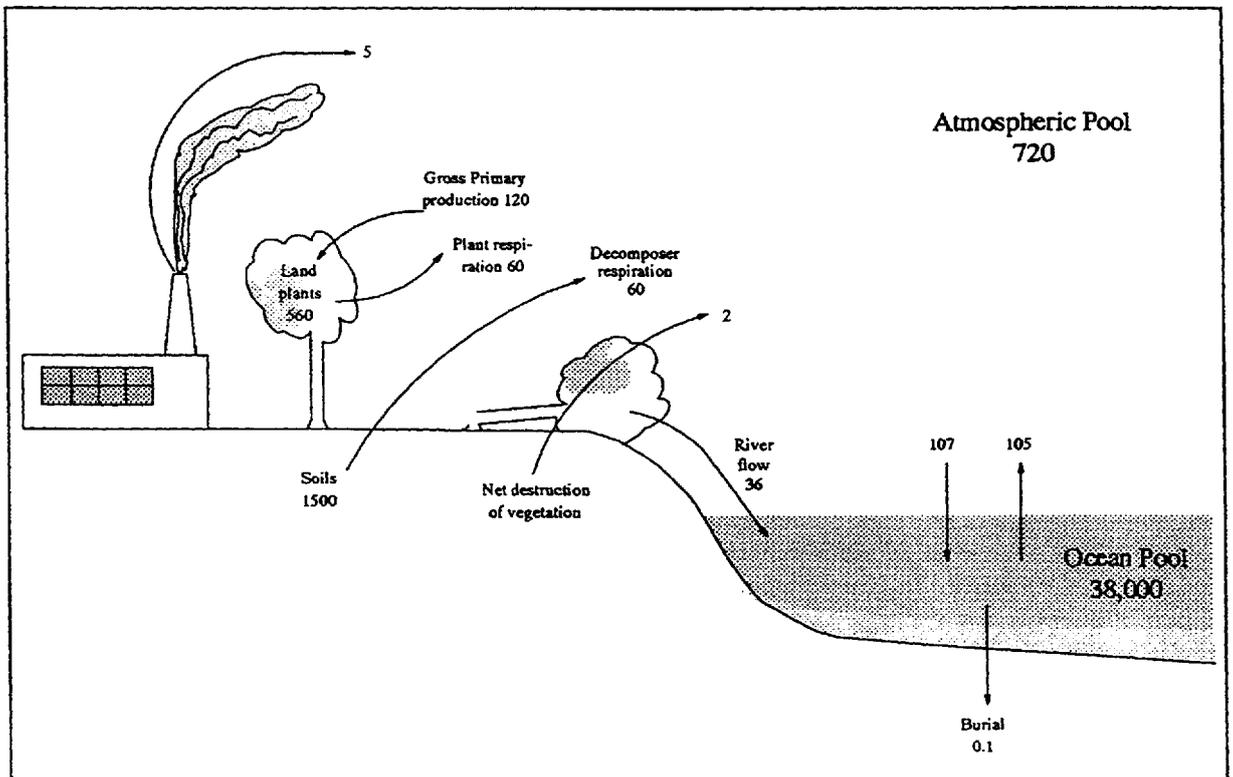


Figure 3. Present-day carbon cycle: intermedia fluxes (10^{15} g c)
 Source: [Schlesinger 1991, Figure 11.1]

There is little direct evidence to support the hypothesis of enhanced plant growth as a "sink" for atmospheric CO₂. However, notwithstanding increased timber and woodpulp harvesting, the forest biomass of the north temperate zones, North America and northern Europe — and perhaps Russia — is actually *increasing* [Kauppi *et al* 1992]. This would tend to compensate for tropical deforestation, thus reducing the apparent anthropogenic emissions below the figure of 7 Pg/yr cited above. It may help explain the "missing" carbon.

The Nitrogen Cycle

In general, vegetation can utilize either soluble nitrates or ammonium compounds, but not elemental nitrogen.⁶ Thus, all life depends on nitrogen fixation. By the same token, the

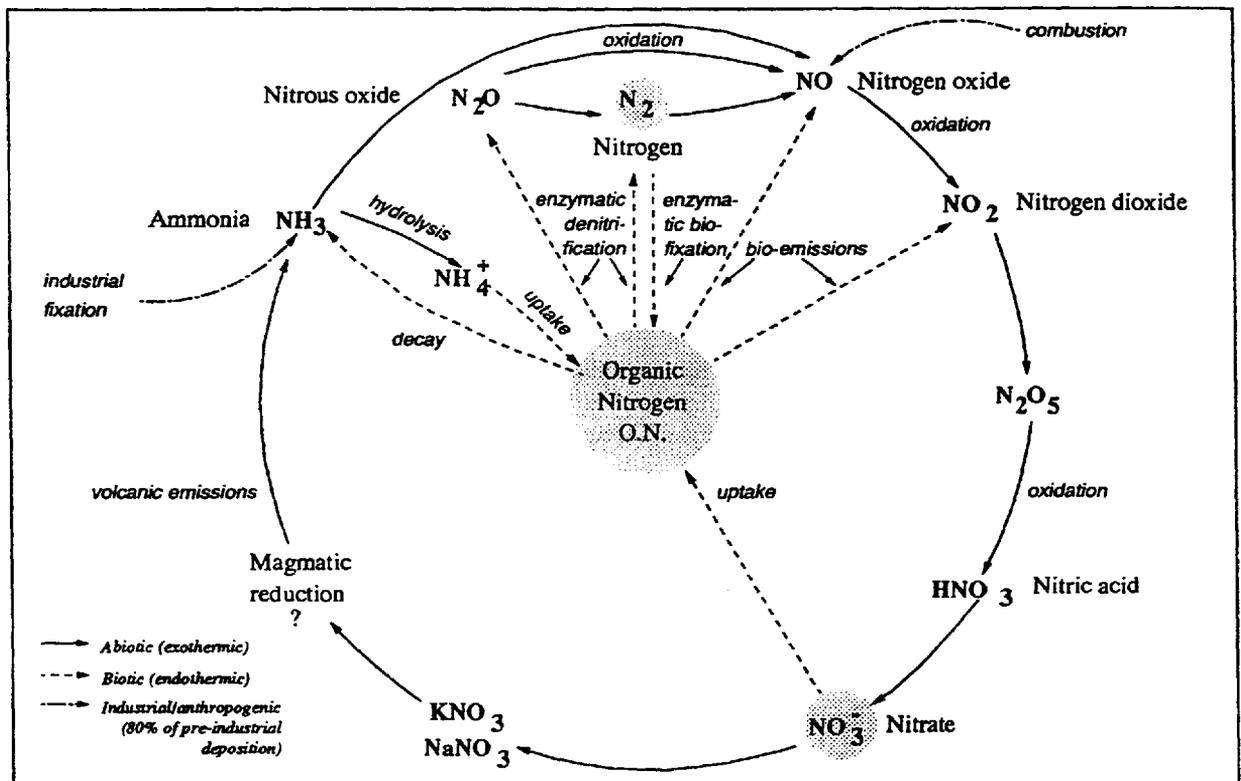


Figure 4. Nitrogen cycle: chemical transformations

nitrogen cycle (Figure 4) depends intimately on living organisms. Because nitrogen was (and is) a limiting factor in many agricultural regions, it has been relatively easy to increase output by supplementing natural sources of available nitrogen by the addition of synthetic sources. For this reason, however, the imbalances in the nitrogen cycle may prove to be the most difficult to correct (or compensate for) by deliberate human action.

