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The Abiotic Nitrogen Cycle

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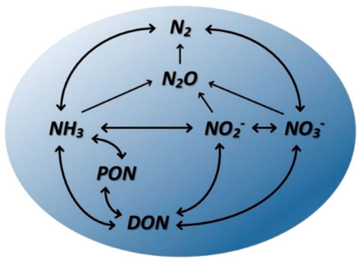
ABSTRACT: Natural environments on Earth are amenable to a diverse array of chemical reactions that can convert one form of nitrogen into another, often with the participation of additional substances such as minerals, dissolved metals, and organic compounds. These processes collectively define a natural chemical nitrogen cycle, analogous to the familiar biologically driven cycle but even more intricate with respect to the number of pathways by which nitrogen can be transformed and transported across land, air, and water. The fully assembled abiotic nitrogen cycle manifests a landscape rich in opportunities for investigation either with or without parallel attention to biological processes.



KEYWORDS: *abiotic, atmosphere, nitrogen cycle, photochemistry, soil, water*

Since the pioneering work of Boussingault, de Saussure, Reiset, and others in laying the conceptual foundation for the natural nitrogen (N) cycle,[1−4] countless researchers have contributed to understanding its architecture, largely by following the microorganisms that change one form of N into another. The same arrows used to represent these changes, however, tell another story: for all of the biological transformations in the N cycle, there are analogous abiotic reactions that can operate in the same environments. Some have been discovered recently, others have faded from view since they were first discovered, but only a few have been assimilated into the prevailing paradigm. The N cycle in current discussions[5−12] is still surveyed and drawn almost exclusively around microbial activity, despite evidence, old and new, that the abiotic reactions relegated to the margins of these discussions may in fact be more than marginal.

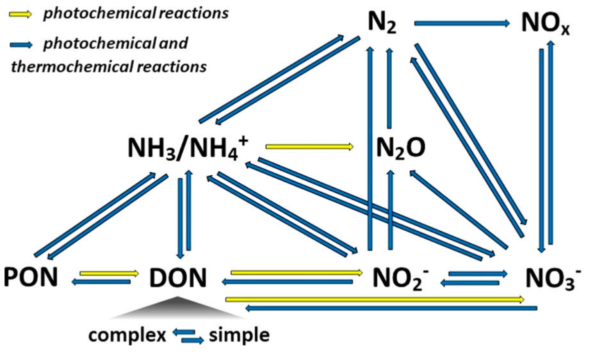


Figure 1. Abiotic nitrogen transformations known to occur under conditions found on the Earth's surface. PON, particulate (solid) organic N, including bulk organic matter such as soil and sediment, and discrete compounds such as chitin and insoluble proteins; DON, dissolved organic N, comprised of simple compounds such as amino acids and relatively complex compounds such as 'humic' substances; NO_x, NO and/or NO_2.

Figure 1 traces the movement of N via abiotic transformations, which include both photochemical and nonphotochemical (thermochemical) reactions. Table 1 compiles these and additional reactions that have been observed naturally or have been shown to occur under conditions found on the Earth's surface. Enzyme-mediated biological processes correspond to most of these abiotic reactions but not all; in fact, more abiotic transformations are possible directly from one form of N to another than biotic transformations, imparting additional complexity to the Earth's "most advanced biogeochemical nutrient cycle".[12]

A look through the literature confirms that most abiotic reactions relevant to N cycling, particularly photochemical reactions, have not attracted more than sporadic interest; their contribution to N cycling therefore remains vague. A good example is the photochemical fixation of dinitrogen (into ammonia or nitrate), a notion still obscure to geoscientists despite "significant evidence that this process occurs spontaneously in terrestrial settings".[13] It has been suggested that 10 Tg of N $year^{-1}$ can be photochemically fixed on the Earth's deserts,[14] which is comparable to what is fixed by lightning (2−20 Tg of N $year^{-1}$),[10,15] and an appreciable amount relative to total biological fixation across land ecosystems, estimated at 100−290 Tg of N $year^{-1}$,[16] 150 Tg of N $year^{-1}$,[17] or 40−100 Tg of N $year^{-1}$.[18] Photochemical fixation may be more consequential in places where biological fixation is low: an estimate for deserts of up to 20 kg of N ha^{-1} $year^{-1}$ based on measurements with sands[19] is similar to biological fixation estimated at 5−11 kg of N ha^{-1} $year^{-1}$.[16] Using data collected with soils,[20] it can be calculated that up to 0.3 kg of N ha^{-1} $year^{-1}$ is photochemically fixed. Only two available assessments of the abiotic process do not afford a robust comparison to the biological process, but nevertheless attest that photochemical

