Environmental Chemistry and Microbiology
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Module - 12
Lecture - 62
Biogeochemical Cycles - I

Welcome everyone. We are now starting a new topic and this is Biogeochemical Cycles. It is divided into 2 parts. Part 1 is lecture 62 of module 12.

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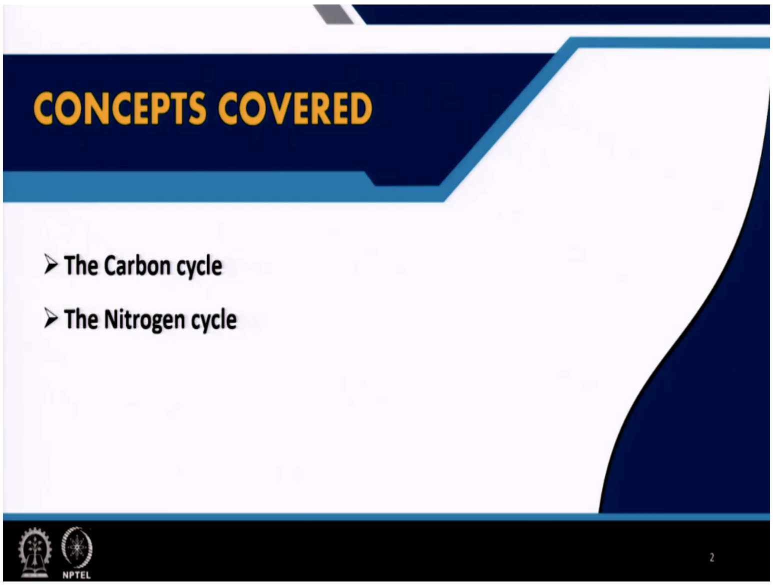

In this first part of the Biogeochemical Cycles, we are going to cover the carbon cycle and the nitrogen cycle. All the other remaining cycles will be covered in part 2.

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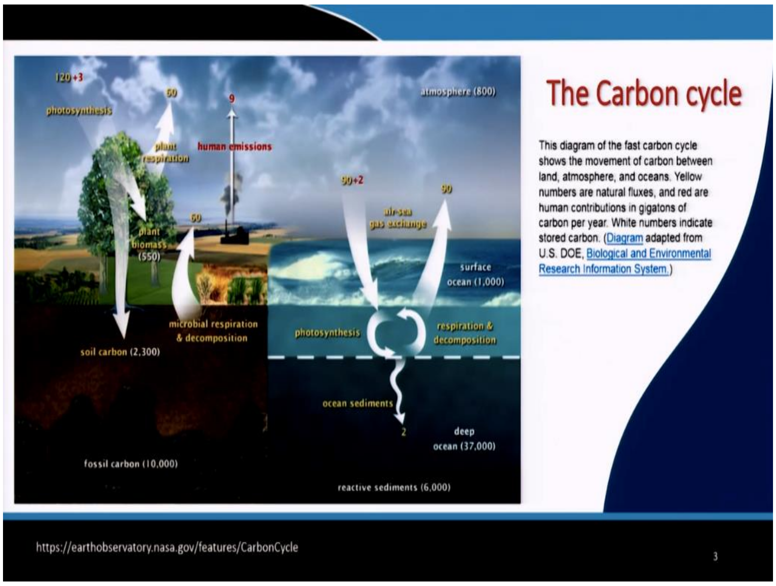

So, this is what is called the fast carbon cycle and the reason for including this; this is actually from the NASA website, and it shows the movement of carbon through different parts of the environment. You can see the flux of carbon. So, the flux of carbon is measured in gigatons per year, and those are the numbers on this slide. What you can see are the main processes.

So, you have photosynthesis, where carbon dioxide that is present in the atmosphere; it is a fair amount of carbon; is converted to biomass. So, here you have photosynthesis and the creation of plant biomass. Some of this in the process of plant respiration or what we call transpiration is given back to the atmosphere and the dead biomass as well as the soil carbon will result in an increase in organic carbon in the soil as well as the deeper layers. This is for the terrestrial part and we also know about anthropogenic emissions. We know that whenever we burn fossil fuels; that is one of the biggest sources of human emissions. So, that is about 9 gigatons per year.

What about the aquatic environment? The aquatic environment is also subject to some of the same processes. So, you have carbon dioxide in the atmosphere being converted to biomass by marine phytoplankton. So, the algal cells, kelp, seaweed, all these are examples of marine phytoplankton that will take up carbon dioxide from the atmosphere and convert it to biomass. When this biomass dies, it becomes part of the ocean sediments, it sinks down to the bottom and you have a high accumulation of organic carbon in the deep sediments. So, in deep ocean sediments, you can see how high the stored carbon is. It is a huge amount, 37,000 (gigatons). That is the biggest amount; it is even bigger than fossil fuel carbon and then you have reactive sediments which are about 6,000 gigatons.

How does the CO_2 in the atmosphere remain; it is not stable (i.e., constant); we know that it is increasing exponentially in the last 50 to 100 years, post-industrialization. So, we are all familiar with the fact that atmospheric carbon dioxide levels are increasing and they are increasing mainly due to anthropogenic emissions.

