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Review

Reduced nitrogen in ecology and the environment

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Half of industrial ammonia production is eventually lost to the global environment with significant effects.

Abstract

Since the beginning of the 19th century humans have increasingly fixed atmospheric nitrogen as ammonia to be used as fertilizer. The fertilizers are necessary to create amino acids and carbohydrates in plants to feed animals and humans. The efficiency with which the fertilizers eventually reach humans is very small: 5–15%, with much of the remainder lost to the environment. The global industrial production of ammonia amounts to 117 Mton NH_3-N year^{-1} (for 2004). By comparison, we calculate that anthropogenic emissions of NH_3 to the atmosphere over the lifecycle of industrial NH_3 in agriculture are 45.3 Mton NH_3-N year^{-1}, about half the industrial production. Once emitted ammonia has a central role in many environmental issues. We expect an increase in fertilizer use through increasing demands for food and biofuels as population increases. Therefore, management of ammonia or abatement is necessary.

Keywords: Reduced nitrogen; Emission; Nitrogen cycle; Ammonia; Effects; Abatement

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1. Introduction

In 1827 the German professor Von Liebig (1827) reported that about 27 kg/ha free fertilizer was obtained by wet deposition from the atmosphere, which was regarded as so much that additional fertilizer was not necessary to grow plants. Since that time a debate was started on the validity of this number and the start of fertilizer and environmental ammonia research was a fact. Von Liebig appeared to be wrong at that time, overestimating the atmospheric deposition as a result of measurement errors. However, in large industrialized parts of the world the current deposition far exceeds this number as the result of increased intensities of agriculture, industrial processes and traffic. The central role of ammonia in environmental problems is now becoming more widely recognized.

Nitrogen, present in amino acids, proteins, and DNA, is necessary for life. While there is an abundance of nitrogen in nature, almost all is in an unreactive form (gaseous nitrogen, N_2) that is not usable by most organisms. In the absence of human intervention, the supply of reactive nitrogen in the environment is not sufficient to sustain the current abundance of human life. Thus humans learned in the early 20th century how to convert gaseous N_2 into forms that could sustain food production. Over 40% of the world's population is here today because of that capability.

There are two major problems with nitrogen: some regions of the world do not have enough reactive nitrogen to sustain human life, resulting in hunger and malnutrition, while other regions have too much nitrogen (mainly due to the burning of fossil fuel and inefficient incorporation of nitrogen into food products) resulting in a large number of major human health and ecological effects (e.g. Vitousek et al., 1997; Mansfield et al., 1998; Langan, 1999; Erisman et al., 1998a,b; Cowling et al., 2001; Galloway et al., 2003). The rate of

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change of the problem is tremendous, probably greater than that for any other major ecological problem. For example, half of the synthetic nitrogen fertilizer ever used on Earth has been used in just the last 15–20 years. Opportunities to reduce these problems are plentiful. A prerequisite to reduce these problems is the development of a sound scientific base on which to begin to discuss policy options.

The least known part of the nitrogen cycle is the reduced nitrogen form. Reduced nitrogen, such as ammonia, ammonium and amines, is essential in food production, in ecology and also in the environment. Emissions of ammonia to the atmosphere can contribute to particulate matter formation affecting human health, contributing to eutrophication and acidification of aquatic and terrestrial ecosystems after deposition and to nitrous oxide formation, contributing to the greenhouse effect. The scientific basis for reduced nitrogen in ecology and in the environment needs to be strengthened. We here summarize the issues associated with increased ammonia emissions and discuss the need and possibilities for abatement measures.

2. The nitrogen cycle

Nitrogen is an important element – the most abundant constituent of the atmosphere. It is also one of the essential elements for the growth of plants and animals. Reduced nitrogen has a crucial role in ecology and in the environment. It is useful to look at the reactions of elements in the form of a closed cycle. Such a cycle is often termed a biogeochemical cycle because chemistry, biology, and geology all provide important inputs. Cycling of elements is often governed by kinetics and may involve the input of energy, so that chemical equilibrium states are not attained. The ultimate source of energy for driving energetically uphill reactions is the sun. The Earth's surface receives an average radiation input of 100–300 W/m^2/day, depending on latitude. Some of this is captured by photosynthesis, and used to produce high-energy content molecules, such as oxygen.

