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A SUMMARY OF THE BIOGEOCHEMISTRY OF NITROGEN COMPOUNDS IN GROUND WATER

JEROLD BEHNKE

California State University, Chico, Calif. (U.S.A.)

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ABSTRACT

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The biogeochemistry of nitrogen compounds in ground waters is exceedingly complex. The exclusive chemical monitoring of nitrates in ground waters is overly simplistic and may lead to errors in data interpretation. Nitrogen compounds are biodegradable and an understanding of the physical, chemical, and biologic systems through which transient water is moving is important in analyzing chemical data. Ground water nitrate contamination is generally encountered in shallow aquifers which have direct or indirect hydraulic continuity with the ground surface. Surface sources of ground water nitrate contamination related to man's activities include domestic sewage, agricultural practices, and high-density animal confinement.

INTRODUCTION

There is an increasing number of articles reporting excessive nitrate concentrations (above 45 p.p.m.) in ground waters appearing in the literature. When I first began investigating ground water nitrate concentrations in 1968 I realized that the biogeochemistry of nitrogen compounds in ground waters is extremely complex and generally poorly understood. Historically, most of the articles in the literature (mine included), have reported only nitrate concentrations emphasizing the cause and effect relationship between nitrate concentrations above 45 p.p.m. and methemoglobinemia (nitrate cyanosis) in infants. This article represents an attempt by the author to briefly summarize the history of nitrogen compounds in the bioshell and to relate nitrates to the biogeochemistry of other nitrogen compounds involved in the nitrogen cycle. Finally, the article summarizes ground water nitrate occurrences, and provides the reader with an updated bibliography on the subject. It is hoped, that this article will provide the reader with a better understanding of nitrates, as they relate to other nitrogen species in naturally occurring waters.

NITROGEN IN THE BIOSHELL

Nitrogen is listed in Group 5 of the periodic table of the elements. Under normal physical-chemical conditions encountered near the earth's surface nitrogen exists as chemical compounds or as the diatomic gaseous molecule N_2.

When nitrogen occurs as a compound, it is attached to from one to four atoms. In natural waters, nitrogen often forms a compound by attaching to 2, 3, or 4 adjacent atoms. Examples of nitrogen compounds found in naturally occurring waters include, ammonia (NH_3), nitrite (NO_2^-), nitrate (NO_3^-), and the ammonium ion (NH_4^+). Nitrogen is also found in many organic compounds such as proteins and protein derivatives including purines and pyrimidines, and urea. Generally, inorganic nitrogen salts are quite soluble in natural waters.

Many experts estimate our planet to be from 5 to 10 billion years old. Scientists generally agree that approximately 4 billion years ago a primoidal atmosphere developed from gasses emanating from the earth's interior. Hutchinson (1944) believes that one of the main gaseous constituents of the initial atmosphere was ammonia. Other experts speculate that approximately 2 to 3 billion years ago, organic molecules were formed by non-biologic activities using electrical discharges (lightning) or sunlight (electromagnetic radiation) as energy sources for chemical reactions. Some biochemists believe that amino acids and other complex nitrogen compounds were originally synthesized in this manner. Once formed, these organic and inorganic nitrogen compounds and molecules slowly accumulated in warm, shallow, primoidal oceans. It is estimated that approximately 2 billion years ago, living organisms evolved from this nitrogen-rich ancestral ocean.

As life continued to evolve, green plants emitted oxygen via photosynthesis and our ancestral atmosphere, composed primarily of methane (CH_4) and ammonia (NH_3) became oxygen (O_2) enriched. As living organisms further evolved, nitrogen became incorporated in biochemical transformations.

Plants consumed inorganic nitrogen compounds and synthesized organic, nitrogen compounds such as proteins. Animals consumed the plant proteins transforming them into animal proteins. After death, plant and animal proteins are biologically decomposed into simpler inorganic forms of nitrogen primarily by the activities of bacteria and fungi. In this fashion the Nitrogen Cycle began, and millions of years later our atmosphere attained its current nitrogen level of 78.09 percent by volume.

Table I shows the estimated geochemical distribution of nitrogen after Bartholomew and Clark (1956). Table I shows that most of the nitrogen (98.03%) is incorporated in the earth's soils and rocks. Atmospheric nitrogen accounts for only about 1.96% of the nitrogen in the total earth system.

