Sources of Nutrients in Wastewater

Dr. Peggy Minnis, Pace University

Man is part of the biogeochemical cycle. The materials of the Earth enter the human system, just as they do with most other living creatures. The chemical composition of the human body is similar to other mammals and the dietary requirements are about the same. Much of what is ingested is converted into body mass and energy. The rest is rich in nitrogen and phosphorus, which is the topic under consideration.

With centralized sewers, there was a belief that, given enough money, most water pollutants could be removed. As the treated water became cleaner, it became increasingly difficult and expensive to remove the remaining pollutants. Depending upon where the treated effluent was finally released, the focus has shifted from removing the organic component to nutrient reduction. This is especially true in sensitive watersheds, where a freshwater lake or saltwater area is impacted by the nutrients. In my home area, on Long Island Sound, nitrogen is the limiting algal nutrient. In places where the effluent goes into fresh water, phosphorus is the limiting algal nutrient.

As a result, there has been an active interest by wastewater professionals on nutrient reduction in wastewater treatment plants. They seem to have a good handle on removing phosphorus, since insoluble precipitates are easily formed. But, nitrogen remains a constant challenge. There are many methods, all of which require picky families of microorganisms to convert chemically-combined nitrogen (ammonia, nitrate, nitrite) through an intricate process to nitrogen gas that goes back into the atmosphere. The municipal wastewater treatment people are constantly trying to improve nitrogen removal through sometimes very innovative methods. Since onsite wastewater treatment systems will probably increase in numbers in the future, nitrogen has become a large concern.

What are Phosphorus and Nitrogen?

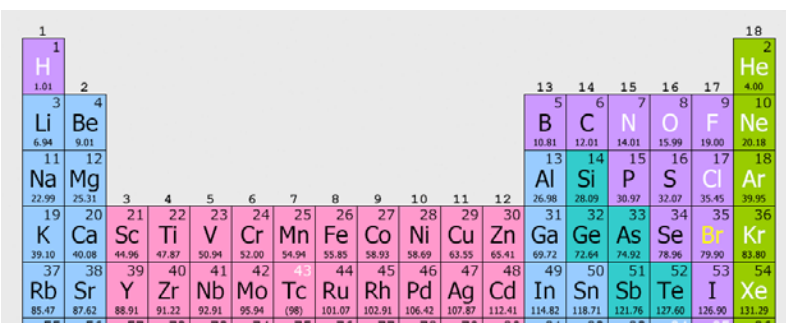


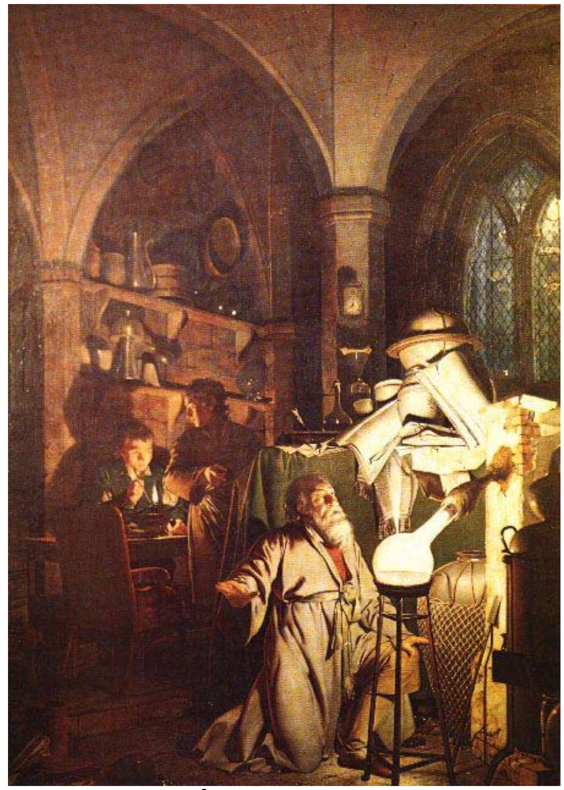
Figure 1 – Part of the Periodic Table

Before we begin to discuss the sources of nitrogen and phosphorus in wastewater, it's important that we all understand the nature of these elements.