Nitrogen fluxes to the atmosphere (the major reservoir of inorganic nitrogen) are of two kinds. Bacterial denitrification from the decay of organic materials, and denitrification of nitrate fertilizers return nitrogen to the atmosphere as inert N₂ or N₂O. This loss must be compensated by fixation. On the other hand, ammonia volatilization from the soil, combustion of organic materials (generating NO_x) and bio-emissions from marine organisms are recycled

as "odd" nitrogen. Fluxes from the atmosphere to the land and ocean surface include deposition of nitrate NO_3 (from "acid rain") and ammonium NH_4 . Fluxes to the biosphere include uptake of soluble nitrates and ammonium compounds, recycling of organic detritus (e.g. manure), and bio-fixation by micro-organisms. None of these fluxes, except the application of synthetic fertilizers, is well-quantified. Recent estimates from the literature are summarized in *Table III*.

Synthetic fertilizers from industrial nitrogen fixation (mainly as ammonia, NH_3) became important only in the present century. Current global annual ammonia production is of the order of 110 million metric tons, or 110 Tg/yr [UN Industrial Statistics 1991]. Of this, about 91 Tg is nitrogen content, of which 82 Tg/yr is used for agricultural fertilizer; the remainder is used to manufacture other industrial chemicals, notably explosives, pesticides, plastics (nylon) etc. These products eventually become wastes and are disposed of, either in landfills or via waterways. This nitrogen eventually finds its way back into the global cycle. As mentioned earlier, the only global reservoir of nitrogen is the atmosphere, which is 78% elemental nitrogen gas N_2 . The total stock of molecular nitrogen (di-nitrogen) in the atmosphere (*Table I*) is estimated to be 3.9 billion teragrams (Tg). Di-nitrogen (N_2) and nitrous oxide (N_2O) are not biologically available. There are only four sources of biologically available ("odd") nitrogen compounds. These are (1) biological fixation, (2) atmospheric electrical discharges (lightning), (3) high temperature combustion and (4) industrial processes for producing synthetic ammonia.

As already mentioned, only a few very specialized bacteria and actinomycetes (yeasts) can utilize (i.e., "fix") elemental di-nitrogen. There are some 25 genera of free-living or symbiotic bacteria. The most important is *Rhizobium*, which attaches itself to the roots of legumes, such as alfalfa. In addition, there are 60 genera of anaerobic cyano-bacteria, such as *anabaena* (leftovers from the early evolutionary history of earth), and 15 genera of actinomycetes (most prominently, *Frankia*). The range of estimates for bio-fixation in the literature is from 44 Tg/yr to 200 Tg/yr on land and from 1 to 130 Tg/yr in the oceans (see *Table III*). Overall, biological N-fixation, from all sources, may be as little as 50 Tg/yr and as much as 365 Tg/yr, although most estimates would be somewhere in the range 150–200 Tg/yr. Our best estimate (*Figure 5*) is that 140 Tg is fixed by terrestrial vegetation, roughly balanced by 130 Tg denitrification flux.

The rate of natural atmospheric nitrogen fixation as NO_x is even less accurately known than the bio-fixation rate. Estimates vary from 0.5 Tg/yr to 100 Tg/yr [Smil 1991; Schlesinger 1991]. Nitrogen oxides (NO_x) are also produced by high temperature combustion processes. Anthropogenic activities, mostly automobiles and trucks and electric power generating plants, currently generate approximately 20 Tg/yr of NO_x . Finally, of the order 5 Tg/yr of ammonia (NH_3) is also discharged by volcanoes and fumaroles, on average, although this can vary a lot from year to year.

Evidently, known anthropogenic inputs of fixed nitrogen are already comparable in quantity to (and may even be significantly larger than) estimated natural fixation rates. Assuming the nitrogen cycle must have been balanced in pre-industrial times (i.e., as recently as 1860) it is safe to say that inputs and outputs to some reservoirs are now out of balance by a large factor. Of course, it would be very difficult to detect any changes in total atmospheric nitrogen content (i.e. pressure) over any short period of time. However, it is known that nitrous oxide (N_2O) has increased in recent years, from approximately 300 ppb in 1978 [Weiss 1981] and is probably close to 315 ppb today. The annual increase has been measured by several investigators. For example, Khalil and Rasmussen estimated the annual increase at 0.2%; and Schnell put the rate at 0.33% p.a. [Khalil & Rasmussen 1983; Schnell 1986].

Table III: Published Nitrogen Balances

Flux			Delwiche & Likens 1977	Söderlund & Svensson 1976	Mc Elroy 1976	Sweeney et al 1977	Burns & Hardy 1975	NAS 1978	Liu & Cicerone 1984	Smil 1991	Ayres, Schlesinger & Socolow 1994
Biofix	N ₂ → ON	terrestrial marine	99 30	139 110 (30-130)	170 10	100 15-90	139 36	139 110 (20-120)		44-200 1-130	140 30
N-fix	N ₂ → NO _x N ₂ → NH ₃ N ₂ → NO _x	atmospheric industry combustion	7 40 18	— 80 19	10 40 40	0.5-3 35 15	10 30 15	30 80 10-200 (bio) 21 (ff)	10 (2-20) 1-10 (bio) 15-25 (ff)	10 (0.5-30) 90 (1985) 5 (bio) 30 (ff)	3 90 — 20
N ₂	from denitrifi- cation	terrestrial marine	122 40	107-161 25-179	210 50	90 50-125	190	197-390 0-120		} 83-575	130 70
N ₂ O	N ₂ → N ₂ O N ₂ O → N ₂ , NO from denitrifi- cation	combustion disappearance terrestrial marine	<i>in N-fix</i> <i>in N₂</i> <i>in N₂</i>	— (N ₂ =15, NO=5) 20 20		<i>in N-fix</i> 10	<i>in N-fix</i> <i>in N₂</i> (5%)	} 10			
Bio-emission of NO _x		terrestrial marine						11-33 11-33		} 20-90	
NO ₃ deposition		terrestrial marine					60	66-200 17-42			
NH ₄ ⁺ deposition		terrestrial marine					140	<i>in NO₃</i>			
NH ₃	NH ₃ → NO _x	atmospheric combustion volatilization		18-45 terr. 18-45 mar.			30 5 165	— 18-45 terr. 18-45 mar.	< 5 1-10	10 100-190 (36-250)	
River runoff			35	13-24	20	30	—	18		15-40	40
To sediments							10	30-40			
Outgassing from volcanoes							5				