In natural waters, nitrogen compounds generally occur in the three following ionic forms: ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-). The action of microorganisms transform gaseous, atmospheric nitrogen, into fixed forms such as ammonium and nitrate. Still other microorganisms are able to denitrify

TABLE I

Geochemical distribution of nitrogen*

Shell distribution	Amount of nitrogen in each geoshell (tons)	Nitrogen percent contained in each geoshell
Atmoshell	$4.25 \cdot 10^{15}$	1.96
Lithoshell	$2.127 \cdot 10^{17}$	98.03
Bioshell	$1.804 \cdot 10^{11}$	0.01

*After Bartholomew and Clark (1965).

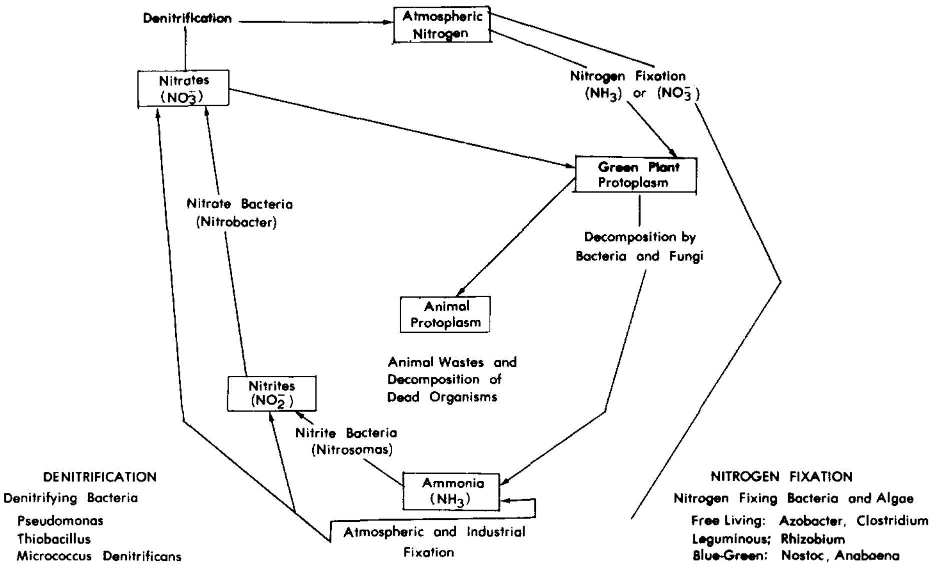

Fig. 1. The nitrogen cycle.

fixed nitrogen back into gaseous forms such as nitrous oxide and free nitrogen.

As Fig.1 suggests, the chemical species nitrogen encountered in underground waters is related primarily to the type of soil microorganisms present, the physical-chemical conditions in the soil-water matrix, and the transient history of the ground water as it moves from recharge to discharge areas. In natural systems, the dynamics of nitrogen transformations are further modified by additional variables such as rainfall, temperature, evaporation, infiltration and percolation rates, and the type of plant cover present in the system.

NITROGEN SPECIES IN NATURE

The relationships between various chemical nitrogen species in water are diagramatically represented in Fig. 2.

Molecular, atmospheric nitrogen may be transformed into organic nitrogen by nitrogen fixing bacteria and algae. Therefore, natural waters may contain dissolved nitrogen gas (N_2), ammonia (NH_3), in addition to ionic forms such as ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) as well as organic nitrogen compounds. Sources of ammonia include decomposition of dead plant and animal material, release from organic soils, and complex photochemical reactions in the lower atmosphere. Rainfall generally contains larger amounts of ammonia than oxides of nitrogen unless the lower atmosphere has been significantly contaminated by gasses from internal combustion engines.