Figure 1 is a portion of the Periodic Table. The numbers on the upper right of each square indicate how many protons there are in the nucleus of each element and are called the atomic numbers. Nitrogen is #7 and Phosphorus is #15. You will notice that they occur in the same column of the periodic table and are said to be in the same family, the Nitrogen Family. Both of them have five electrons in their outer shell, but phosphorus is a larger atom and has more bonding options than nitrogen does. They can form similar compounds with other elements. Both are considered essential for most plant and animal life and are called macronutrients. Let us look at each of these elements in a little more depth.

Examining the Elements Phosphorus and Nitrogen

Phosphorus



In 1669, Henning Bran, a German merchant in Hamburg who was also an amateur-alchemist, was the first to obtain elementary phosphorus. He had boiled down 60 buckets of urine, collected over many weeks, and kept it away from air. He discovered a snow-white substance at the bottom of the container. This substance burned with a dark and choking smoke. The most interesting thing about that substance was that it also glowed in the dark and Bran was able to read by its light. The name of phosphorus is Greek in origin, meaning "it possesses brilliance". So, in 1669 a chemical element was discovered when an alchemist was trying to turn urine into gold. Figure 2 shows a painting is by Joseph Wright of Derby, England that depicts this great discovery.[i]

The method of producing phosphorus by evaporating urine was used until 1775, when it began being extracted from bones. In 1769, bones had been found to contain calcium phosphate ($Ca_3(PO_4)_2$).[ii]

Phosphorus is usually combined with oxygen as the orthophosphate (PO_4^{-3}), shown in Figure 3. This polyatomic molecule has a tetragonal shape and an overall electrical charge of –3. The free phosphate ion does not survive long in solution. It is either taken up rapidly by living organisms in the water or it precipitates out with various positively-charged metal ions may be in solution. For example, a common way of removing the phosphate ion is to use Alum ($Al_2(SO_4)_3$) to turn soluble phosphate into insoluble aluminum phosphate ($AlPO_4$**)**

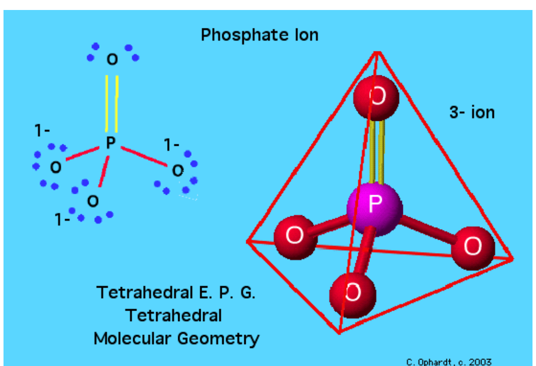


Figure 2 – The Structure of the Phosphate Ion.

Phosphorus in our bodies

Phosphorus makes up about 1% of bodyweight and 85% of phosphorus in the body occurs in bones and teeth. Almost every food contains phosphorus, since phosphate is also needed for plant and animal growth.

Phospholipids are major structural components of cell membranes. Energy production and storage are dependent on phosphorus-containing compounds, such as adenosine triphosphate (ATP) and creatine phosphate. Nucleic acids (DNA and RNA), responsible for the storage and transmission of genetic information, are long chains of phosphate-containing molecules. A number of enzymes, hormones, and cell-signaling molecules depend on phosphorus-based reactions for their activation. Phosphorus also helps to maintain normal acid-base balance (pH) in its role as one of the body's most important buffers. The phosphorus-containing molecule 2,3-diphosphoglycerate (2,3-DPG) binds to hemoglobin in red blood cells and promotes oxygen delivery to the tissues of the body.

Dietary phosphorus is readily absorbed in the small intestine, and any excess phosphorus is excreted into urine by the kidneys. Children need about 0.5g phosphorus per day and adults need 0.8g - 1.2g/day. We excrete about 3-4g/day, depending upon what we have eaten. Table 1 shows the percentage of phosphorus in various foods.

Table 1[iii]
Phosphorus content of Foods

Food	**Serving**	**Phosphorus (mg)**
Milk, skim	8 ounces	247
Yogurt, plain nonfat	8 ounces	383
Cheese, Mozzarella;	1 ounce	131
Egg	1 large, cooked	104
Beef	3 ounces, cooked	173
Chicken	3 ounces, cooked	155
Turkey	3 ounces, cooked	173
Fish, halibut	3 ounces, cooked	242
Fish, salmon	3 ounces, cooked	252
Bread, whole wheat	1 slice	64
Bread, enriched white	1 slice	24
Carbonated cola drink	12 ounces	44
Almonds[#]	1 ounce	139
Peanuts[#]	1 ounce	101
Lentils[#]	1/2 cup, cooked	356