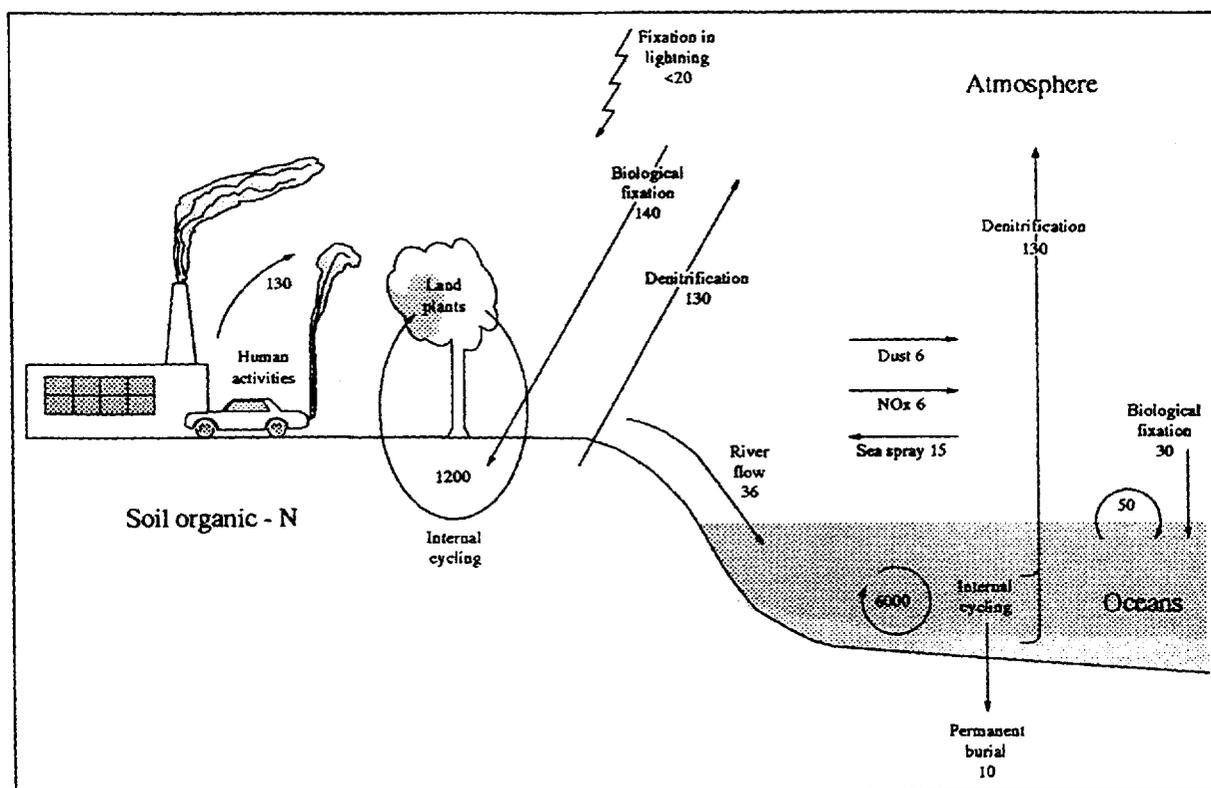


Figure 5. Present-day global nitrogen cycle: intermedia fluxes (10^{12} g n)
 Source: [Schlesinger 1991, Figure 12.2]

Nitrous oxide is not oxidized in the troposphere. In the stratosphere it is photolyzed yielding N_2 and O, or it is oxidized by ozone to NO_x . In fact, oxidation of nitrous oxide is the major source of stratospheric NO_x . The disappearance rate by these two mechanisms in combination is estimated to be 10 Tg/yr [Weiss 1981; Liu & Cicerone 1984; McElroy & Wofsy 1986]. This process has aroused great interest in recent years because of the discovery by Crutzen [Crutzen 1970 1974] and others that this set of processes governs the stratospheric ozone level, at least in the absence of chlorine compounds (which also catalytically destroy ozone).

N_2O is a co-product (with N_2) of natural denitrification by anaerobic bacteria and other micro-organisms. Aggregated data on the $\text{N}_2\text{O}/\text{N}_2$ ratio is scarce. However, such data as does exist (for fertilized land) implies that the ratio of N_2 to N_2O production on land is probably in the range 10-20, with a most likely value of about 16:1 [CAST 1976]. In other words, N_2O is about 1/16 of the total terrestrial denitrification flux. There is no *a priori* reason to assume this ratio should not hold true for marine conditions or pre-industrial times. It follows that the current N_2O flux of 13 Tg/yr should be accompanied by a corresponding N_2 flux of about $16 \times 13 = 208$ Tg/yr. (This compares with 240 Tg/yr in Figure 5; however, the numbers are subject to considerable uncertainty).

It now appears that denitrification of nitrate fertilizers accounts for 0.7 Tg/yr of N_2O emissions at present. According to one source, approximately 0.3% of fertilizer nitrogen is converted to N_2O [Galbally 1985]. A calculation by Crutzen sets the figure at 0.4%, which would correspond to N_2O emissions of 0.25 Tg/yr at current fertilizer production levels.⁷ An industrial source of N_2O , recently recognized, is the production of adipic acid, an intermediate in nylon manufacture [Thiemens & Trogler 1991]. This source could theoretically account for as much as 0.4 Tg/yr or 10% of the annual increase, in the absence of any emissions controls.

However, the actual contribution from this source is probably much less. One other possible source of N_2O is explosives. Virtually all explosives are manufactured from nitrogenated compounds (such as nitrocellulose, ammonium nitrate, trinitroglycerine, and various amines); according to simulation calculations, under conditions of rapid oxidation and decomposition up to 9% of the nitrogen may end up as nitrous oxide [Axtell 1993].

Denitrification is the complementary process to nitrogen fixation (as utilized by plants). Hence, the terrestrial contribution to denitrification must have increased in rough proportion to overall terrestrial and atmospheric nitrogen fixation, taking into account both natural and anthropogenic sources. On this basis, natural fixation (approx. 160 Tg/yr) has been increased by anthropogenic contributions of about 115 Tg/yr, or 70%. Absent other evidence, it is tempting to assume that global denitrification should increase proportionally, along with the percentage increase in nitrous oxide (N_2O) emissions, since pre-industrial times. This argument is not affected by uncertainties in the $N_2:N_2O$ ratio. On this basis, it would follow that the overall rate of denitrification — including N_2O emissions — may have increased by over 50% in little more than a century. Yet, there is no direct evidence of such an increase, and it is difficult to reconcile all the numbers.