2.1. Ammonia in the early atmosphere

Before the Earth's crust was formed, we speak of the First Atmosphere, comprising probably entirely of H_2 and He. These gases are relatively rare on Earth compared to other places in the universe and were probably lost to space early in Earth's history because Earth's gravity was not strong enough to hold lighter gases. Once the core differentiated the heavier gases could be retained and the Second Atmosphere was formed mainly by volcanic out gassing. Gases produced were probably similar to those created by modern volcanoes (H_2O, CO_2, SO_2, CO, S_2, Cl_2, N_2, and H_2), NH_3 (ammonia) and CH_4 (methane). No free O_2 existed at this time (not found in volcanic gases). As the Earth cooled, H_2O produced by out gassing could exist as liquid in the Early Archean, allowing oceans to form. Today, the atmosphere is ~21% free oxygen. Produced O_2 levels by breakup of water molecules by ultraviolet were approx. 1–2% current levels. At these levels Ozone (O_3) can form to shield Earth's surface from UV. Photosynthesis combined $CO_2 + H_2O +$ sunlight into the formation of organic compounds and O_2, produced by cyanobacteria, and eventually higher plants – supplied the rest of O_2 to the atmosphere. The amount of O_2 in the atmosphere has increased with time. Chemical building blocks of life could not have been formed in the presence of atmospheric oxygen. Chemical reactions that yield amino acids are inhibited by the presence of very small amounts of oxygen. Oxygen prevents growth of the most primitive living bacteria such as photosynthetic bacteria, methane-producing bacteria, and bacteria that derive energy from fermentation. Since today's most primitive life forms are anaerobic, the first forms of cellular life probably had similar metabolisms. Today these *anaerobic* life forms are restricted to anoxic (low oxygen) habitats such as swamps, ponds, and lagoons.

Whereas the (Second) atmosphere was composed of high concentrations of ammonia, the current atmosphere has a high oxidizing capacity. We learn from the past that volcanic emissions are an important source for ammonia in the atmosphere.

Nowadays the atmosphere contains mostly elemental dinitrogen, along with other trace gases (ammonia, nitric oxide, nitrogen dioxide, and nitrous oxide). Aquatic systems primarily contain soluble forms of nitrogen, such as nitrate and ammonia/ammonium ion, as well as biological nitrogen found in proteins, DNA, RNA, and other compounds that make up living systems. Since lone pairs of electrons on nitrogen are usually basic, ammonia coexists in both the protonated and de-protonated forms near neutral pH. The most important aspect of the environmental nitrogen cycle is the dynamic exchange of species that occurs between the atmosphere and the surface landmasses and oceans. Fig. 1 shows the nitrogen cycle in its most elemental form.

Living systems are essential for maintaining the balance between nitrogen's reduced and oxidized forms. They play an important role in providing reduced nitrogen compounds for the global cycle, by de-nitrification processes (the conversion of nitrate to N_2 and N_2O), biosynthesis (making amino acids, DNA, and RNA), and *nitrogen fixation* (reduction of N_2 to NH_3 by bacteria in root nodules). Nearly all organisms can use ammonia for biosynthesis (*ammonia assimilation*). Ammonia is also a major metabolic end product, as in the bacterial decomposition of dead organisms (*ammonification*). Mammals eliminate ammonia; however, the liver transforms it into the less toxic compound urea before excreting it. Urea, which is prepared industrially at high pressure from the reaction between ammonia and carbon dioxide, is hydrolysed readily in the environment into ammonia and carbon dioxide, which accounts for ammonia emissions from animal feedlots.

Although reduced nitrogen is preferred for biosynthetic reactions, plants have also learnt to capture the nitrogen they need by *assimilatory nitrate reduction.* This was an evolutionary necessity because nitrate is the dominant soluble form of nitrogen in aerated soils. Formation of reduced nitrogen compounds is energetically uphill. Besides plant use of nitrate, its