Organic Matter Content of Wastewater and Manure

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Organic Matter (OM) plays a large role in the environment. The OM content of soil affects nutrient retention, water holding capacity, and the soil's ability to provide nutrients for plant growth. The OM content of wastewater discharged to a stream determines how much oxygen is available for fish to breathe. This Fact Sheet defines OM in byproduct materials, and shows how the many different measures of OM are used to predict the material's behavior in the environment.

What is Organic Matter?

To a chemist, an Organic Chemical is any compound that contains Carbon. To a biologist, OM is living material or material that was once alive. Soil Scientists define a special type of OM called humus as, "the all-but-stable fraction of soil OM remaining after the plant and animal residues have decomposed." Environmental Engineers have an even simpler definition, if it burns at 550° C, it is organic. Running through these definitions is a constant theme. Organic matter is connected to life. And as you will soon see, OM is also connected to energy.

The Connection between Organic Matter and Energy

Simply put, nature stores energy using carbon. Take crops growing in a field. Plants use energy from sunlight, carbon dioxide (CO_2) from the air, and moisture from the soil to create carbohydrates (CH_2O) through photosynthesis (Figure 1). Carbohydrates are the building blocks of life. In other words, they are the basic ingredients of OM.

Conversion of energy to organic matter, sometimes called Primary Production, also takes place in aquatic environments (Figure 2). Aquatic plants, plankton, and some microorganisms use photosynthesis to create OM and pass it further up the food chain.

Written as a simple chemical formula, photosynthesis is:

$$CO_2 + H_2O + \text{energy} \rightarrow CH_2O + O_2$$

This is simplifying things, so don't get hung up on minerals, nitrogen, and other nutrients vital to the process. Also, remember plants use photosynthesis to clean CO_2 and add oxygen (O_2) to the atmosphere. We will come back to the O_2 a little later. For now, think of photosynthesis as storing a portion of the sun's energy as OM. If you don't believe OM is stored energy, stand in front of logs burning in a fireplace, or try to outrun a grass fire. The heat you feel was once sunlight before photosynthesis converted it to OM.

Fortunately for life on earth, other living creatures can unlock the energy stored in OM for their own use (Figure 1). When

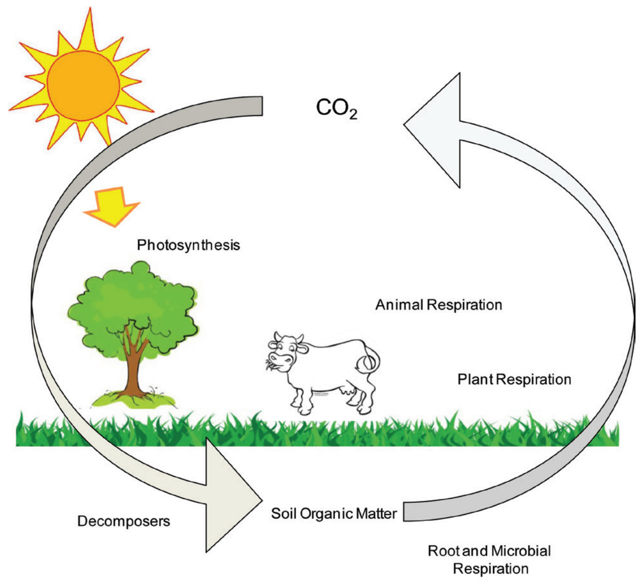

Figure 1. The Carbon Cycle in Terrestrial Ecosystems.

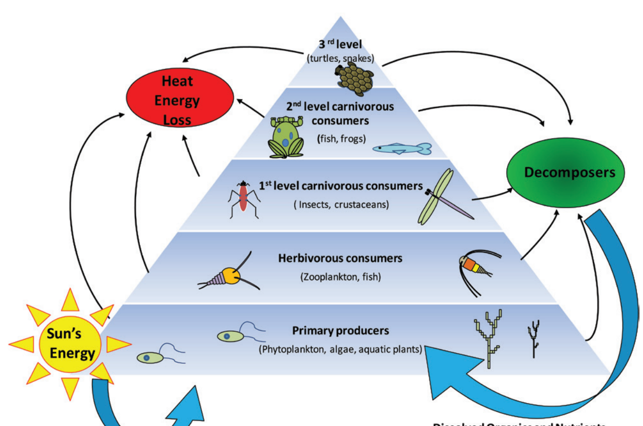

Figure 2. Trophic Levels and Energy Flow in Farm Ponds.

a cow eats grass, she is harvesting the same energy that the prairie fire releases. Some types of OM contain more energy than others. It is easier to fatten a cow on grain than grass, because OM in the grain (starch) is more digestible than OM in grass (cellulose). The cow stores energy as fat – which is even more energy rich than cellulose or starch.