However, there are other sources of atmospheric carbon dioxide. So, what you see in this particular graphic is the respiration and decomposition of biomass that is generated by the processes of photosynthesis as well as bacterial respiration; all of that also contributes to the production of CO_2. Even though bacteria and algae grow in aquatic systems, this CO_2 that is produced in water is also going to enter into the atmosphere because of air-sea gas exchange. So, that is what is governed by Henry's law and that is beyond the anthropogenic emissions. That is the other biggest source of CO_2 in the atmosphere. CO_2 in the atmosphere diffuses into the aquatic systems, whether it is oceans, lakes, rivers, whatever it is. So, there is a gas-water equilibrium, and that will maintain CO_2 in equilibrium with the atmospheric CO_2. So, aquatic biomass or terrestrial biomass is created.

And when you get this deposition of dead organic biomass at the bottom of the oceans, it will over geological timescales be converted into different forms of carbonate in the lithosphere. So, you have carbonate-containing rocks and so on. So, limestone, dolomite, all these are examples of calcareous sediments being converted into carbonate-containing rocks. You also have the creation of fossil fuels.

So, coal and oil which contain organic carbon are basically stored in the lithosphere. This dead terrestrial biomass is going to eventually become part of soil organic matter, where it will be decomposed. Because of the processes of decomposition and respiration, some of it will be converted back to CO_2 and some of it will remain dead matter in the soil.

And we have already seen fossil fuel burning. So, that in a nutshell, is how carbon in the environment is continuously recycled.

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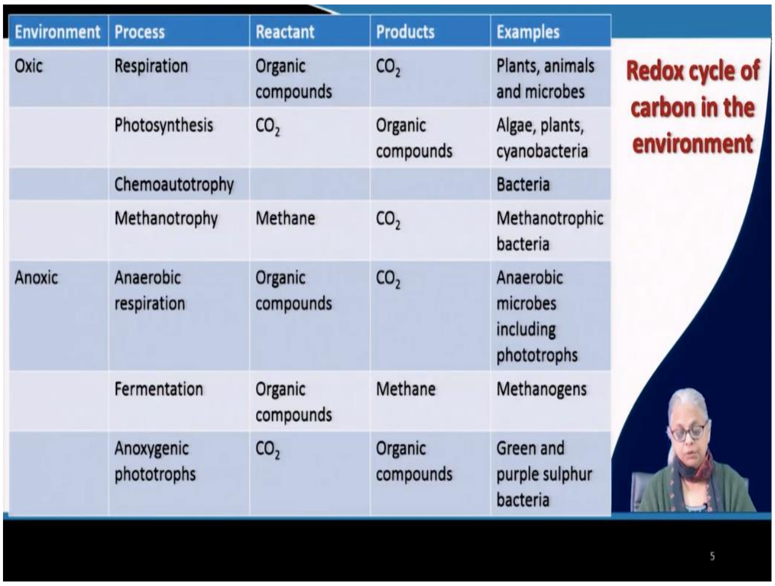

Environment	Process	Reactant	Products	Examples
Oxic	Respiration	Organic compounds	CO_2	Plants, animals and microbes
	Photosynthesis	CO_2	Organic compounds	Algae, plants, cyanobacteria
	Chemoautotrophy			Bacteria
	Methanotrophy	Methane	CO_2	Methanotrophic bacteria
Anoxic	Anaerobic respiration	Organic compounds	CO_2	Anaerobic microbes including phototrophs
	Fermentation	Organic compounds	Methane	Methanogens
	Anoxygenic phototrophs	CO_2	Organic compounds	Green and purple sulphur bacteria

What does that have to do with the microbial world? It is almost entirely dependent on microbial activity. Some of it is; it is not 100% dependent, but the predominant reactions are mediated by microorganisms. So, let us take a look at all the different microorganisms that are responsible for the redox cycling of carbon in the environment. So, we will start with carbon dioxide; if it is present in the aerobic environment, what happens to it? and if it is present in the anaerobic environment, what happens to it?

So, here we have CO_2 in the aerobic environment. As I mentioned, the processes of photosynthesis are mediated by algal cells; by green plants, the larger ones; and cyanobacteria. So, out of these 3 groups, 2 of the groups are microorganisms, and they are converting CO_2 to biomass. This organic matter is what we feed on. All higher eukaryotes, animals and other organisms, we are all dependent; all heterotrophic, aerobic heterotrophic organisms are dependent on this biomass for their food and existence. So, respiration, the processes of respiration where; if you remember, in the previous lectures I spoke about glucose plus oxygen being converted to CO_2 and water. That is the beginning and end of an entire series of biochemical reactions. So, here we are looking at the same thing.

So, this biomass is taken up by higher organisms as well as microorganisms and plants and during their respiration process and converted back to CO_2 and water. What happens in the anaerobic environment? In the anaerobic environment, several things are possible. So, let us take a look at that. So, CO_2 along with methane is generated by a group of bacteria called methanogens and this is a microbial consortium that is required for converting organic material to CO_2 and methane. So, we will go into those details in a little bit. Then you have another group of bacteria called homoacetogens. Homoacetogens are going to take up CO_2 and convert it to biomass. And there are also anoxygenic phototrophic bacteria that can also convert CO_2 to biomass, under anaerobic conditions. They utilize hydrogen sulphide or elemental sulphur. Then you have anaerobic respiration and fermentation. Remember, we have gone through both the biochemical pathways of respiration and fermentation under anaerobic as well as oxic conditions. So, these anaerobic microorganisms which also include phototrophic bacteria are capable of returning the organic material back to CO_2 under anoxic conditions. We have already taken a look at these organisms under the topic of metabolic diversity.