A faster rate of global denitrification could, in principle, be attributed to either of two factors: (i) more rapid turnover of stored organic nitrogen in soils or (ii) an increase in the total (nitrogenous) biomass. At first sight the former hypothesis seems more plausible. Unquestionably, global agricultural activity has increased sharply over the past two centuries, both in scope and intensity. The nitrate content of riverine runoff from land to oceans has increased sharply. At the same time, the organic (humus) content of most agricultural soils has declined. This would seem to be intuitively consistent with the notion of accelerated turnover.

The declining organic content of soils is mainly due to plowing and exposure to oxygen. It is oxidation that is mainly responsible for the loss of organic material in soils. Increased exposure to oxygen would, *ceteris paribus*, probably tend to *decrease* the rate of denitrification (notwithstanding the fact that some N_2O and NO are apparently produced in aerobic soils). It must be remembered, after all, that denitrification is essentially a process whereby anaerobic bacteria "steal" oxygen from nitrates in the absence of molecular oxygen (air). Thus, the only major agricultural activity that would plausibly result in increased denitrification is wet rice cultivation. On the other hand, the drainage of wetlands would tend to have the opposite effect, decreasing denitrification.

An alternative to the hypothesis of increased global denitrification is that global nitrogen fertilization (from acid rain) has increased the uptake of nitrogen in biomes like grasslands and forests that are not cultivated. This explanation would be qualitatively consistent with the observations of increased forest biomass in northern Europe by Kauppi [Kauppi *et al* 1992]. It would also simultaneously provide an explanation of the "missing carbon" problem mentioned previously.

The Sulfur Cycle

The global sulfur cycle resembles the nitrogen cycle thermodynamically, insofar as reduced forms of sulfur (S , H_2S) are gradually oxidized by atmospheric oxygen, ending in sulfur oxides (SO_2 , SO_3) and finally sulfuric acid (H_2SO_4). See Figure 6. Sulfate (SO_4) is eventually deposited in wet or dry form (e.g. as ammonium sulfate). The reverse part of the cycle, which converts sulfur back to states of higher thermodynamic potential, is accomplished either by biological activity or by high temperature magmatic reactions in the earth's mantle.