Oxygen is a key ingredient in unlocking the energy stored in OM. Whether chemical (combustion) or biological (metabolism), O_2 is consumed in aerobic conversion of OM to energy. A simplified chemical formula for the process is:

$$OM + O_2 \rightarrow CO_2 + H_2O + \text{energy}$$

Notice that this is basically the opposite of photosynthesis. Oxygen is consumed in the aerobic conversion of OM to energy. Fire removes O_2 from the atmosphere. If the available O_2 is consumed, the fire will go out. Likewise, aerobic microorganisms remove dissolved oxygen (DO) from water. Take enough DO from the water, and fish die.

In combustion, energy is released as heat. Living creatures use metabolic energy from OM to live, grow, and reproduce. They release some of the energy as heat. Warm blooded creatures use a portion of the metabolic heat to maintain an elevated body temperature.

Not all life on earth requires oxygen to live. Anaerobic organisms, organisms that live in the absence of O_2, also tap into the energy stored in OM. Anaerobic digestion is an industrial process that harnesses energy from OM conversion. A simplified chemical formula for anaerobic digestion is:

$$OM + \text{heat} \rightarrow CH_4 + CO_2 + H_2O + \text{energy}$$

Notice that energy in the form of heat appears on the left hand side of the formula. Anaerobic organisms need warm temperatures (20^o C and above) to make the process work efficiently. Some of the energy released from OM is stored as CH_4 (Methane). Methane is a flammable gas, and we can release its stored energy through combustion:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O + \text{heat}$$

So, if a digester uses heat from burning methane, and we combine the metabolism and combustion parts of digestion, we end up with the same equation as aerobic conversion to energy:

$$OM + O_2 \rightarrow CO_2 + H_2O + \text{energy}$$

Organic Matter in the Environment

Soil Environment

The OM content of soil affects moisture holding capacity, nutrient holding capacity, and particle aggregation. Soil OM supplies nutrients to the soil environment. Think of soil OM as a pool. The OM pool is constantly being built up and broken down through chemical and biological action. Decomposition of the pool releases CO_2 and plant nutrients. Manure is sometimes given the euphemism “organic nutrients.” This is because land application of manure adds both OM and nutrients to the soil. Plant materials (in particular plant roots) also add to the soil OM pool. Adding inorganic nutrients (chemical fertilizer) increases soil OM by increasing plant growth.

Soil microorganisms use the energy as well as the nutrients stored in OM to reproduce and grow. When OM is added to the soil, soil microorganisms respond to the input of energy by growing and reproducing. If the soil OM pool contains more nutrients than the microorganisms need, nutrients are released for plant uptake. If the soil is deficient in nutrients, microorganisms will either not grow or they will take nutrients from the soil to digest the OM.

The process of microorganisms removing nutrients from the soil is called immobilization. Immobilization’s effect on soil fertility is usually temporary, but can be devastating to plant growth. When a high carbon, low nutrient material such as wheat straw or saw dust is added to the soil, soil microorganisms remove nutrients from the soil in order to digest the high carbon material. They are basically robbing nutrients from plants. Eventually, the microorganisms use up the available digestible energy, die, and release the nutrients stored in their bodies to the soil.

Since nitrogen is the most limiting nutrient for plant growth, the amount of organic matter to nutrients is expressed as the ratio of carbon to nitrogen, or C:N ratio. As a general rule of thumb: materials with C:N < 20 release nutrients to soil as soon as they are added; materials with C:N > 20 immobilize soil nutrients for some time after they are added.

The nutrient and moisture holding ability of soil OM is related to the amount of nearly completely decomposed material or humus in the pool. The other benefits of organic matter, aggregation and release of nutrients, are related to the actively decomposing portion of the pool. Healthy soils require a constant replenishing of the OM pools to remain productive.

Aqueous Environments

The oxygen supply is much more difficult to maintain in aqueous compared to terrestrial or soil environments. Oxygen must dissolve into water before it can be useful. If animals or microorganisms use DO faster than it can be replaced, O_2 is depleted and aerobic organisms die.