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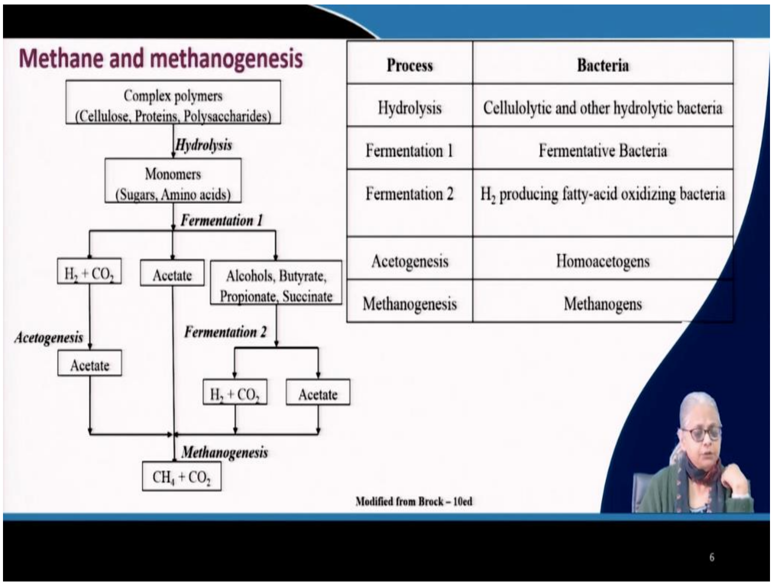

The point here in the carbon cycle for you to remember is that in all biogeochemical cycles, microorganisms play the most important role, because the entire cycle of nutrient recycling through the environment by Nature is dependent on microorganisms and higher organisms, but the main work is done by microorganisms.

Let us take a look at what happens in anaerobic digestion. Now, those of you who are familiar with wastewater treatment, you know that the sludge from the activated sludge process or from a trickling filter or any other aerobic wastewater treatment process, that sludge can be digested further and biogas can be obtained. Now, this biogas is a mixture of methane and CO_2. So, this is our end product. This is what we call biogas. How is this biogas generated in an anaerobic digester?

All of this, like I said, is done by a consortium of microbial organisms, mainly bacteria. And it is not very different from what happens inside the stomach of a ruminant. Ruminants are cows, buffaloes; these are animals that are called ruminants. Their stomach has compartments and each of these compartments can be compared to an anaerobic digester. So, let us take a look at how that works.

So, this sludge that we are taking from the aerobic process is nothing but complex polymers. So, this is complex organic matter, cellulose, polysaccharides, proteins, nucleic acids, all of it. The first thing that the bacteria need to do is to exude what are called extracellular enzymes. These extracellular enzymes have one job, and that is hydrolysis of the polymers to break them down into monomers, because, remember, the cell wall of most of these bacteria is relatively impermeable. So, for these large molecules to enter into the cell is very difficult. So, the only way they can enter into the cell is, first they have to be broken down into monomers and this is hydrolysis. So, you have cellulolytic as well as hydrolytic bacteria and their extracellular enzymes that are responsible for breaking down these polymers into monomeric form. These monomers can then be brought into the cell.

So, here we have several groups of bacteria. We have fermentative bacteria. Within the fermentative bacteria, we have homoacetogens (can be anaerobic autotrophs and heterotrophs as well), we have acetogenic bacteria, we have methanogens and some of them are syntrophs. We have already gone through all this in syntrophy; so, that was in the previous topic. So, these fermentative bacteria which are several species, several groups of bacteria. Now, they can take up these sugars, amino acids, etcetera and convert them to hydrogen and carbon dioxide.

They can also generate acetate. Acetate is a C2 compound. CH_3COOH is your acetic acid and acetate is the salt and then we have higher C-containing, higher carbon-containing compounds. We have propionate which is C3, butyrate which is C4, succinate which is C6, alcohols which may be any number from methanol to higher amounts of carbon. So, all these can be generated by these fermentative bacteria.

So, this hydrogen plus carbon dioxide can further be modified to acetate. Acetate itself will be converted to a combination of methane and carbon dioxide. And this conversion of acetate to methane and carbon dioxide is done by methanogens. So, these are the methanogenic bacteria. And you can see the hydrogen-producing fatty acid oxidizing bacteria, the syntrophs are also present.

Now, there has to be a very precise equilibrium between the hydrogen-producing fatty-acid oxidising bacteria and the methanogens, because any shift in that equilibrium between these groups will result in a digester that does not perform. So, these are some of the things that you can keep in mind about anaerobic digestion.

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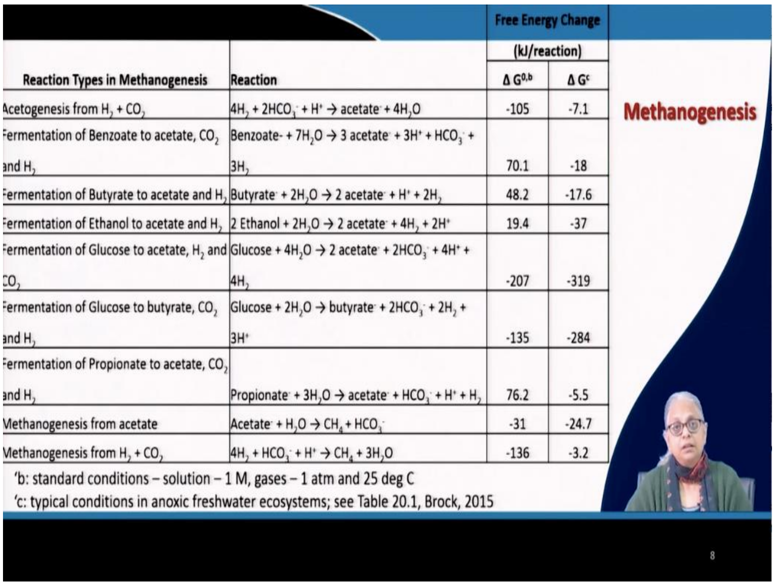