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Table 1. Abiotic Reactions That May Participate in the Earth's Natural Nitrogen Cycle

transformation[a]	photochemical reactions[b]	thermochemical reactions[c]	biological counterpart[d]
NH_3/NH_4^+ → DON and PON	non-specific photoconsumption[62]	formation of N-containing heterocycles and aromatic compounds[71−74]	synthesis in general
	photoamination of quinones[63] possibly including those derived from lignin photodegradation[64] or present in organic matter[65,66]	reaction with phenolic compounds and quinones, including those present in or derived from lignin and tannins[75−77]	
	addition of NH_3 to products of irradiation of fatty acids[67]	reaction with sugars[78]	
	formation of N-containing heterocycles[68]	reaction with existing organic matter in soil[29,79,80]	
	photoamination of alkenes[69]		
	amino acids produced from hydroxycarboxylic acids[70]		
NH_3 → N_2	on TiO_2[81]	by MnO_2[82]	feammox [concurrent Fe(III) reduction]
NH_3 → N_2O	on TiO_2[81,83]		ammonia oxidation
NH_3 → NO_x	on TiO_2[84,85]		ammonia oxidation
NH_3 → NO_2^-	on TiO_2[83,85]		nitrification, feammox
NH_3/NH_4^+ → NO_2^-	24	H_2O_2 + Cu(II)[91]	nitrification, feammox
	by MnO_2, TiO_2, ZnO, Al_2O_3, and SiO_2[86−88]		
	by singlet oxygen generated from riboflavin[89] and possibly other photosensitizers (e.g., chlorophyll derivatives and humic acids[90])		
NH_3 → NO_3^-	on TiO_2[85,88]		
	by singlet oxygen generated from riboflavin[89]		
NH_4^+ → NO_3^-	86	on mixed Fe−Mn oxide,[92] on Fe_2O_3, TiO_2[93]	nitrification, feammox
NH_4^+ + NO_2^- → N_2	soil, Fe_2O_3, TiO_2, and ZnO[85,94−96]	spontaneous reaction[97,98]	anammox
NH_4^+ + NO_3^- → N_2O	on Al_2O_3[99]		
complex DON → simple DON	release of amino acids[100−102]	on clays[105]	decomposition in general
	protein fragmentation by MnO_2[103]		
	depolymerization of chitosan[104]		
simple DON → complex DON	protein aggregation[106,107]	reaction of amines (including amino acids) with carbonyl compounds[72]	synthesis in general
	photoamination of quinones with amines[108]	by MnO_2[109−112]	
		reaction of amino acids and peptides with phenols: alone[113] or on clays[114−117]	
		polymerization of proteins with sugars[118]	
DON → NH_4^+	23, 100, and 119−122	by MnO_2[109]	mineralization (ammonification)
	on TiO_2[123,124]	on clays[105,114,125]	
DON → PON	photochemical flocculation of organic matter[126,127]	precipitation of proteins with tannins and lignin[128,129]	humification
		adsorption of DON onto minerals and organic colloids[130−132]	
		reaction of amino acids and phenols and retention of products on clays[117]	
DON → N_2	on TiO_2[123]	by MnO_2[82]	
DON → NO_2^-	133 and 134		
DON → NO_3^-	on TiO_2[123,124]		
PON → NH_3/NH_4^+	100, 135, and 136	heating by solar radiation[41]	
	protein decomposition[137]	by burning[138−140]	
PON → DON	135, 136, 141, and 142		decomposition in general
	release of amino acids[100]		