One way DO is depleted occurs when excess plant nutrients in the water cause the primary producers (algae, plankton, aquatic plants) to flourish. During the day, primary producers pump O_2 into the water, at night they remove O_2. If nighttime removal outpaces daytime replenishment, DO is depleted. This process, called eutrophication, takes place in lakes, reservoirs, and estuaries, often far downstream from where the nutrients were introduced.

A second method of O_2 depletion occurs when secondary producers (the decomposers) remove O_2 faster than it can be replaced. Excess OM is usually the cause of this sudden flourishing of decomposers. Dissolved oxygen depletion due to microbial blooms happens close to the source of OM addition. This is why the OM content is usually the limiting factor of wastewater discharge to streams.

Treatment Systems

You have already seen how methane production in digesters is directly related to OM content of waste. The OM content of wastewater is also important in aerobic liquid treatment systems such as lagoons and sewage treatment plants. Think of these as souped-up farm ponds. Aerobic life depends on adequate levels of DO. The amount of DO added through photosynthesis, natural aeration, or mechanical aeration must closely match the OM removed from the system. A compost pile is a solid aerobic treatment system. As in liquid treatment systems, O_2 must be added by turning or blowing air through the pile to match the rate of OM reduction.

A compost pile is also a good example of the energy stored in OM. Because the pile provides insulation, some of the metabolic heat released during the decomposition of OM is trapped in the pile. As a result, the pile heats up – sometimes as high as 180^o F before the heat begins to kill off the very organisms that create it. Compost piles hardly ever get hot enough to spontaneously combust. But, wet hay, carelessly stacked, will catch fire because of overheated aerobic activity.

Measuring Organic Matter in Byproduct Materials

Organic matter plays a variety of roles in different environments. Likewise, a number of methods have been devised to measure OM content, each with its own uses. We can categorize the various methods of measurement into basic groups: carbon content, loss on ignition, oxygen demand and respiration, and methane production.

Carbon Content

One definition of OM is that it contains carbon. A direct method to determine OM content is to measure a material's carbon content. **Total Carbon (TC)** content is divided into **Inorganic Carbon (IC)** and **Total Organic Carbon (TOC)** content. Inorganic carbon is comprised of carbonate, bicarbonate and dissolved CO_2. Organic carbon is the carbon atoms in the structure of organic compounds. The most common method of determining TC is to combust a sample and measure the CO_2 released. Before combustion, the IC content is measured by injecting a liquefied sample into a reaction chamber packed with phosphoric acid coated quartz beads. Under these acidic conditions, IC is converted to CO_2, but the organically bound carbon is not. Total organic carbon is calculated by subtracting IC from TC.

Loss on Ignition

Another definition of organic versus inorganic material is that OM is combustible. A sample is first dried to determine the **Total Solids (TS)** content. The dried sample is then placed in a 550° C furnace for one to two hours. The material remaining after combustion is **Fixed Solids (FS)** or **Ash** content, and the mass that disappears is **Volatile Solids (VS)** content. Volatile solids analysis is useful because it gives a rough measure of the total mass of OM in a sample --regardless of its specific chemical makeup. It is often used to define total mass of OM, and other analyses are used to partition the VS content into other groups. More information on VS and Solids Testing can be found in OSU Fact Sheet, BAE 1759, *Solids Content of Wastewater and Manure.*

Oxygen Demand and Respiration

Organic Matter content of a pollutant is measured indirectly by observing the amount of oxygen needed to digest it. The two basic measurements of oxygen use are **Oxygen Demand** and **Respiration Rate**. Oxygen demand is the total amount of O_2 required to aerobically degrade OM. Oxygen demand is further divided into **Biochemical Oxygen Demand (BOD)** and **Chemical Oxygen Demand (COD)**. Respiration rate is the rate at which O_2 is removed from the atmosphere or water.

The relationship between oxygen demand and respiration rate is illustrated in Figure 3. Pretend that an OM rich liquid is placed in a sealed container with an infinite amount of DO. The curve in Figure 3 represents the cumulative amount of DO removed from the liquid as microorganisms eat the OM. To calculate the amount of O_2 removed from the liquid (or *demanded* by the OM) at any point in time, draw a line up from the x axis until you reach the curve, then pivot 90° to the left, and extend the line until you reach the y axis. Oxygen demand is value given on the y axis, cumulative O_2 removed (mg), divided by the volume of liquid (l). To calculate respiration rate, pick any point on the curve and draw a line with a slope equal to slope of the curve at that point. Respiration rate is slope (mg/time) divided by the volume (l).