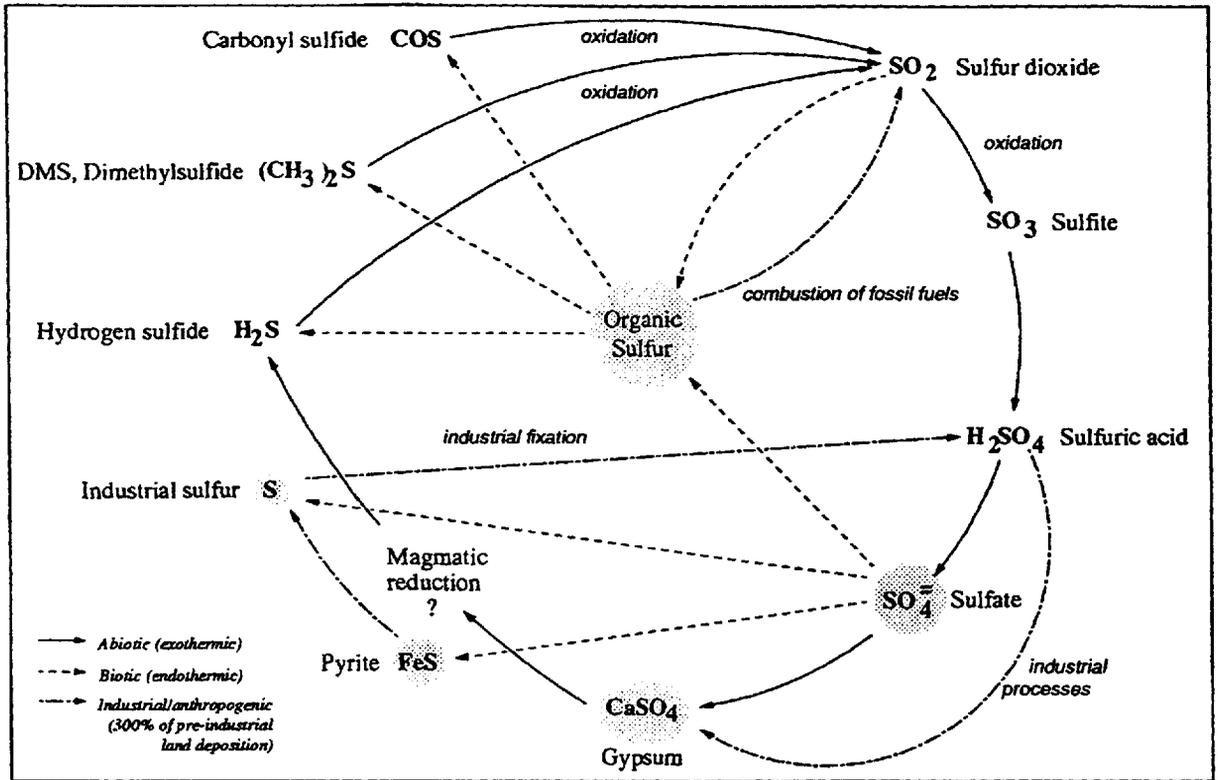


Figure 6. Sulfur cycle: chemical transformations

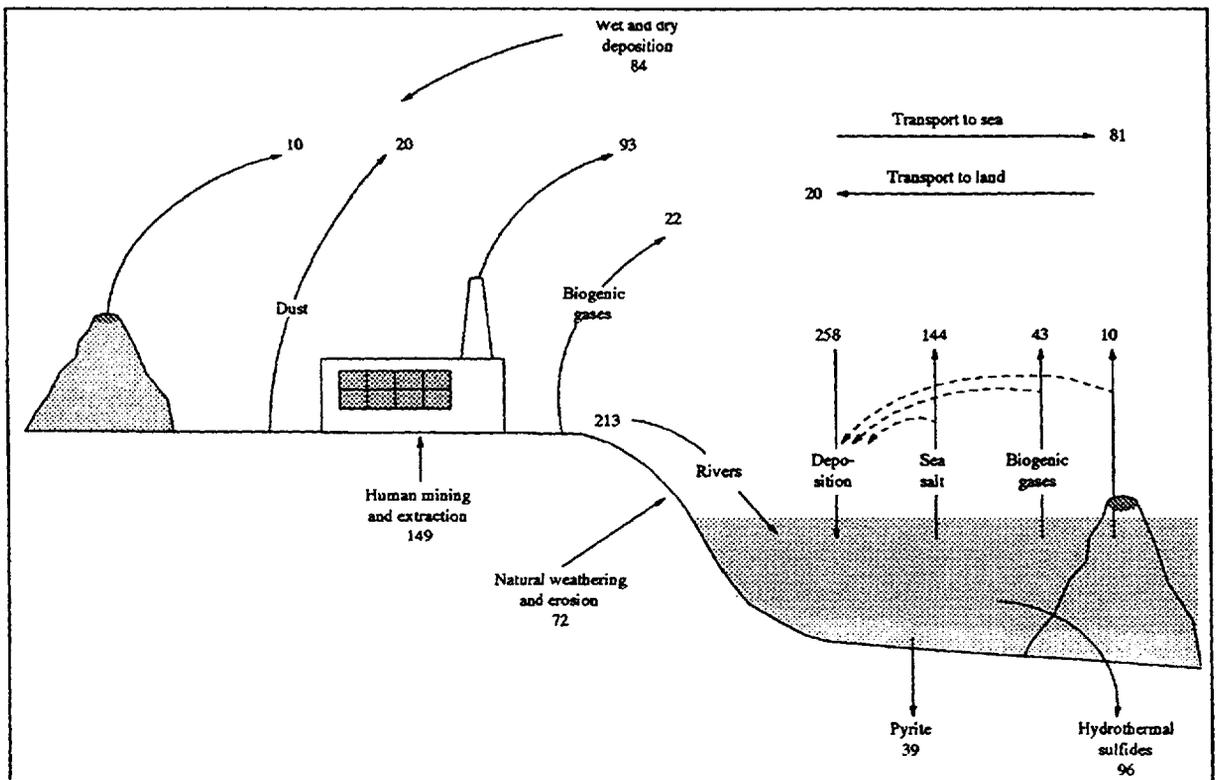


Figure 7. Present-day global sulfur cycle: intermedia fluxes (10^{12} g s/yr)
 Source: [Schlesinger 1991, Figure 13.1]

Table IV: Estimates of Sulfur Fluxes

(Tg/yr)	<i>Eriksson 1960</i>	<i>Junge 1963</i>	<i>Robinson & Robbins 1970</i>	<i>Kellogg et al 1972</i>	<i>Friend 1973</i>	<i>Granat et al 1976</i>	<i>Ivanov & Freney 1983</i>	<i>Brimblecombe et al 1989</i>
Combustion, smelting, etc.	39	40	70	50	65	65	113	93
Fertilizer	—	—	—	—	—	—	28	
Volcanic gases	—	—	—	1.5	2.0	3.0	28	land 10 ocean 10
Aeolean emission (dust)	—	—	—	—	—	0.2	20	20
Biogenic, land	77	70	68	90	58	5	16	22
Biogenic; coastal & ocean	190	160	30		48	27	20	43
Sea spray	44		44	43	44	44	140	144
Long-lived reduced S-compounds	—	—	—	—	—	—	5	—
Uptake of SO ₂ by land & terr.veg.	77	70	26	15	15	28	17	—
Washout of SO ₄ over land		55	70	86	86	43	51	84
Dry sulfate deposit over land	57	15	20	10	20	—	16	
Uptake of SO ₂ by oceans	70	70	25	72	25	10	11	258
Washout of SO ₄ over ocean		60	71		71	63	230	
Dry SO ₄ deposition over ocean	146							
River runoff: natural							104	213
River runoff: anthropogenic							104	
Abrasion from shores							7	
Underground river seepage							11	
Erosion & runoff								72
Ocean sediments, SO ₄							28	—
Ocean sediments, reduced (pyrite)							111	135
Atmospheric transfer, land to sea							total 102 anthropo- genic 65	81
Atmospheric transfer, sea to land								20

From another perspective, of course, the S-cycle consists of transformations of insoluble and biologically unavailable forms of sulfur (notably sulfides (pyrites) and calcium and magnesium sulfates) to available forms. These are utilized by organisms and finally returned once again to unavailable forms. From this perspective, the cycle can also be seen as a complex set of transfers between air, land and sea, as shown in *Figure 7*. Assuming the pre-industrial version of the cycle was really balanced (which is open to question) the controlling rate, or "bottleneck" in the system must have been the rate at which insoluble sulfides or sulfates were deposited in oceanic sediments. In the very long run (on the average) this deposition rate must have been equal to the rate at which sulfur was re-mobilized by pre-industrial geo-chemical processes, with or without biological assistance. It must also equal the pre-industrial net rate of deposition of sulfur compounds on the ocean surface, plus the pre-industrial runoff from rivers, abrasion of shores, etc.

Various estimates of sulfur fluxes are shown in *Table IV*. Roughly, the pre-industrial inputs to the land surface must have been about 26 Tg/yr, as compared to 84 Tg/yr from atmospheric deposition (c. 1980) and a further 28 Tg/yr as fertilizer. In short, the sulfur flux to land has more than quadrupled since the beginning of industrialization. It is likely that river runoff has doubled, e.g. from 72 Tg/yr pre-industrial to 213 Tg/yr currently. It is clear that the global sulfur cycle is now extremely unbalanced. Inputs to oceans appear to exceed deposition to the ocean bottom by as much as 100 Tg/yr [Schlesinger 1991].

It must be acknowledged that there is no known or obvious reason to worry unduly about this aspect of the anthropogenic perturbation of the sulfur cycle *per se*, however massive. Clearly, however, the oxidation of large amounts of reduced sulfur will continue to acidify the soils and the ocean. Deposition of heterogeneous sulfite/sulfate (SO_2/SO_4) and nitrate (NO_3) onto the land or water surface as "acid rain" — with measurable changes in pH — is currently much higher than the pre-industrial case. Atmospheric haze, consisting mostly of sulfuric acid/ammonium sulfate aerosols in the micron-size range, has increased by orders of magnitude. This phenomenon is sufficient to measurably increase the earth's albedo and, possibly, compensate for greenhouse warming in recent decades [Wigley 1989]. On the other hand, sulfate haze is proportional to the current rate of sulfate emissions, whereas the greenhouse phenomenon is a function of the atmospheric concentration, or total buildup, of greenhouse gases. Thus, the greenhouse warming and sulfate cooling will not continue to cancel each other indefinitely.

Thermodynamic Equilibrium

One important point needs to be emphasized again with regard to the grand nutrient cycles. It is that the atmosphere and lithosphere are emphatically *not* in thermodynamic equilibrium with the oceans. All three of the cycles discussed above consist of two distinct branches, a geochemical and a biological branch. In the geochemical branch, as schematically represented in *Figures 2,4,6*, reduced forms of carbon, nitrogen and sulfur are gradually oxidized by a multi-step sequence of processes, approaching the most stable (i.e., lowest energy) thermodynamic state. The latter would be one in which buried carbon and sulfur, and atmospheric nitrogen, combined with oxygen (and water) to form acids, *viz.*





These acids would react with all alkaline species in the environment and eventually accumulate in the ocean. For instance, if the nitric acid formation reaction (8), alone, proceeded to chemical equilibrium it has been calculated that almost all the oxygen in the atmosphere would be used up and the pH of the ocean would decrease to 1.5 [Lewis & Randall 1923]. More recent equilibrium calculations (below) have confirmed and refined this result.