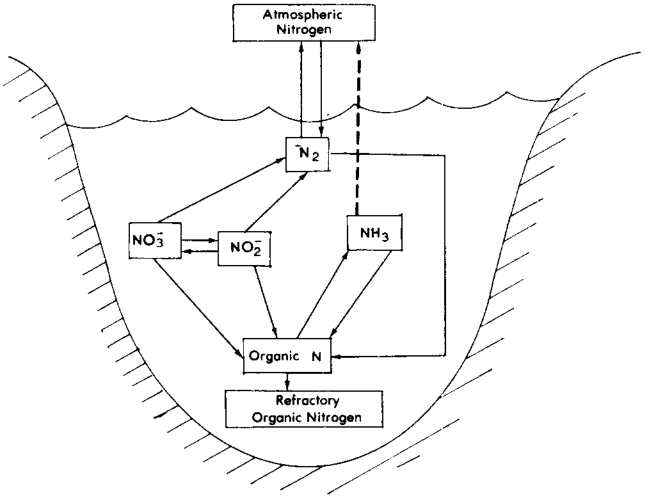

Fig. 2. The nitrogen cycle in water.

Only a few species of bacteria and algae can directly use molecular nitrogen. Generally, most plants use organic nitrogen, ammonia, nitrite, or nitrate for protein synthesis. Animals cannot exclusively use inorganic nitrogen for protein synthesis and they therefore must consume organic nitrogen contained in plants and/or other animals. When plant and animal material aerobically decomposes, organic nitrogen is biologically converted to other nitrogen species by autotrophic, nitrifying bacteria. Ammonia may be partially oxidized to nitrite or more completely oxidized to nitrate. Within the root zone, nitrates may be utilized directly by plants as a source of nitrogen, or under anaerobic conditions (little or no oxygen present) the nitrates may be reduced by heterotrophic denitrifying bacteria to nitrite and eventually to gaseous nitrogen.

CONCENTRATIONS OF NATURALLY OCCURRING NITROGEN SPECIES

With the exception of gaseous N_2, most of the nitrogen existing near the earth's surface is organic nitrogen. Inorganic nitrogen compounds seldom exceed a concentration of a few parts-per-million (generally less than 10 p.p.m.) in uncontaminated natural waters. Ground waters have attained concentrations of more than 100 p.p.m. where inorganic nitrogen compounds are not subject to biologic uptake or bacterial conversion.

The bulk of the nitrogen in domestic wastewaters is in the form of ammonia (NH_3) or ammonium (NH_4^+). These two forms will be rapidly oxidized to nitrites and nitrates in the presence of oxygen and autotrophic bacteria.

Agricultural drainage waters may contain nitrate concentrations in excess of 100 p.p.m. Even higher concentrations may be encountered in subsurface drainage waters which dissolve the highly soluble nitrate nitrogen formed by the oxidation of ammonia nitrogen in percolating waters by autotrophic bacteria. Feth (1966) indicated an average nitrate concentration of 0.8 p.p.m. for U.S. rivers. Hutchinson (1957) believes that the two most important nitrogen species in lakes are nitrates and organic nitrogen.

PHYSICAL—CHEMICAL PROPERTIES OF THE VARIOUS NITROGEN SPECIES

Elemental nitrogen

Elemental nitrogen occurs as a diatomic molecule N_2. Gaseous nitrogen is considered inert chemically. Fig. 3 shows the solubility—temperature relationships for molecular nitrogen.

At 20°C, 15 p.p.m. molecular nitrogen would be found in surface waters. This relatively high concentration is generally of little consequence because of the chemical inertness of molecular nitrogen. However, molecular nitrogen

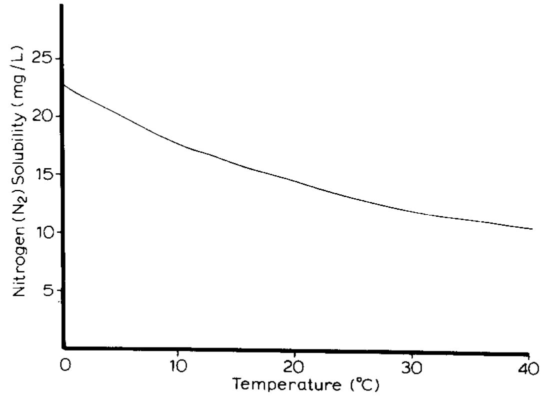

Fig. 3. Solubility of molecular nitrogen in equilibrium with dry air at 1 atm of pressure.

may be reduced by heterotrophic bacteria or used in the cellular material of blue-green algae.