Biochemical oxygen demand is determined by placing a known amount of pollutant in a sealed flask along with seed organisms and enough pH buffered, nutrient rich liquid to fill the flask. At the start of the test, the liquid in the container is saturated

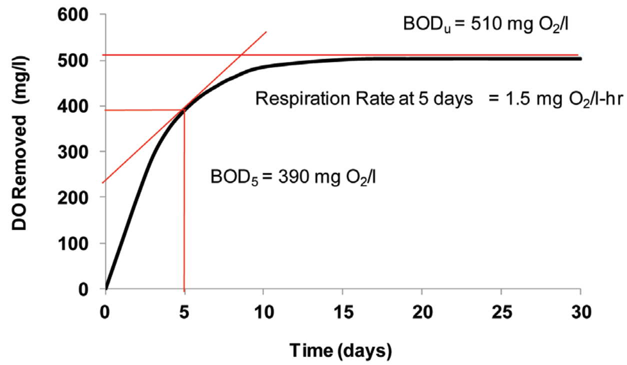

Figure 3. Relationship between Respiration Rate, BOD_5, and BOD_u from DO Removal Curve.

with DO. BOD is divided into two values: BOD_5 and BOD_u. **Five day BOD or BOD_5** is determined by measuring DO removed after five days. The mass of DO removed from the liquid after five days is divided by the sample volume to give BOD_5. **Ultimate BOD or BOD_u** is measured by allowing the test to run as long as DO can be removed from the liquid (generally 30 to 60 days). The DO content of the test flask is usually close to zero well before the long running BOD_u test is finished. To keep the microorganisms alive, the liquid is periodically removed from the flask and reaerated. Dissolved oxygen is measured using probes.

Nitrogen compounds also have an oxygen demand. For instance, ammonia (NH_3) removes DO as it is oxidized to nitrate (NO_3). **Carbonaceous Biochemical Oxygen Demand or CBOD** is determined by adding nitrate inhibitors to the BOD flask before the test begins, so theoretically, only carbon is oxidized while removing DO.

The **Chemical Oxygen Demand or COD** is similar to BOD in that it measures the amount of oxygen needed to digest OM, except that a strong chemical oxidant (usually a mixture of Potassium dichromate and Sulfuric Acid) is used instead of microorganisms. A dilute sample of pollutant is mixed with the oxidant in a heated flask and digested for two hours. After two hours, the mass of dichromate needed to digest the organic matter is measured, and COD is calculated by dividing O_2 equivalents removed by sample volume.

Chemical oxygen demand is related to $CBOD_u$ in that it measures the maximum amount of O_2 used to consume carbonaceous OM. Ammonia is not oxidized in the COD test unless excess chloride is present in the sample. A little caution is needed, though. A pollutant will have a COD even though the chemicals in sample may be toxic to microorganisms. Also, like the BOD tests, the amount of oxidant consumed is related to the time of digestion. If the analyst does not dilute the sample sufficiently, or the test is stopped before all chromate is consumed, oxygen demand will be underestimated.

As seen in figure 3, the **Respiration Rate**, or slope of the cumulative O_2 removal cure, is constantly changing during the digestion of OM. Oxygen removal rate is great early on in the test as the organisms consume the readily available energy. Further along, oxygen consumption slows as the food supply dries up. Respiration rate is a good measure of the energy content of organic matter as it undergoes decomposition. This is why respiration rate is often reported as the oxygen removal rate per VS concentration of the material (mg O_2/mg VS-min). A byproduct with a high respiration rate contains more digestible energy than one with a low respiration rate with the same mass of OM.

Respiration rate can be determined in both liquids and solids. There are two basic methods of determining respiration rate. In both methods, a sample is placed in an air tight container. In the first method, a known amount of O_2 is added and the rate at which CO_2 is released is measured. In the second method, a strong base (KOH) is placed in the sealed container along with the sample. The base removes CO_2 as it is released. Pressure drops as the CO_2 is absorbed. Respiration rate is determined by measuring the amount of O_2 needed to bring pressure in the container back to atmospheric. Newer respirometers have sensors to detect the pressure drop, and replace the consumed O_2 by electrolysis of water. Measuring the electric current required to create the makeup O_2 gives an instantaneous reading of respiration rate.