As I said, methanogenesis is not a single reaction. In fact, none of the biochemical reactors that we talk about, none of them is based on a single reaction, they are all based on series of reactions and in our lab studies, we often rely on 1 group or 1 species of bacteria, but anaerobic digestion and the conversion of organic compounds to methane requires a large number of species and a large number of reactions for complete conversion of the organic matter to methane and CO_2.

So, these are some of the reactions that are mentioned over here and these are ΔG^0 for each of these reactions. You can see some of them have ΔG^0 values that are negative and some of them are positive. So, you might say, how can a positive ΔG^0 result in the formation? how will that reaction proceed? Look at what happens under the conditions of the anaerobic digester.

So, under real conditions, with the concentrations that are typical in anoxic, in this case, freshwater ecosystems, it is negative. Otherwise, under standard conditions, they are positive. So, under real conditions, under real environmental conditions, the net ΔG for these reactions is the actual free energy released from these reactions is negative and therefore, the bacteria are capable of obtaining energy for their survival as well as for their reproduction.

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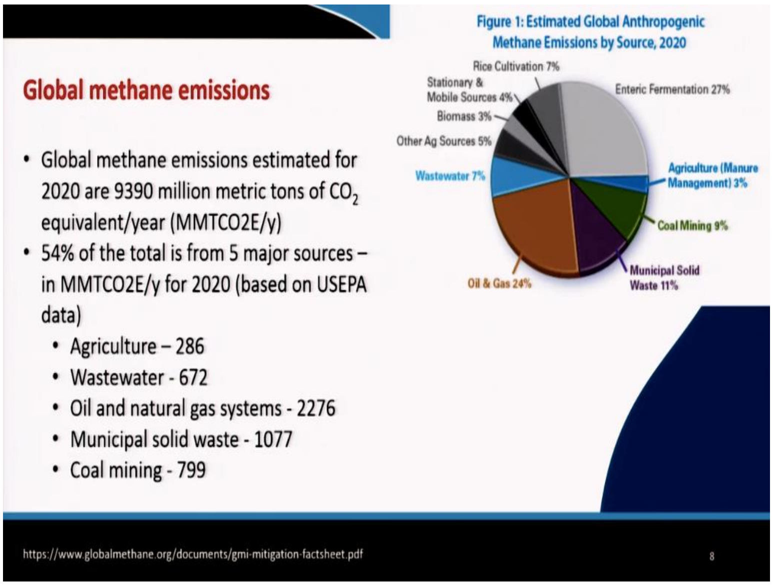

Let us also take a look at something that has become a major topic today, and that is global methane emissions. So, global methane emissions that were estimated for 2020 was 9,390 million metric tons in terms of carbon dioxide equivalence per year. So, this is the shortened form, MMTTCO2E. So, this is the general parameter that is used for quantifying and comparing methane emissions from different sources.

So, if you look at this figure over here, on my right, on the right of your screen, you will see that enteric fermentation is, I think, the largest one. So, enteric fermentation is literally methane generated by ruminant animals. So, I have already mentioned that the livestock population on the planet is fairly high and you have cows, buffaloes and so on. These kinds of animals are called ruminants and they are responsible for about 27% of the global methane emissions. That is the first thing.

Second thing is that 54% of the total comes from 5 major sources which can be controlled by human beings. For example, enteric fermentation, we can assume that it is out of control, so, we are not going to do anything about that. What can we do to control methane emissions? Because you already know it is a greenhouse gas and it is about 25 to 30 times it has higher greenhouse gas potential compared to CO_2, so, it is more important for us to control methane emissions. So, let us take a look at what is the biggest one, within what anthropogenic emissions can; what can we control?

So, what you can see in this pie chart is that out of the sources of methane emissions that can be controlled, the biggest one is oil and natural gas systems. So, anytime you pass by oil refineries or natural gas handling refineries and so on, you will probably notice that many of them have fires at the top of their stacks. That is called flaring of the residual material. Or sometimes what you have is passive venting of the natural gas that is not utilizable. So, that accounts for the bulk of the methane emissions. 24% of the global methane emissions are from oil and natural gas systems.

The next big one is municipal solid waste. So, municipal solid waste, whether it is in a landfill or in an open dump is contributing 11% of the global emissions.

After that, I think we have coal mining. Coal mining contributes 9%. Again, it is release of natural gas during the mining operations.

Wastewater treatment ends up releasing 7% and agricultural management, the manure management releases about 3%. So, these are what are called controllable sources of methane; basically, that can be controlled to reduce global methane emissions.