Ammonia nitrogen

Ammonia is highly soluble in water. At 20°C and 1.0 atmosphere pressure, approximately 525 g/l of ammonia will dissolve in water. When ammonia reacts with water, it forms ammonium and hydroxide ions according to the following reaction:

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \qquad (1)$$

Fig. 4 shows that pH is a critical factor in determining which nitrogen species, ammonia or ammonium, will be present in water.

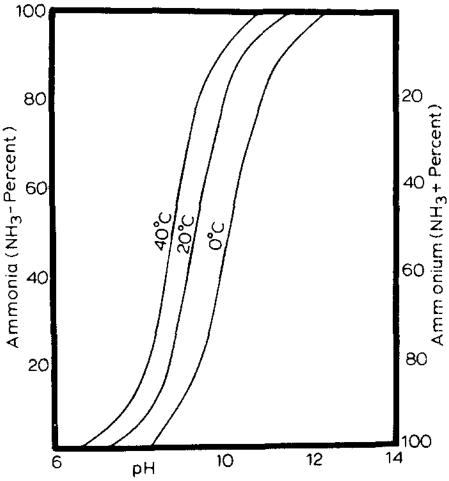

Fig. 4. Effect of pH and temperature on the distribution of ammonia and ammonium ion in water.

Ammonia (NH_3) is present at high pH's while ionic ammonium (NH_4^+) is present at low pH's. This is why wastewaters are adjusted to a high pH before ammonia stripping towers are used in advanced waste treatment.

Ammonia and ammonium tend to be absorbed by clay particles in soils. In fact, the ammonium ion will generally displace other monovalent cations already occupying absorbtion sites on clay particles.

At a neutral pH (7.0) in most surface waters, ammonium will be converted to other nitrogen forms by biologic action (bacteria and plants). A species of autotrophic bacteria called *Nitrosomas* are especially effective in converting ammonium to nitrite according to the following equation:

$$NH_4^+ + 3/2\ O_2 \longrightarrow NO_2^- + 2H^+ + H_2O \qquad (2)$$

The nitrification process depends primarily upon the presence of oxygen, temperature, pH, and concentration of nitrifying organisms in the soil or water system. Therefore, in lakes having long retention times, and in well aerated surface soils containing slowly percolating waters, one would expect that most of the organic ammonium would be converted to nitrites or nitrates.

Nitrite nitrogen

Nitrite nitrogen is a rather unstable nitrogen species which will generally be reduced or oxidized. Nitrite nitrogen seldom exists in surface waters in concentrations as high as 1.0 p.p.m. The bacteria *Nitrobacter* will take the nitrite formed in eq. 2 and further oxidize it to nitrate according to the following equation:

$$2\,NO_2^- + O_2 \longrightarrow 2\,NO_3^- \qquad (3)$$

In the absence of oxygen, nitrates may be reduced to nitrites by heterotrophic bacteria. This process is called denitrification, and the end product is molecular nitrogen.

Nitrate nitrogen

Nitrate nitrogen is quite soluble in water and is not significantly absorbed by clay-rich soils. It represents the stable end product of the nitrification process. Nitrates are quite stable unless they are biologically denitrified under anaerobic conditions or taken up by plants.

Organic nitrogen

Organic nitrogen is generally formed and decomposed by biologic activity. The most common forms of organic nitrogen include proteins and protein derivatives such as purines and pyrimidines, and urea. Globular proteins, the major components of muscle tissue, tend to be biodegradable. Urea, formed during the degradation of proteins or amino acids, is enzymatically hydrolyzed in natural waters into ammonia and carbon dioxide. This explains why urea-derived nitrogen (ammonia) is readily available to the plant community.

NITROGEN STANDARDS FOR WATER

Although nitrogen contamination of natural waters may result from dissolved organic and/or inorganic nitrogen species, nitrate is commonly monitored and generally accepted as the primary pollution parameter. Nitrates represent the end products of the biologic nitrification process. It should be noted that septic tank waters would contain essentially no nitrates because the nitrogen species in this water would be ammonia or ammonium, however, the soil-water immediately outside the leach line in a well aerated soil may contain nitrates in excess of 100 p.p.m.