Methane Production

The set up of a **Biochemical Methane Potential or BMP** test is similar to a BOD test. A sample is placed in a sealed container with seed organisms and nutrient rich, buffered liquids. Only in a BMP test, the liquid is free of oxygen, and mass of CH_4 released over time is measured rather than O_2 consumed. Sample size is adjusted relative to seed so that OM will be digested in about 30 days. A word of caution must be given. The BMP test determines the potential CH_4 released per mass of VS *under ideal conditions*. The amount of biogas released in an actual digester depends on the conditions present in the digester and the presence or absence of toxic compounds in the material. For more information on the BMP test read OSU Fact Sheet BAE-1762 , *Anaerobic Digestion of Animal Manures: Methane Production Potential of Waste Materials*.

Organic Matter Stability

Stability is the measure of how rapidly carbon is altered in OM. Some organic matter is extremely stable. Diamonds and graphite are pure carbon, but a diamond will not change its composition for thousands of years. There are three basic facets of OM stability. If mixed with the soil, will OM take nutrients away from plants? If stacked, will OM heat up? If left on the soil surface, will OM create odors, draw flies, or invite larger animals to feed?

We have already shown how C:N ratio is used to predict immobilization in soil. A direct method to predict autoheating ability of solid manure or compost is to place a sufficient quantity of material into an insulated container, add water to bring moisture content to approximately 50 percent, and measure temperature rise in the container after one day. A step by step procedure to use this method is given in OSU Factsheet, BAE-1761, *The Icebox Test: an Easy Method to Determine Autoheating Potential of Compost and Byproduct Materials.*

Putrescibility is a measure of a waste's ability to release noxious odors and attract flies. The general definition of a non-putrescible waste is that it cannot undergo "significant biological transformation." Decomposing animal bodies undergo a huge transformation from muscle protein to soil organic matter. Composted manure is non-prutescible because it lies at a much lower energy state. First, the animal removed energy from the feed before it was excreted. Then, microorganisms removed more energy from the manure during composting. We generally rely on other indirect measures, such as the ability of the material to autoheat to determine the putrescibility of wastes. It is difficult to predict the autoheating potential of OM -- especially with liquids. Therefore, the energy level of OM, as measured as resipiraiton rate, is usually used to indirectly measure putrescibility.

The **Solvita**™ compost stability test is a commercial product that uses respiration and ammonia volatilization rates to estimate stability. The mass of CO_2 and NH_3 released by a compost sample in an airtight container is measured using standard color changing panels. Organic matter stability is determined by consulting standard charts (Figure 4).

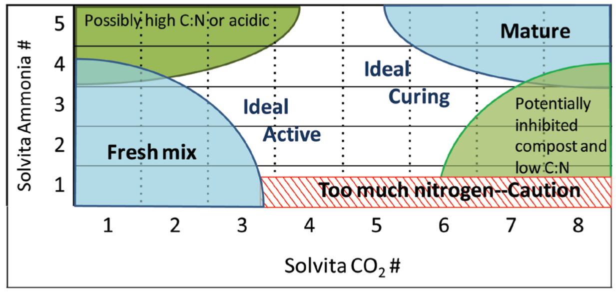

Figure 4. Determining Compost Stability from Solvita CO_2 and NH_3 results (from Woods End Laboratory, 2009)

Using measurements of OM in Waste Management Systems

An awareness of OM, and the measures used to describe OM, can be used to ensure successful operation of waste handling systems.

Say a dairy farmer uses manure to fertilize corn. Naturally, he would measure plant nutrients (Total N, Total P_2O_5, and K_2O) to determine an application rate to match a yield goal. Adding TC to the analysis would allow him to calculate C:N, and determine if he should plant immediately following application, or wait a few months after spreading manure.

A horse farm, wanting to market compost to local nurseries and gardeners, would characterize their product using C:N, VS:TS ratio, and respiration or Solvita™ tests to guarantee its quality.

A wastewater treatment plant is required by its permit to test BOD before discharge. They might also want to measure TOC and respiration rate at point of discharge to better predict the effect of OM on the receiving stream.

A swine farmer wants to add an anaerobic digester. He can predict the amount of carbon available for conversion to biogas using the TOC or COD tests. To get a better estimate of manure's potential to produce methane; he would use VS and BMP tests.

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