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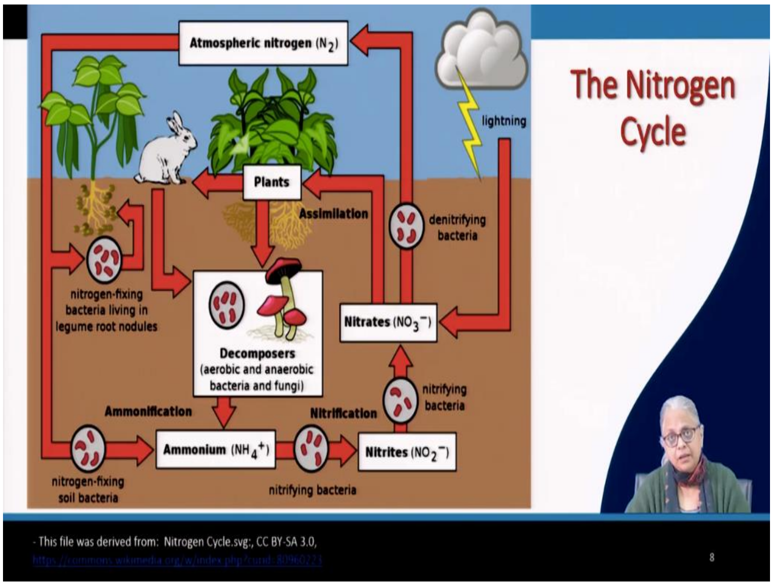

Let us now come to the next one and that is the nitrogen cycle. Now, you have probably studied in high school that nitrogen which is an inert gas is not in bioavailable form. So, even though we have so much nitrogen in the atmosphere, it is not bioavailable nitrogen. The bioavailable forms of nitrogen are ammonium or ammonia and nitrite or nitrate.

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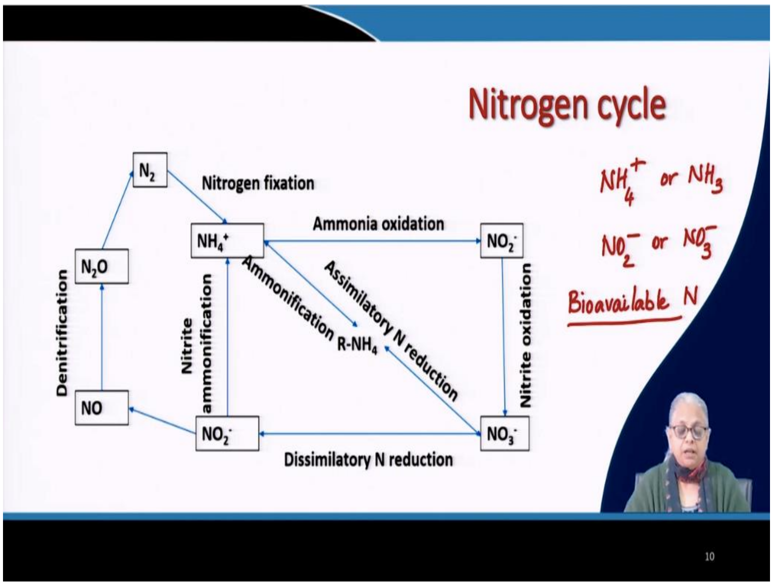
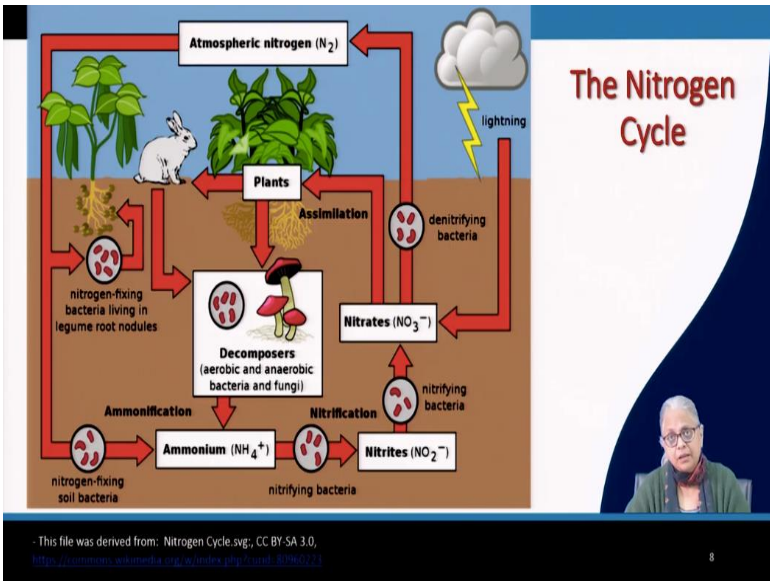


These are the bioavailable forms. N_2 is not bioavailable. So, this is an important point to remember because, even though we have a huge amount of nitrogen in the atmosphere, it is not bioavailable; and therefore, it really does not do any good. So, how is it converted?



So, nitrogen fixation, the conversion of nitrogen to the bioavailable forms is very difficult. So, you can do it industrially. Nature does it in 2 ways. This is the natural cycle.

So, nature has only 2 methods of converting inert nitrogen gas to bioavailable nitrogen. One is during lightning strikes and the second is biological. So, we are going to focus on the biological aspect because microbes are the ones that are responsible for converting N_2 gas into bioavailable nitrogen. So, that is the first thing. So, during precipitation, during a thunderstorm event, you get the conversion of nitrogen gas to nitrate and this nitrate comes with the rain water and enters the terrestrial cycle. So, here it can be taken up by plants, it can be taken up by microorganisms, it can be converted into biomass, and that is how we are utilising plant or animal-based nitrogen. So, that nitrogen (utilizable by plants and animals and other organisms) can be in the form of ammonium, ammonia, nitrite, nitrate; these are the forms. Microorganisms do the same thing.