Elevated nitrate concentrations in drinking water create a human health hazard illustrated by a disease known as methemoglobinemia or nitrate cyanosis. This disease is caused by the bacterial reduction of nitrate to nitrite in the intestinal tract. The nitrite then enters the blood-stream and combines with the hemoglobin to form methemoglobin, which reduces the blood's capacity to transport oxygen. The reduction to nitrite occurs primarily in infants because their gastric juices are more nearly neutral in pH than those of adults and provide a better environment for nitrogen-reducing bacteria. In its uncomplicated acute form, methemoglobinemia is generally easily diagnosed and its treatment understood (National Academy of Sciences Report, National Research Council, 1972).

The United States Public Health Service (USPHS) Drinking Water Standards (Anonymous, 1972) recommends a limit of 45 p.p.m. nitrate or 10 p.p.m. nitrogen. Moreover, the USPHS recommends that at this concentration the public should be warned of the potential health hazard associated with using the water for infant feeding. The California Department of Water Resources Bulletin 143-6 states that nitrate concentrations exceeding this standard are not uncommon. California has recommended nitrate limit of 45 p.p.m. and mandatory limit of 90 p.p.m. Most methemoglobinemia cases reported in the U.S. and Europe have been associated with waters containing more than 50 p.p.m. nitrate. The bulk of the reported cases involve shallow wells located near barnyards, irrigated fields or domestic waste disposal facilities.

The National Academy of Sciences (1972) compiled statistics on incidence of methemoglobinemia and reported source of nitrate or nitrite which caused the disease. Throughout the United States, 278 cases caused by well water nitrate were reported for the years 1945 through 1950 resulting in 39 known deaths. For the year 1952—1966, forty cases were reported with no fatalities; and for 1960—1969, approximately 10 cases are reported with no fatalities. Other cases of methemoglobinemia were attributed to nitrates obtained from food.

NITRATES IN GROUND WATERS

Elevated nitrate concentrations have been encountered in ground waters at many locations. Most of these ground water bodies were in direct or indirect hydraulic continuity with decaying plant or animal material, agricultural fertilizers, domestic sewage, areas of high density animal confinement, or geologic materials containing soluble nitrogen compounds.

Nitrate and nitrite anions are not absorbed by clay soils because both the soil particles and the anions have a negative charge. The ammonium ion however, carries a positive charge and will be adsorbed on the surface of negatively charged soil particles. Ammonium ions electrostatically bound to negatively charged clay particles may be oxidized via the action of microorganisms, and resulting negatively-charged nitrite or nitrate ions are then free to migrate with the percolating soil waters.

Nitrate reported in a chemical analysis would include nitrate originally present in the water but, also, could include oxidized ammonia, ammonium, and nitrite originally present. Ammonium has been found in thermal waters, and, unless proper sampling and analysis techniques are used, will tend to oxidize and be reported as nitrate (Robertson and Whitehead, 1961).

Summary of elevated nitrate concentrations in ground waters

Minnesota

Schroepfer and Preul (1964) describe the movement of nitrogen species in laboratory soil columns and beneath waste stabilization ponds in the field. They further state that by 1964, Minnesota had experienced over 200 cases of methemoglobinemia. They also found indications that there were no cases of methemoglobinemia associated with waters containing nitrate concentrations less than 45 p.p.m. Schroepfer and Preul (1964) felt that the primary cause of the nitrogen contamination of ground waters was the release of nitrogen bearing waste waters at or near the ground surface. They considered soil absorption systems for septic tanks, waste stabilization ponds, waste treatment plant effluents, sludge lagoons, irrigation systems, privies, barn yards, leaking sewers, and agricultural fertilizers as sources of nitrogen contamination.

Delano, California

Nitrate concentrations in ground water used by the City of Delano, were in excess of the 45 p.p.m. recommended by the USPHS as reported by the California Department of Water Resources in their Bulletin No. 143-6 (1968). They concluded that nitrate of undetermined origin was being transported to ground water by water applied at the ground surface. As a temporary solution, Delano pumped only wells which contained lower nitrate levels.

Fresno, California

Behnke and Haskell (1968) and Schmidt (1970) discuss ground water nitrate concentrations beneath the City of Fresno. Behnke and Haskell (1968) constructed a ground-water nitrate contour map beneath a portion of the City of Fresno. The nitrate contour map showed two areas having elevated nitrate concentrations. One of these areas was overlain by a subdivision containing septic tanks and leach fields and the other by sewage treatment plant oxidation ponds.