[#]Phosphorus from nuts, seeds, and grains is about 50% less bioavailable than phosphorus from other sources

Nitrogen

Daniel Rutherford, a medical student in Scotland, was the first to publish the discovery of nitrogen in 1772. Joseph Priestley, Henry Cavendish and Carl Wilhelm Scheele also discovered it about the same time. Antoine Lavoisier first recognized the gas as an element and called it azote (Greek - "without life") because of its inability to support life. The name nitrogen, from "nitre" (saltpetre, or potassium nitrate KNO) plus "gen" (forming), was coined in 1790.[iv]

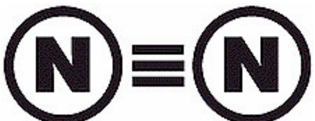


Figure 3 – Nitrogen gas, showing the triple bond

The element nitrogen does not normally exist as a single atom, but is usually combined with another nitrogen atom very tightly in a triple bond, as shown in Figure 4. This molecule, nitrogen gas, N_2, is the predominant gas in our atmosphere, making up over 79% of air. The bond is so tight that it is only broken by very energetic natural events, like lightening. When this happens, and it happens often, various compounds of nitrogen and oxygen are formed in a process called *nitrogen fixation*. Sometimes, fixed nitrogen is called *reactive nitrogen*. The most oxidized form is called nitrate. The nitrate ion is another polyatomic ion and it has a net charge of –1. Figure 5 shows the geometry of the nitrate molecule. It, like phosphorus, is in a tetragonal configuration, but there is an unshared pair of electrons taking up one corner of the tetrahedron.

Nitrogen can also be fixed by natural processes in the soil and in water. Blue-green algae can fix gaseous nitrogen and several plants can fix nitrogen through the nodules on their roots, as shown in Figure 6.[v]

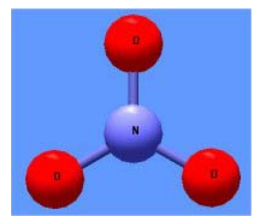


Figure 5 – the Nitrate ion

The amount of nitrogen in the environment for plant fertilization was limited to natural nitrogen fixation and to the mining of limited deposits of guano. Therefore, food production was limited because of the unavailability of fixed nitrogen.

Figure 6 – the roots of a legume, showing nitrogen-fixing nodules

The Growth of Agriculture

A paper on the increase in the amount of reactive nitrogen in the environment was written by James N. Galloway of the University of Virginia and Ellis B. Cowling at North Carolina State University. They reviewed the growth in reactive nitrogen in the environment from 1890 to the present.[vi] The crucial event, around 1908, that created the beginnings of a dramatic increase and sparked the growth of agriculture was the work of Fritz Haber. By using high temperature, high pressure, and an iron catalyst, Haber could force relatively unreactive gaseous nitrogen and explosive hydrogen gas to combine into ammonia. This furnished the essential precursor for many important substances, particularly fertilizers and the explosives used in mining and warfare. He received the Nobel Prize in 1918 for his discovery.

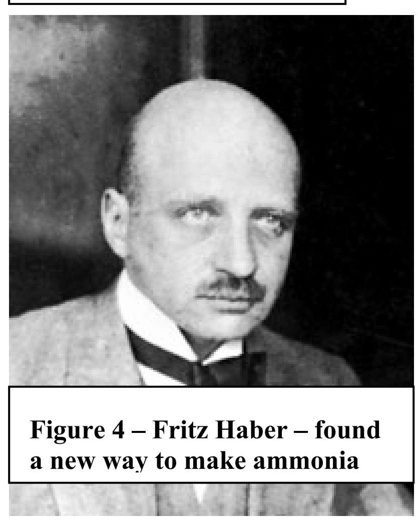


Figure 4 – Fritz Haber – found a new way to make ammonia

Galloway and Cowling reported that the change in reactive, available nitrogen in the environment has spiraled upwards since Haber's discovery. They also tracked how reactive nitrogen moves through the food chain. Their net finding was that only 4% of the reactive applied nitrogen actually winds up being ingested by humans as food. The rest of it enters the environment and causes a multitude of problems, including acidifying soils and providing the limiting nutrients for oceanic algae blooms. So, clearly the production of reactive nitrogen by artificial means has had serious consequences for man, both good and bad.