Now, organic residues, both from dead biomass as well as from excreta is basically organic matter with amine; remember amino acids. So, amine groups are the form that nitrogen is present in (any biomass). This can be mineralised to NH_4 or NH_3, NH_4^+ or NH_3, ammonia gas. Ammonium, NH_4^+ can adsorb to clays or any other minerals in the subsurface. It can get converted to nitrite and nitrate.

So, in nitrification processes with oxygen as the terminal electron acceptor, we have autotrophic bacteria, *Nitrosomonas* and *Nitrobacter* that are capable of converting ammonium to nitrite and nitrate. All these forms, ammonia, nitrite, nitrate, can be taken up by plants and converted to organic nitrogen. This nitrate is then under certain conditions converted by denitrifying bacteria to various gases.

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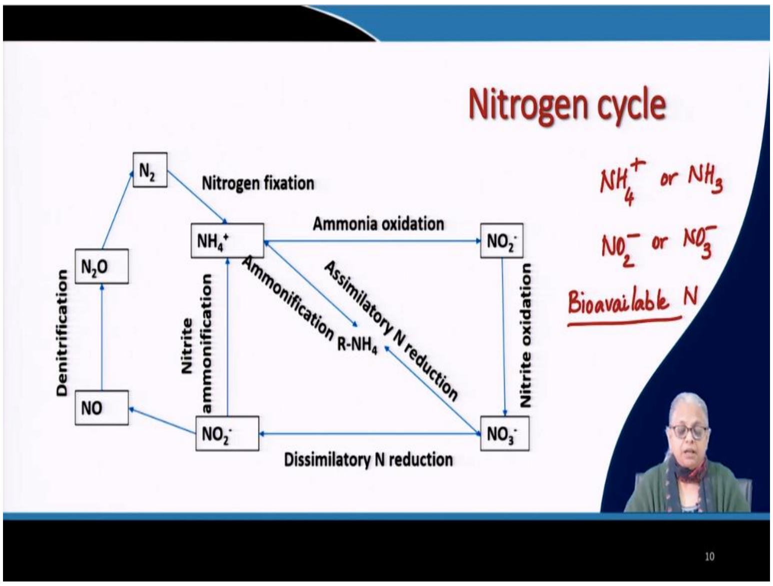

So, nitrogen gas, nitrous oxide, all these are gaseous outputs from the denitrification process. So, a very simple schematic to explain all these processes is shown over here. So, you have nitrogen gas in the atmosphere. It is fixed by; and each one of these processes is mediated by either 1 group or 1 species of bacteria or by several bacterial species. So, you have nitrogen fixation which is the conversion of inert nitrogen to ammonia.

Ammonia oxidation to nitrite and nitrate, so, that is nitrite oxidation. Then, what we call dissimilatory nitrogen reduction and nitrite ammonification. So, the conversion of nitrite and nitrate to ammonia and into the biomass. Now, the final step is nitrate going to nitrite going to nitrous oxide, dinitrogen oxide (nitric and nitrous oxide) and back to the inert form. So, these are the various forms of nitrogen that are present in the environment and converted by different bacterial species.

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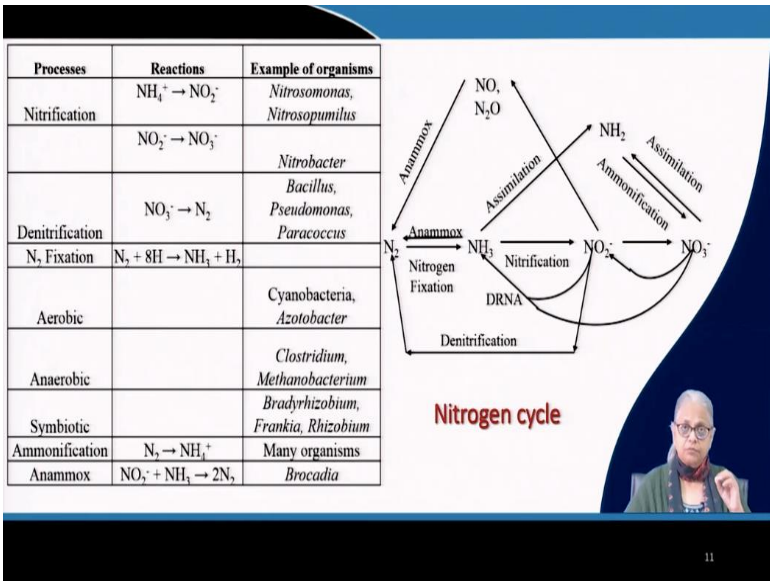

Here are some examples of the bacterial species that are responsible for mediating all these reactions. So, you have the nitrification reaction. Ammonia to nitrite is done by *Nitrosomonas*; nitrite to nitrate is done by *Nitrobacter*. Denitrification where nitrate and nitrite are converted to N_2, is done by *Bacillus* species, *Pyrococcus*, *Pseudomonas*; they are all capable of doing denitrification.

We have several nitrogen-fixing bacteria, where nitrogen is converted to ammonia form. Aerobic conditions, it is done by *Azotobacter* and cyanobacterial species. Under anaerobic conditions, we have *Clostridium*, purple and green phototrophic bacteria, Methanobacterium; these are all possibilities. Then we also have symbiotic organisms. So, we have *Rhizobium, Bradyrhizobium, Frankia*. These are bacteria that colonise the roots of certain plants.