Fortunately, some of these thermodynamically favored oxidation reactions do not occur at significant rates on the earth's surface — including the atmosphere and the oceans — under current conditions. In the case of carbon and sulfur, this is because biological reduction processes, combined with sedimentation and burial, regenerate and sequester reduced forms (e.g., kerogen and sulfides).

In the case of nitrogen, where physical sequestration is not a factor, there are two barriers. The first is kinetic. The formation of nitric acid is thermodynamically favored, to be sure. But it can only proceed by a sequence of reversible reactions involving a number of intermediate oxidation stages. These can only occur when the appropriate species are present in significant concentrations. In several cases the energy required for "ignition" of the reaction is extremely high. Thus, the *rate* at which this reaction occurs in nature is very low. Even so, the nitric acid level of the oceans would gradually build up, except for another barrier. There are several enzymatically catalyzed biological processes that convert soluble nitrates back to reduced forms, including NH_3 and even N_2 , thus restoring the non-equilibrium situation.

In the absence of these biological denitrification processes, most of the atmospheric oxygen would end up as dissolved sodium nitrate in the ocean. Ahrendts has calculated that an atmosphere-ocean-crustal system (equilibrated to a depth of 100 meters) would have an atmosphere of 95% N_2 , with only a trace amount of oxygen (0.3ppm and a pressure of 0.77 atmospheres [Ahrendts 1980]. The atmospheric oxygen would end up mostly as NaNO_3 in the ocean, where it would constitute 0.4% of the dissolved solids, and the surface layer would consist largely (54.5%) of silicic acid (H_4SiO_4) [ibid].

If the equilibration in the earth's crust were taken to a deeper level (e.g. 1000 meters), the silicic acid, ferric iron (hematite), and sulfates would be reduced to silica, magnetite, and sulfides respectively. Calcium carbonate and silica would also recombine to produce calcium silicate (CaSiO_3) and CO_2 (the reverse of equation 3). Essentially all of the sequestered carbon and hydrocarbons in the earth's crust would be oxidized (releasing CO_2 to the atmosphere). Ammonia and methane would also exist in the atmosphere [ibid]. Atmospheric pressure and temperature would then rise. But, in any case, there would be no free oxygen in the atmosphere.

In summary, the earth system does not (for the present) closely approach thermodynamic equilibrium. This is lucky for us, since the true equilibrium state — or anything close to it — would be antithetical to life. It is possible to estimate roughly what earth would be like if all of the thermodynamically favored chemical reactions went to completion without biological interference. In addition to Ahrendt's work, noted above, this has been done using two different approaches (Table V). "World #1" is based on a computer simulation of the

earth as a chemistry experiment, in which all favorable chemical reactions go to completion [Sillén, quoted by Lovelock 1979]. "World #2" is based on an interpolation between observed conditions on Mars and Venus, allowing for the earth's intermediate orbit and slightly greater gravitational field (*ibid*). It can be seen that the two are very similar to each other, and roughly consistent with Ahrendt's equilibrium calculations [Ahrendt's *op cit*]. The conditions are far different from conditions on the actual earth as we know it.

The ability of the biosphere to maintain the earth system far from thermodynamic equilibrium is the essence of the "Gaia" hypothesis. A thermodynamic measure of the earth's "distance from equilibrium" is the exergy (or availability) content of the atmosphere, ocean and crustal layer. Ahrendt has actually computed the stored exergy values of the major components of the actual state (actually a slightly simplified "model" version) *vis a vis* several possible reference (equilibrium) states [*ibid*]. Without the biosphere, this stored exergy would be dissipated and lost (as entropy).

Stored environmental exergy has increased, on average, over geologic time at least until human industrial activity began in earnest, two hundred years ago. Since then, there has been a reversal. Environmental exergy has certainly decreased, although probably not yet by a very significant amount. (For example, the amount of free oxygen in the atmosphere is essentially unchanged), and the fraction of sequestered carbon that has been consumed by burning fossil fuels is still infinitesimal compared to the amount stored in shales, not to mention carbonates. Nevertheless, there are potential risks.

Table V: The Stabilizing Influence of the Biosphere (Gaia)

<i>Reservoir</i>	<i>Substance</i>	<i>Actual world</i>	<i>Ideal world I</i>	<i>Ideal world II</i>
Atmosphere	Nitrogen	78%	0%	1.9%
	Oxygen	21%	0%	trace
	CO ₂	0.03%	99%	98%
	Argon	1%	1%	0.1%
Hydrosphere	Water	96%	85%	?
	NaCl	3.4%	13%	Not
	NaNO ₃	—	1.7%	?
			much	?
			Water	?
Temperature	Degrees Celsius	13	290 ± 50	290 ± 50
Pressure	Atmospheres	1	60	60

Note: Life is impossible if average temperature is too high for liquid water, or if salinity exceeds 6%.

Acidification of the Environment

Acids are associated with H⁺ ions and bases are associated with OH⁻ ions. A strong acid such as HNO₃ is one that ionizes easily in water, viz. HNO₃ ↔ H⁺ + NO₃⁻. Obviously the total number of positive and negative ions (due to overall charge neutrality) remains constant. However, acidification can increase if the number of H⁺ ions increases. For this to happen without a corresponding increase in OH⁻ ions means that there must be a buildup of other negative ions to balance the positive charges.

Acidification results largely from oxidation of atmospheric gases. In particular ammonia (NH_3) and hydrogen sulfide (H_2S) were present in the primordial atmosphere. Ammonia dissolved in water is ammonium hydroxide, a base. These gases can be oxidized (in several steps) to nitric and sulfuric oxides, respectively. In water, these become acids. The oxygen buildup, of course, resulted from the evolutionary "invention" of photosynthesis and the sequestration of carbon (as hydrocarbons) in sediments.

Acid rain is a well-known phenomenon. It contributes significantly to both the sulfur and nitrogen cycles, as they function currently, although playing little role prior to industrialization. The basic mechanism for sulfur is that sulfur dioxide (SO_2) from combustion products oxidizes in the atmosphere to sulfur trioxide (SO_3) which subsequently dissolves in water droplets to form sulfuric acid (H_2SO_4). In the case of nitrogen, the sequence also starts with combustion, except that the nitrogen is from the air itself. The two nitrogen oxides are NO and NO_2 . Further oxidations occur, producing N_2O_5 and finally (with water), nitric acid (HNO_3).

These strong acids increase soil and water acidity (i.e. reduce the pH). They react immediately with ammonia or any other base. Many metallic ions — including toxic metals — that are bound quite firmly to soil particles when the soil pH is high (alkaline) are likely to be mobilized as the alkaline "buffering" capacity (Ca^{++} and Mg^{++} ions) in the soil are used up. Aluminum is one example. Aluminum poisoning, caused indirectly by acid rain, may be one of the causes of the European *Waldsterben* that has decimated some forests in central Europe. Similar problems may arise in the future as toxic heavy metals like Pb, Cd, As and Hg continue to accumulate in soils and sediments.