Nightengale (1970) studied historical ground water nitrate trends beneath urban and agricultural zones in the Fresno area. He found that nitrates were increasing faster beneath the agricultural areas than they were beneath the urban areas.

Grover City — Arroyo Grande, California

Stout et al. (1965) compared ground water nitrate accumulations beneath a sewage treatment plant, cropped areas and areas having native vegetative cover. Stout (1965) found many wells within his study area had nitrate concentrations near 100 p.p.m. He also stated that the sewage waters of the basin contained an average nitrogen concentration of 172 p.p.m. NO_3^- equivalent. He also found high nitrate concentrations in the soil solution beneath cropped and uncropped areas. Stout (1965) stated that on an area basis, legume plant covers (such as alfalfa) can fix 880 lbs. NO_3^- per acre, per year, while grass covers fix from 44 to 132 lbs. NO_3^- per acre, per year.

South Platte Valley of Colorado

Stewart et al. (1967) encountered similar nitrate concentrations in shallow soil profile beneath areas cropped to alfalfa and areas covered by native grasses. In the uppermost 22 ft. of soil, they found 62.5 lbs. per acre nitrate-nitrogen beneath alfalfa (*Medicago sativa*) and 72.3 lbs. per acre beneath native grass cover. They encountered nitrate concentrations ranging from 26 p.p.m. to 50 p.p.m. in the uppermost 0.44 ft. of the soil profile.

Their chemical examination of the soil profile did not extent to depths greater than 39.4 ft. The authors cite a hydraulic conductivity of 2.5 cm/yr. (0.99 inch/yr.) for both sod and cultivated areas. This low value of $0.79 \cdot 10^{-7}$ cm/sec indicates a surface limiting condition in terms of downward water percolation probably due to soils having high clay contents. Their nitrate distribution with depth profiles for irrigated fields and cultivated dryland fields further indicate a surface limiting condition involving thick, clay-rich, surface soils.

Coachella Valley, California

Oertli and Bradford (1973) studied nitrate concentrations in drainage waters from cropped fields under different types of agricultural management practices. They found high nitrate concentrations in drainage waters associated with the cultivation of corn, carrots and asparagus, and lesser concentrations associated with the growing of grapes and citrus crops. The White River draining the valley receives most of its flow from agricultural and sewage effluents. The concentration of nitrates in the White River increases approximately 100 fold over a 12.4 mile distance.

Upper Santa Anna River Basin, California

Perhaps one of the most comprehensive ground water nitrogen investigations ever undertaken was conducted by Ayers and Branson et al. (1973) in the Santa Anna River Basin. They established nitrogen pools and fluxes for the 356,000 acre Upper Santa Anna River Basin. They concluded that most of the high nitrates encountered in the Basin's ground waters were associated with open, permeable soil profiles and irrigated agriculture using chemical fertilizers. Citrus is the major crop grown within the basin.

Bushland, Texas

A study conducted by Scalf et al. (1969) at Bushland, Texas, is interesting, because he found that after recharging, it was possible to recover 94 percent of the recharged water and nitrates by pumping the recharge well. This indicates that because ground water movements are relatively slow, shallow wells located within cropped areas, intentionally or non-intentionally can be efficient collectors of leached nitrogen.

SUMMARY OF NITRATE OCCURRENCES IN GROUND WATERS

Reported sources for ground water nitrate contamination include decaying plant and animal material, organic sediments, agricultural fertilizers, domestic sewage, and areas of high density animal confinement. Nearly all the reported cases of excessive nitrate build-ups in shallow ground waters appear to be related to the downward leaching of nitrogen by surface water. The downward leaching of surface water requires a relatively open geologic profile between the ground surface and the water table. Once the nitrates reach the water table, they generally form a thin layer (usually less than 10 ft.) capping the shallow ground water body. The literature indicates that deep wells (deeper than 500 ft.) show little or no evidence of nitrate contamination. Most of the reported instances of nitrate contamination appear to be related to irrigated agriculture and the use of chemical fertilizers or to domestic sewage.

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