Table 1. continued

transformation[a]	photochemical reactions[b]	thermochemical reactions[c]	biological counterpart[d]
PON → NO_x		heating by solar radiation[41]	
PON → N_2, N_2O, and NO_x		burning (pyrodenitrification)[10,143]	
N_2 → NH_3	on TiO_2 and Fe_2O_3,[13] TiO_2 containing Fe, Co, Mo, and Ni oxides,[14,144] FeOOH,[145] Fe_2O_3–Fe_3O_4,[146] ZnO and CdS[147]	by $Fe(OH)_2$[149]	symbiotic and asymbiotic fixation
	$Fe_2Ti_2O_7$ plus humic acid[148]		
	on sand[19]		
N_2 → NO_x	on TiO_2[150]	by lightning[10,15]	
N_2 → NO_2^-	on Fe(III) oxide,[151] ZnO–Fe_2O_3[152]		
N_2 → NO_3^-	on ZnO and TiO_2[13,20,88,153,154]	by TiO_2 above 50 °C[20]	
	on soil[20]	by soil above 70 °C[20]	
N_2O → N_2	on TiO_2, Fe_2O_3, ZnO, and Cu zeolites[155−158]	$Fe(OH)_2$ plus catalytic Cu(II) (aq)[161]	denitrification
	on sand[44]	on Cu_2O above 60 °C[162]	
	by e^- (aq),[159] itself generated upon irradiation of organic matter[107,160]	on sand[44]	
NO → NH_3 and N_2O		by FeS[163]	denitrification
NO_2 → NO		on Al_2O_3, Fe_2O_3, and TiO_2[164]	
NO_x → DON and PON	165	166 and 167	
NO_x → N_2O	on TiO_2[168,169]	on Al_2O_3 and TiO_2,[164] Fe(III) nontronite[170]	
NO_x → NO_2^- and NO_3^-	on TiO_2[85,171]	disproportionation of NO_2 in water[172]	
		sorption by moist limestone,[60,173] calcareous soil,[174] and clays,[170] by Al_2O_3, Fe_2O_3, and TiO_2[164]	
NO_2^- → NH_3/NH_4^+	on TiO_2 containing Fe(III) or other metals,[175] on ZnS[176]	172	respiratory ammonification
		Fe(II) (aq)[161]	
		green rust,[177] $Fe(OH)_2$[145]	
NO_2^- → DON and PON	photonitration, enhanced by TiO_2[178]	reaction with organic matter[28,29,56,180]	
	conversion to amides and lactams[179]	reaction with lignin, other polyphenols, and humic acids[77]	
NO_2^- → N_2	on TiO_2[181]	172	denitrification
		reaction with polyphenols and organic matter[28,182−184]	
		by Fe(II) (aq)[161]	
NO_2^- → N_2O	on TiO_2[181]	172	denitrification
		decomposition of HNO_2[98]	
		reaction with lignin, other polyphenols, and organic matter[28,182,183,185]	
		reaction with amines[182]	
		by Fe(II) (aq)[161,186−188]	
		by Fe(II) in minerals: silicates,[189] siderite,[190] and magnetite[191]	
NO_2^- → NO_x	133, 192, and 193	172	nitrite reduction (to NO)
		disproportionation of HNO_2[98,182,194]	
		by Fe(II) (aq)[161,187]	
		reaction with organic matter[185]	
NO_2^- → NO_3^-	179 and 193	172	nitrification (nitrite oxidation)
	on Fe_2O_3, TiO_2, and ZnO[88,181,195]	disproportionation of HNO_2[98,182]	
		by dissolved oxygen[196]	

Table 1. continued

transformation[a]	photochemical reactions[b]	thermochemical reactions[c]	biological counterpart[d]
		by Mn oxides[39]	
$NO_3^- \rightarrow NH_3/NH_4^+$	on TiO_2 plus an organic electron donor,[197] on TiO_2 containing Fe(III) or other metals,[175,198] on ZnS[176]	by Fe(II) plus catalytic Cu(II) (aq)[199,200] by green rust,[201] $Fe(OH)_2$,[145] FeO,[202] and Fe(II) plus goethite[199]	respiratory ammonification/ dissimilatory nitrate reduction to ammonium
$NO_3^- \rightarrow$ DON and PON	photonitration[178,203,204]	29 and 180	
$NO_3^- \rightarrow N_2$	on TiO_2 containing Cu(II)[198]	by Fe(II) in silicate minerals[205] by Fe(II)[187] or Fe(II) plus catalytic Cu(II) (aq)[200] by Mn(II) (aq)[82]	classical denitrification and denitrification coupled to other reactions, such as Fe(II) oxidation
$NO_3^- \rightarrow N_2O$	on Fe_2O_3, Al_2O_3, SiO_2, and TiO_2[206,207]	by Fe(II) plus catalytic Cu(II) (aq)[200] by Fe(II) in silicate minerals[189]	denitrification
$NO_3^- \rightarrow NO_x$	on Fe_2O_3, SiO_2, TiO_2, Al_2O_3, ZnO, and zeolites[206−209] on sand[208]	by Fe(II) plus catalytic Cu(II) (aq)[200]	denitrification
$NO_3^- \rightarrow NO_2^-$	24, 179, 210, and 211 on zeolites[209] by organic matter[212,213] on TiO_2 containing Cu(II)[198]	by Fe(II) plus catalytic Cu(II) (aq)[200] by Fe(II)-containing silicate minerals[205]	nitrate reduction
plant foliage $\rightarrow N_2O$	214		
plant foliage $\rightarrow NO_x$	215		