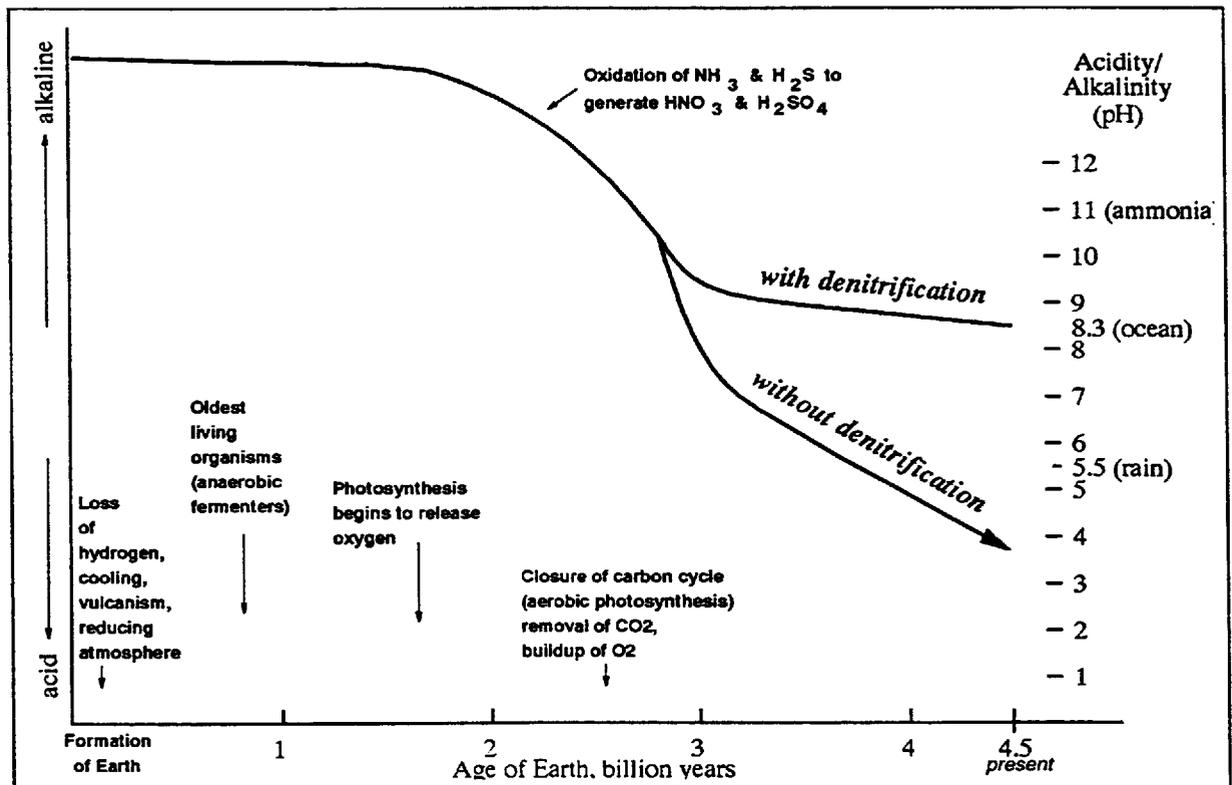


Figure 8. Biospheric stabilization by denitrification

Although virtually all of the literature on acid rain pertains to localized effects, it may be important to consider the global implications. The buildup of NO_3^- and $\text{SO}_4^{=}$ ions in the

environment is matched by a corresponding buildup of H^+ ions. This long-term acidification trend has been under way throughout geologic time. Natural sources of atmospheric hydrogen ion (H^+) production amount to around 9 Tg/yr⁸ [Schlesinger 1991]. Of this amount, only 3 Tg/yr is neutralized by NH_3 from natural sources such as volcanos and soil volatilization [Warneck 1988].

In preindustrial times, the long-term trend toward environmental acidification was mainly driven by nitrogen fixation followed by oxidation. It gradually slowed — and perhaps came to a halt — due to the evolution of bacterial nitrogen recycling (denitrification). An hypothetical trajectory is indicated schematically in *Figure 8*. In a sense, these anaerobic nitrate-consuming soil bacteria can be regarded as a necessary stabilizing element in the biosphere, without which acidification would continue indefinitely until all of the atmospheric oxygen was consumed and the ocean became too acid for life.

The case of sulfates is different. While there are soluble sulfates (ammonium, sodium and potassium) sulfates do not build up in the ocean because they are gradually converted to insoluble calcium sulfate which precipitates out (as gypsum). Thus sulfate acidification is also limited, but by a rather different (non-biological) mechanism.

The industrial activities of humans have considerably acidified the atmosphere (pH = 5.5) as compared to the oceans (pH = 8.3). Even without human intervention, the soils and the ocean are gradually acidifying. In other words, the pH of the environment is decreasing. Meanwhile, however, anthropogenic sources of H^+ (HNO_3 and H_2SO_4) add another 7.4 Tg/yr to the 9 Tg/yr of natural origin. Moreover, the anthropogenic contribution to acidity is rapidly increasing. It already almost equals the natural contribution. Indeed, in many locations the very slow carbonic-acid-driven process of rock weathering is now being replaced by a much faster sulfuric and nitric acid driven weathering process. The geological implications of this are difficult to foresee.

A Risky Experiment

Non-linearity is one of the essential features of a complex system existing in a stable state far from thermodynamic equilibrium. In recent years the dynamics of non-linear systems has been a subject of considerable interest among mathematicians, ecologists and others. There is a well-known tendency for non-linear systems to have multiple "solutions" or stable trajectories. They can suddenly "flip" from one (apparently) stable state — or branch — to another. The mathematician René Thom has classified the various possible "flips" (or "catastrophes") in topological terms.

Under certain circumstances such systems can also become "chaotic". Chaotic trajectories may (or may not) be bounded by "strange attractors". It is as though the trajectory were a planetary orbit influenced by large, invisible gravitational masses whose existence can only be inferred from irregularities in the planetary motion. Scientists ability to predict chaotic behavior is obviously limited.

The weather is an example of chaotic behavior within a bounded region. Short-term predictions can be reasonably accurate, and there seems to be some possibility to predict long term climate changes. The climate of a region is, effectively, the "strange attractor" for the weather in that region. But the climate itself is probably a chaotic variable on a longer time-scale. The earth system as a whole is so complex, and so non-linear, that accurate predictions of some kinds of behavior are probably impossible. The best that can be done is to construct models with the requisite degree of non-linearity and to use these models in simulation experiments to explore the bounds of various "strange attractors" in the system.

Yet models of a system can never capture all of the features of the original, and one of the most important features of non-linear systems is that small — even infinitesimal — changes in initial conditions can cause unbounded changes in trajectories after some time has passed. This is called the "butterfly effect", from the fanciful notion that even the flight of a butterfly in the Amazon forest might have some unpredictable future impact on the weather in Chicago.