Nitrogen in Foods

Nitrogen in foods comes from amino acids in protein and from purines, pyrimidines, free amino acids, vitamins, creatine, creatinine, and amino sugars. The amount of nitrogen in foods varies over a wide range. But, it's hard to chemically analyze for proteins and other nitrogen-based molecules. Not all the nitrogen in food is protein, but most proteins are between 13-19 percent nitrogen. The usual way to test for nitrogen is by the Kjeldahl method to determine total nitrogen and then use a multiplier to estimate the amount of protein. .[vii] The 1896 USDA Bulletin #28 shows the protein content of almost every food imaginable at that time, which is shown in Table 2.

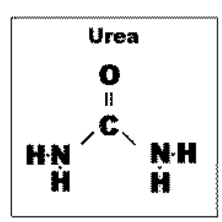
Table 2[viii]
Protein Content of Various American Foods (percentage, based on 6.35 x TKN)

Food	Percentage Protein
Carrots	2
Eggplant	1.2
Peas	2.2
Lettuce	1.8
American cheese	28.8
Flour	7 – 14
Beef	10-25
Chicken	~22
Bass	18
Whole Milk	8.8
Skim Milk	8 .4
Condensed Milk	24.2
Eggs	17.4

Nitrogen in Human Bodies

The average human body needs roughly 2.0 grams of nitrogen per day. However, most humans consume much more nitrogen than would be needed for the building of proteins. The typical American diet supplies approximately 13 grams of nitrogen per day. So, approximately 11 grams will go into the waste stream.

Nitrogen gets into wastes because proteins contain amino acids and they are constantly being broken down in the body. The amino acids have to break down in order to be excreted. There is an important cycle that regulates this process.



When an amino acid breaks down, it turns into an acid and ammonia. Ammonia is a toxic base that would be fatal to us if the liver were not able to quickly convert the ammonia, along with carbon dioxide, to the less toxic urea. This is excreted in the urine. Along with proteins that are flushed into the wastewater from kitchen sources, ammonia is the prime nitrogen source in wastewater.

Wastewater Constituents

We turn our attention now to wastewater and the nutrients that can be generated in a household to eventually become a part of the onsite system effluent. We will review the general sources of nutrients in the materials that are sent down household drains.

Some interesting data tracks how much human excrement enters the wastewater stream per day. Rein Laak from UCONN reviewed multiple sources of data and found the average amount of excrement produced by a person per day, shown in Table 3. Obviously, there can be wide fluctuations, but this takes into account all kinds of people, from children to adults.

Table 3[ix] Average Per Capita Human Excrement per Day	
Feces	120 grams 4.4 ounces
Urine	1.1 Liter 2.3 pints

A more recent study was done in Thailand to assess the value of human excrement as a fertilizer and they noted about the same numbers[x]. They noted that there was little variation among humans, except that older people larger amounts of total wet matter than younger people, probably because they drank more water to avoid constipation.
Accepting these figures as the average value per person per day, let us look at Table 4 to see how the chemical composition of these two substances line up with respect to nutrients:

Table 4[xi]
Pollution Character of Excrement in grams

Excrement Type	BOD_5	Total Nitrogen	PO_4^{-3}
120 grams feces	12	1.2	0.36
1.1 liter urine	11	11	3.30

Characteristics of Wastewater

The character of wastewater varies widely. Many researchers have quoted figures and the EPA 1980 Design Manual takes into account that variability.[xii] Table 5 shows the average strength of residential wastewater going into a septic tank.

Table 5[xiii] Characteristics of Typical Residential Wastewater	
	Concentration in Water mg/Liter
BOD_5	200-290
Total Nitrogen	35-100
Ammonia	6-18
Nitrates and Nitrites	<1
Total Phosphorus	18-29
Phosphate	6-24

Table 6 shows the average strenth of wastewater coming from different household fixtures. If you look, then at the different water-using fixtures in a house, you have a different way of looking at nutrient sources. It is obvious that the use of a garbage disposal should be avoided if nutrients are a problem.