[a] DON, dissolved organic N; PON, particulate organic N. Ammonia and ammonium are listed together when either form may be present in the same reaction environment but are treated separately when only one form participates in a given reaction or when there is a useful distinction (e.g., gas phase versus aqueous reactants or products). Similarly, nitric oxide and nitrogen dioxide are listed together (as "NO_x") when both undergo a given reaction but listed separately when only one species participates. [b] All of the cited photochemical reactions operate at wavelengths greater than approximately 290 nm, i.e., solar radiation that reaches the Earth's surface. [c] Except where indicated, the cited thermochemical (non-photochemical) reactions occur at typical ambient temperatures, i.e., about 40 °C or less. Solid compounds (e.g., metal oxides) generally act as catalysts in both photochemical and thermochemical reactions, while dissolved compounds, such as Fe(II), are typically consumed as reactants. [d] Analogous biological processes that directly accomplish the same transformation.

fixation may be more than negligible, a conclusion upheld by other studies with materials known to occur naturally.[13] Biological fixation, the traditional natural entry point of uncombined nitrogen (N_2) into terrestrial and aquatic N cycling, may not be the only natural entry point, and investigation of abiotic fixation may help resolve some pending "remarkably large uncertainties" on land[21] or provide insight into "elusive marine nitrogen fixation".[22] In the (at least) 7 decades since the light-driven chemical fixation of N_2 was first hypothesized, only three studies have been published in which this process was directly investigated with materials taken from the environment (i.e., soil and sand),[13] so there is certainly room to prospect.

In contrast to reactions like the abiotic fixation of dinitrogen, the one abiotic N transformation that has been vigorously studied in an environmental context is the photochemical generation of ammonium from dissolved and particulate (sediment) organic N. Numerous studies have described this process in water bodies, a process that generates from 0.001 to 1 μM NH_4^+ h^{-1} and can sometimes supply more than half of an ecosystem's bioavailable N.[23] While photoammonification is an established part of aquatic N cycling, it is not yet seriously considered among soil scientists as part of their N cycle, which still gives microorganisms exclusive command of the arrow from soil organic N to ammonium. A related arrow is treated similarly: from the time nitrifying bacteria were discovered, "it has been tacitly assumed that nitrification in soil is entirely a biological process".[24] Given that production of plant-available N is central to terrestrial N cycling inasmuch as it drives primary productivity and other ecosystem processes,[5,10,25−27] another look at N mineralization with abiotic reactions in mind might contribute to this "exciting time to study the soil N cycle".[11] Photochemical mineralization at the soil surface may be particularly significant in dry and/or cold environments, where biological mineralization, normally active throughout a soil profile, is hindered by unfavorable conditions. Non-photochemical abiotic mineralization is, of course, not limited to the soil surface.

Abiotic and biotic N transformations in the environment generally do not depend upon each other, but they are nonetheless connected through coupled biotic−abiotic processes: hydroxylamine and nitrite, for example, are produced by microorganisms but can undergo subsequent abiotic reactions.[28−30] Abiotic and biotic reactions also share some similarities, most conspicuously in that both have periodically challenged long-standing presumptions in the N cycle. When they were first reported, several microbial N transformations, including feammox,[31] respiratory nitrite ammonification,[32] and aerobic or nitrifier denitrification,[33,34] were shown to bypass the pathways previously thought to convert one form into another. Many abiotic reactions do the same thing, such as the direct photochemical conversion of organic nitrogen into nitrite and nitrite into organic nitrogen. Another similarity is found in the connection between elemental cycles: just as there is a biological link between the movement of carbon and N, abiotic N transformations imply simultaneous transformations of carbon whenever organic compounds are involved, as is the case for the incorporation of inorganic N into organic matter and for photochemical dissolution and mineralization.