Similarly, a seemingly trivial change in the specification of a complex non-linear model can have a surprising — maybe unbounded — impact on the dynamical behavior of the model. What this means, in effect, is that it is virtually impossible for scientists to determine some of the features of the dynamics of the earth-system. The system may be the only adequate model of itself.

To bring this discussion to a conclusion, one can envision the present climatic regime as a "strange attractor" in the above sense. It is a stable state, far from thermodynamic equilibrium. Are there other branches? Other stable states suitable for life support? How far can the system be perturbed before it becomes unstable? How rapidly would the transition

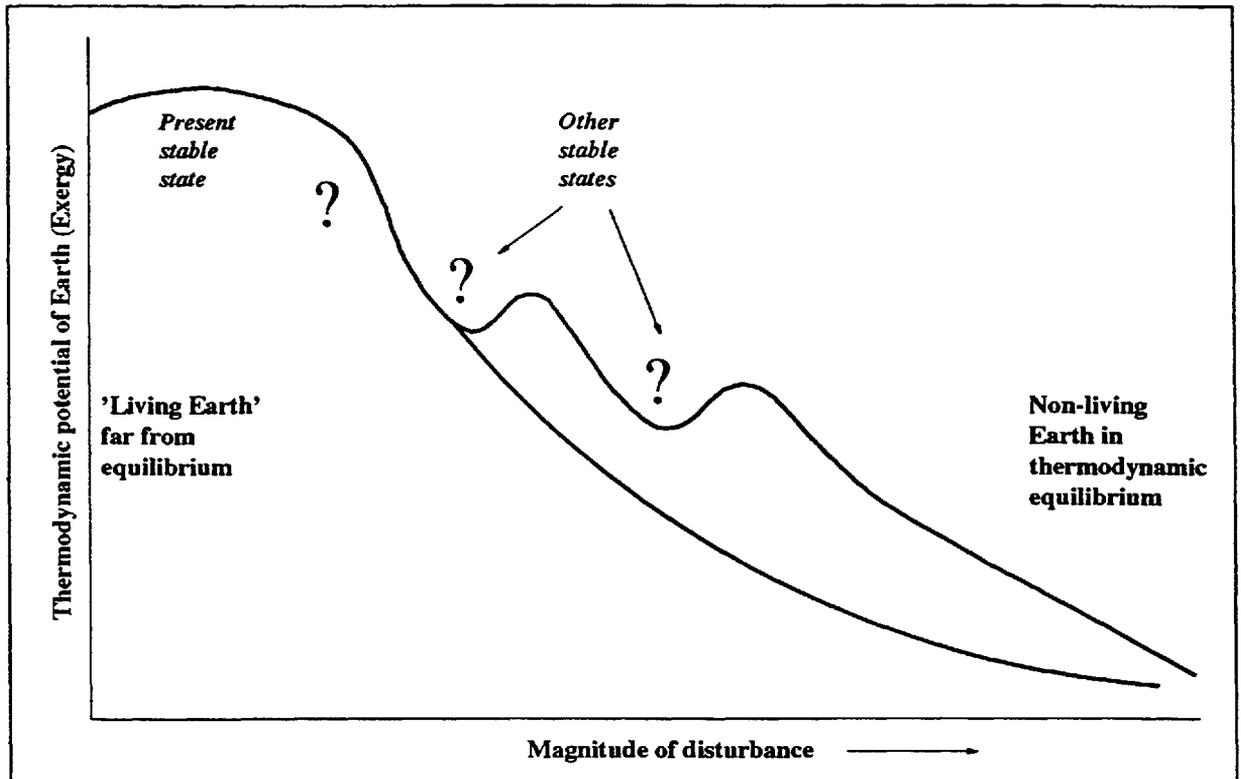


Figure 9. A risky experiment

("catastrophe" in Thom's terms) occur? This question is illustrated by *Figure 9*. It is impossible to answer such questions now. Because of the complexity and non-linearity of the system, it may never be possible, no matter how wide the reach of future science.

Meanwhile, humans are perturbing the grand nutrient cycles, and the climate, in major ways. Some people seem to have great faith in the ability of the Earth system to adjust to any perturbation. But, in my view, there is no rational basis for such confidence. The fact that no catastrophe has yet occurred is not evidence of inherent stability. The only safe course for Man is to consciously restrain anthropogenic impact on the environment to levels that are within the range of past deviations and excursions of natural origin. In this context, it is vital

to bear in mind that the time-scale is critical. Biological evolution is a comparatively slow process, except for micro-organisms. Thus evolutionary adjustment is not possible as a means of accommodation to changes that occur with extreme rapidity.

Endnotes

1. Opal is a form of silica used for the shells of diatoms.
2. If the oceans were to freeze the weathering rate would fall to zero, allowing the atmospheric CO₂ level to rise due to volcanic action. It has been shown that this feedback is sufficient to assure that the oceans would not have been frozen over, even during the earth's early history when the sun was emitting 30% less energy than it does today [Walker *et al* 1981].
3. In the more general case, the rate of photosynthesis can be expected to depend on the concentrations of all the essential nutrients — especially C,N,S,P — in biologically available form.
4. The origin of natural gas is currently in doubt. For a long time it was assumed that natural gas was entirely biogenic and associated mainly with petroleum. Now it is known that gas deposits are much more widely distributed than petroleum deposits. It has been suggested by several astronomers that much of the hydrogen in the earth's crust may have originated from the sun (via the "solar wind" proton bombardment).
5. To be more precise, an environment lacking nitrates, manganese oxide, iron oxides or sulfates. Recall the earlier discussion of "redox potential" and bacterial sources of oxygen for metabolism.
6. Most bacteria and animals can only utilize organic nitrogen, mainly as amino-acids.
7. Denitrification bacteria reduce nitrates (NO₃) to obtain oxygen for metabolic purposes. They do not metabolize ammonia. Thus the denitrification flux from fertilizers depends somewhat on the chemical form in which it is applied. The N₂O/N₂ proportion depends on local factors, such as carbon content of the soil, acidity and dissolved oxygen. It must be acknowledged that the combined uncertainties are quite large. Thus, for instance, a recent US study sets the N₂O emissions from fertilizer at 1.5 Tg/yr, as compared to only 1 Tg/yr from fossil fuel combustion. Other estimates in the literature range from 0.01 to 2.2 Tg/yr [Watson *et al* 1990].
8. A more detailed breakdown of the sources of H⁺ in the atmosphere is as follows: carbonic acid 1.25 Tg/yr; volcanic SO₂ 1.3 Tg-yr; NO_x formation by atmospheric electrical discharges (lightning) 1.4 Tg/yr; oxidation of biogenic sulfur compounds 4.1 Tg/yr. The total for all the above natural processes is of the order of 9 Tg/yr.

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