They have a symbiotic relationship with these plants, especially leguminous plants and that is why legumes are richer in nitrogen compared to other food crops. And that is because of this symbiotic relationship between the bacterial species and the plant. Then we have ammonification, where organic nitrogen is converted to ammonia. Many bacterial species are capable of doing that, and, in fact, I think we are also capable of doing that. Anammox, where you have nitrite and ammonia converting to inert nitrogen gas. This is a very specific reaction that is mediated by *Brocadia*.

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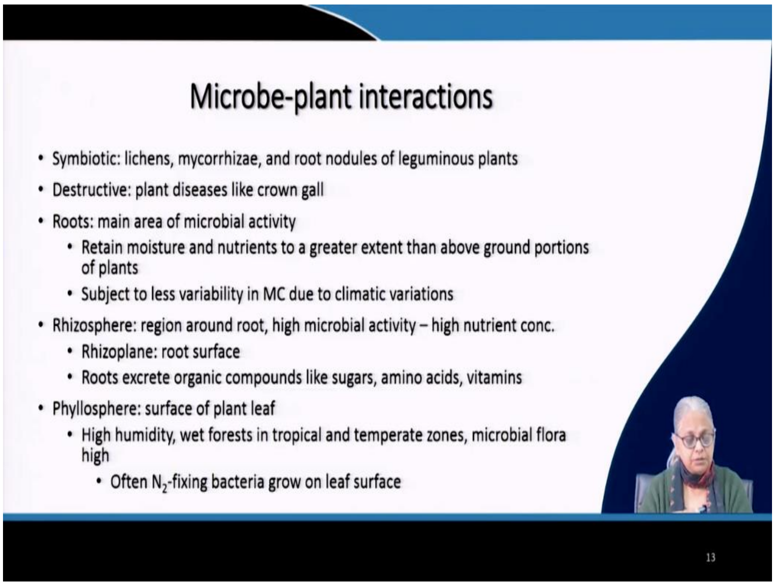

Let us then come to microbe-plant interactions. So, there are several symbiotic relationships between microbes and plants that are responsible…... They are all beneficial relationships. Symbiotic means beneficial to both. So, you have lichen, which I have already explained. What we are going to look at now is mycorrhizae and the root nodules of leguminous plants.

You can also have destructive relationships. So, you have certain plant diseases like crown gall, which we are not going to go into. It is there in the textbook, so, you can go through it. But we do have certain examples over here. So, you have the root zone. Now, those of you who may have done some lab work, you may know that the soil and the root zone of a plant is where the microbial activity is highest. Why is that the case? For 2 reasons. 1, moisture is highest and nutrient concentration is also the highest. So, retention of moisture and nutrients is much greater in the root zone compared to the above ground portion of the plant. There is also less variation in the moisture content; MC stands for moisture content; despite climate variation. So, if you remember, if you just observe, you can do it even with pots and so on. If you have potted plants, you can observe it. From daytime to nighttime, the temperature varies, but the moisture content in the soil does not vary to the same extent as the ambient temperature and the humidity. So, this is an area that is very stable (in terms of temperature and humidity) and has a high level of microbial activity. Then you have rhizosphere. Rhizosphere is the region around the root. Very high microbial activity; very high nutrient concentrations. You can probably find other examples in the textbook.

There are photos that show you the rhizoplane which is the root surface and also remember that the root region, the root zone is the area where organic compounds are excreted from the roots. This allows these heterotrophic bacteria to thrive and survive in that root zone. So, the rhizosphere, like I said, is extremely essential for the health of plants. And I will show you examples of that.

Phyllosphere is the surface of the plant leaf. You can have nitrogen-fixing bacteria growing on these plant leaves. It is an area especially in tropical and temperate zones, if the humidity and moisture is very high, then you get high microbial activity even on the leaf surface.

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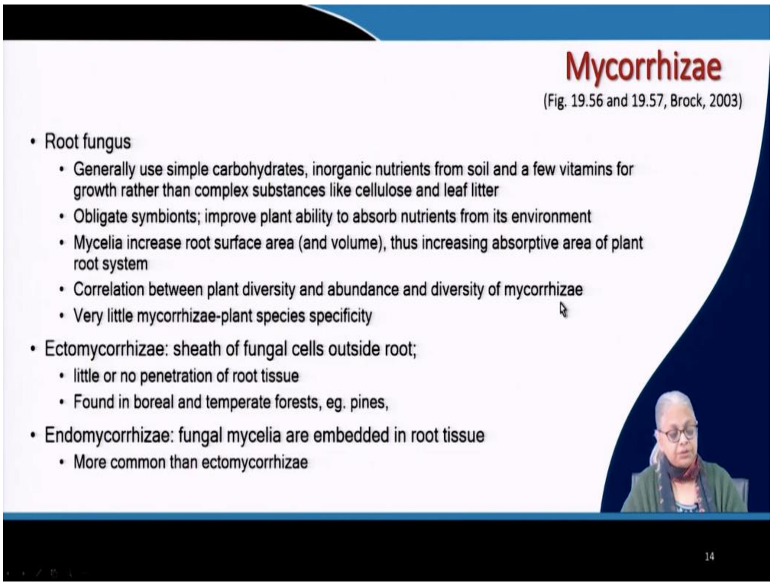

Let us take a look at mycorrhizae. You can refer to these figures in the textbook, but the root fungus is another essential. This is root fungus which is in a symbiotic relationship with the plant. So, these root fungi, they use simple carbohydrates, inorganic nutrients, vitamins from the root zone, and they are able to survive based on these substrates. They do not use complex matter like cellulose and leaf litter. They are obligate symbionts. They cannot survive on their own, they need the plant to survive…... Let me put it in 2 different ways.