Despite some similarities, abiotic processes also differ from biotic processes in important ways. Because they operate via different mechanisms, general features of biological processes are not always applicable to their chemical counterparts and vice versa. Biotic and abiotic reactions may consequently drive distinct facets of the same arrow. For example, organic N compounds that are difficult for microorganisms to decompose into ammonium are often quite easily decomposed by sunlight;[23,35,36] both pathways of decomposition constitute N mineralization. Another noteworthy distinction concerns the environmental scope of abiotic and biotic reactions. Although the domain of microorganisms is extensive and diverse, their activity is ultimately limited to a defined spectrum of favorable conditions. Abiotic N transformations are not constrained to the same spectrum, occurring under hot, cold, acid, alkaline, salty, dry, and other conditions where even the most robust microorganisms are dormant at best. Abiotic processes themselves are not without limitations − an obvious example is that photochemical reactions do not occur at night − but their broader potential distribution invites broader (and more interdisciplinary) inquiry concerning their participation in N cycling on a global scale or in some of the Earth's more anomalous environments.

Regardless of the scale or the environment, advances in constructing the N cycle have been most often prompted by advances in microbiology, as novel metabolism is discovered, new explanations are proposed, or fresh calculations of biological processes are presented. The ways in which N moves through most environments indeed constitute a biogeochemical cycle, but biological processes may nonetheless operate in various degrees of "intricate interplay"[37] with an autonomous, strictly geochemical cycle. In general, any aspect of the N cycle for which there is a discrepancy between biological activity and actual observations[38−41] logically suggests the existence of reactions not mediated by biological activity. Allowing for the participation of abiotic reactions has facilitated the solution of puzzles such as that of litter decomposition in deserts, where "the classical ecological paradigm... has limited our imagination for exploring other controls on the cycling of carbon and nutrients".[42] Exploring beyond our limited imagination, then, would certainly sharpen discussions of N cycling, from debates about its regional singularities to surveys of its global trends. More imagination may even expedite more "surprising findings on unanticipated pathways and mechanisms",[11] including, for example, the (re)discovery of abiotic sinks for nitrous oxide (N_2O), which is tenaciously believed to disappear from the Earth's surface only if microbes are available.[10,11,43] One such abiotic sink, the photochemical destruction of N_2O on mineral surfaces, was demonstrated[44] and circumstantially validated[45] in the 1970s but has received only a few passing glances since then.[46−49] This is understandable given that almost no data are available to ponder. Using one measurement of 0.04×10^{-5} molecules of N_2O decomposed on sand per incident photon,[44] and a cumulative solar photon flux (290−700 nm) of 1.2×10^{17} cm^{-2} s^{-1},[50] this process may be grossly estimated to remove several kilograms of N_2O−N ha^{-1} $year^{-1}$ over dry particulate mineral surfaces (i.e., deserts). Using another measurement from the same primary data set, it was proposed that up to 45 Tg of N_2O−N $year^{-1}$ worldwide could be removed.[51] Current understanding of N_2O consumption on land (attributed to biological activity) has been discussed in surveys of studies that indicate removal of up to 40 kg of N ha^{-1} $year^{-1}$,[48] up to about 1 kg of N ha^{-1} $year^{-1}$,[52] or up to 17 (median 0.4) kg of N ha^{-1} $year^{-1}$.[53] Identification and quantification of N_2O sinks at the Earth's surface is an important part of improving the global

N_2O budget,[43,47,48,52−55] and such efforts might benefit from another glance at abiotic phenomena.

In the meantime, meager reservoirs of data permit at best only cursory assessments of the environmental significance of this and other abiotic processes such as immobilization of inorganic N;[29,56−58] studies of biological processes are hundreds of times more abundant than studies of their abiotic counterparts. A recent statement about N trace gases (NTGs)[59] can be extended to practically all of the arrows in the N cycle: "There is general knowledge about the abiotic formation of NTGs, but little is known about the magnitude of these chemical processes in the global N cycle... These abiotic and coupled biotic−abiotic processes are neglected in most studies, although they can occur over a wide range of soil properties at relatively large rates". Almost 200 years before this, Thomas Graham wrote a critical review of abiotic "nitrification",[60] by which nitrate was known to accumulate spontaneously on calcareous minerals exposed to air, a phenomenon that had intrigued other chemists, including Lavoisier.[61] This was in contrast to the prevailing theory, which maintained that nitrate is formed during the (biotic) decomposition of organic matter, and Graham's candid finger still points in the right direction: "There is reason to doubt... the prevailing theory".

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Notes

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