Table 6[xiv] Concentration of Pollutants from Household Fixtures (mg/L)			
	BOD_5	Total Nitrogen	PO_4^{-3}
Toilet	300	200	100
Bath	200	2	1
Bathroom Sink	200	2	1
Kitchen	700	5	10
Laundry	300	10	1
Garbage Disposal	2380	79	13

*check figures

Other Sources of Nutrients

Besides excreting, people do other tasks around the house that can contribute to the nitrogen and phosphorus loading in a wastewater system. Phosphates in detergents were effective sequestering agents for dissolved mineral ions found in hard water. They were also used to avoid dirt being re-deposited on clothing. Laundry detergents contained high amounts of phosphates in the 1960s, but the formulations were changed to remove them in response to clean water regulations. In the clothes washing machine, even with phosphorus-free detergent, there is the likelihood that children's pajamas treated with flame retardants can leach out phosphorus. Many of these flame-retardant products, as showin in Table 7 are phosphate compounds and they wash out easily.

Table 7
Organo-phosphorus Flame retardants.[xv]

- Triphenyl phosphate
- Tricresyl phosphate
- Resorcinol bis(diphenylphosphate)
- Phosphonic acid, (2-((hydroxymethyl)carbamyl)ethyl)-, dimethyl ester
- Phosphorus and nitrogen constituents for thermosets

At the time the Clean Water regulations were written, few people had automatic dishwashing machines. Trisodium phosphate is the effective cleaner in dishwashing detergent. Dishwasher detergent contains 0.8 grams of phosphate per tablespoon. The concentrated dishwasher detergent tablets contain 1.75 grams of phosphate. It has been estimated that adding one gram of phosphate to a waterbody can grow 400-700 grams of green algae.[xvi]. There are non-phosphate options and these clearly should be used in sensitive environments.

Illinois Association of Wastewater Agencies introduced a bill in the Illinois General Assembly this year to help control problems with phosphorus in waterbodies, intended to limit phosphorus in cleaning agents used by businesses and homeowners.[xvii] This action may be necessary in other districts.

Many people also use ammonia liberally for cleaning, which is a non-toilet source of nitrogen. If you check the labels on products used around the house, you will find that ammonia figures prominently in many cleaners.

Conclusion

In conclusion, there are many inevitable sources of nutrients in the wastewater from a household. The amounts can be calculated. There are other sources of nutrients that can be eliminated or minimized, depending upon the watershed needs. It is important to understand the practices of the household in order to estimate the nutrient output. As an example, a friend spends most of his day at his job in the City and only liquid wastes enter the system, but he washes clothes and uses the dishwasher. Next door to him, there is a family of four that spends much of their time at home. While the houses look identical, the wastewater from each is very different.

References

[1]http://www.metaweb.com/wiki/wiki.phtml?title=Stephenson:Neal:Quicksilver:18:...a_specimen_of_white_phosphorus..._(Alan_Sinder)
[1] ibid.
[1] http://lpi.oregonstate.edu/infocenter/minerals/phosphorus/
[1] http://www.historyoftheuniverse.com/nitrogen.html
[1] http://helios.bto.ed.ac.uk/bto/microbes/nitrogen.htm
[1] Galloway, James N. and Cowling, Ellis B. "Reactive Nitrogen and the World: 200 Years of Change." Ambio Vol 31 no. 2, March 2002, pp. 64-71.
[1] Jones, D. Breese, "Factors for Converting Percentages of Nitrogen in Foods and Feeds into Percentages of Proteins" USDA Circular No. 183, August 1931, revised February 1941.
[1] http://www.nal.usda.gov/fnic/foodcomp/Data/Classics/es028.pdf USDA Bulletin #28, 1896.
[1] Wagner, E.G. and Lanois, J.N., Excreta Disposal for Rural Areas and Small Communities, Geneva, Switzerland: World Health Organization (1958)
[1] Schouw, N.L, Danteravanich, S., Mosback, H., Tjell, J.C. "Composition of Human Excreta – a Case Study from Southern Thailand." Science of the Total Environment 2003 Mar8;286(1-3):155-66.
[1] Laak, Rein, Wastewater Engineering Design for Unsewered Areas, 2nd edition, Technoiviic Publishing Co, Inc. Lancaster, PA, 1986, p.21
[1] http://www.epa.gov/ORD/NRMRL/pubs/625180012/625180012.htm
11.EPA Design Manual – Onsite Wastewater Treatment and Disposal Systems. Publication 625, 1980, Office of Water Program Operations, Washington, D.C. 20460.
[1] Laak, Rein. Page __ modified.
[1] http://www.mst.dk/udgiv/Publications/1999/87-7909-416-3/html/kap08_eng.htm
[1] http://www.mnaction.org/showalert.asp?aaid=479
[1] Personal Communication, Jennifer Hause, National Environmental Services Center, August 29, 2005