They thrive on the carbohydrates that are excreted by the roots. And the inorganic nutrients from the soil are available both for the plant as well as for the fungal cells. And their ability to absorb material from the root zone is much higher. So, in fact, if you look at these figures, they will show you how they are extensions, the mycelia of these fungal cells create extensions of the root zone. So, the rhizosphere becomes much bigger; and therefore, the plant is able to thrive in a much bigger way. So, the mycelia increase the root surface area and volume, thus increasing the absorptive area of the plant root system. There is a significant correlation between plant diversity and abundance and diversity of the mycorrhizae. Very little specificity. Mycorrhizae and plant species are not necessarily specific combinations. They can be non-specific relationships.

There are 2 types of mycorrhizae that are listed in the book. One is ectomycorrhizae, which is the sheath of the fungal cells outside the root; and endomycorrhizal, where the fungal mycelia are embedded in the root tissue. You can see all these figures in the text. So, in the first case, there is little or no penetration of the root tissue, unlike the second one. And those are more common in boreal as well as temperate forests, so pines and so on.

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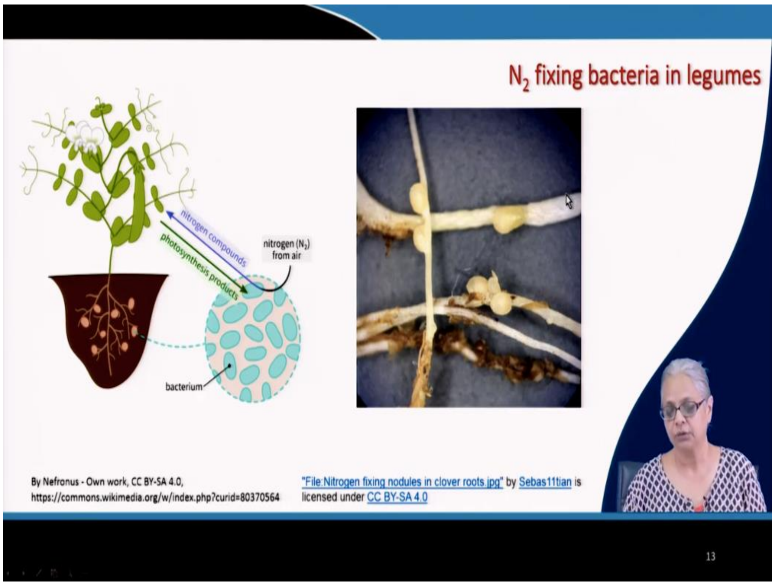

So, here we have some graphics about nitrogen fixing bacteria in legumes. Now, these nitrogen fixing bacteria can be present in both leguminous as well as non-leguminous plants. And what you see here in the first graphic is the nodules. These are the nodules which contain the bacteria that infect the root system of these plants. So, these are the nitrogen-fixing bacteria. They are present in these nodules and that is where the nitrogen from the atmosphere is fixed into bioavailable forms. It is converted into bioavailable forms and made available for plant growth. And that is how these plants are able to survive even in a nitrogen-deficient soil. So, this was as graphic, and here you can see a photograph of these root nodules. So, you can see these root nodules in these clover roots.

So, this is very common in several types of plants, alfalfa, clover, soybeans, many leguminous plants. Most of them have nodules of various types of nitrogen-fixing bacteria that convert atmospheric nitrogen to bioavailable forms of nitrogen.

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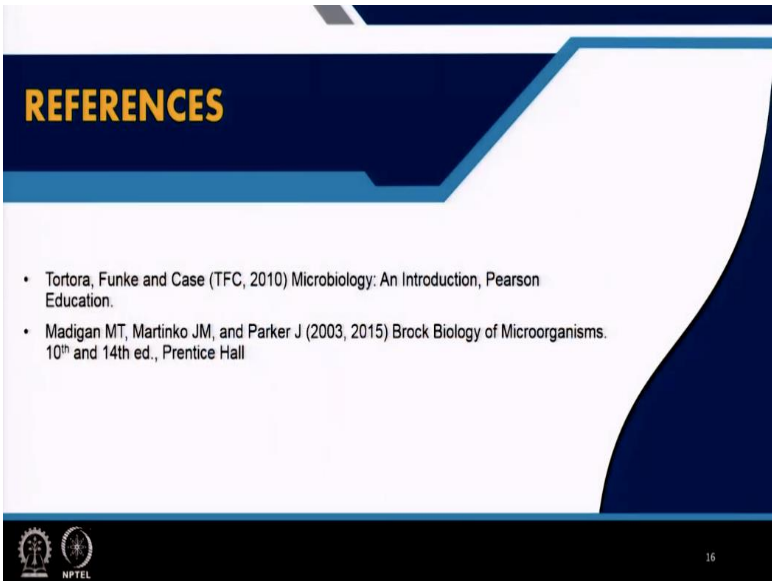

I will stop at this point.