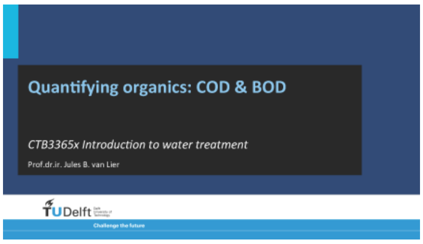
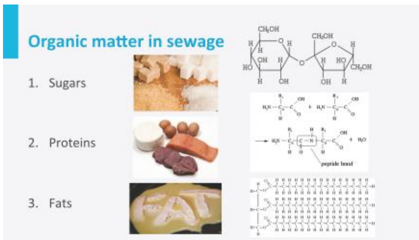
CTB3365x – Introduction to Water Treatment

W1d – Quantifying organics: COD & BOD

Jules van Lier



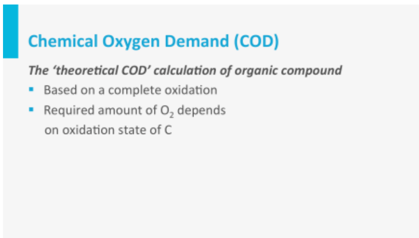
Many different organic pollutants are present in domestic sewage. Do we need to measure them individually?
In this lecture, the basics of quantifying the organic pollution will be discussed: the COD and BOD measurement.
The organic pollutants in domestic sewage are causing oxygen depletion in surface water when discharged untreated.
How do we assess the degree of pollution?
Or the impact that these compounds have in surface water?



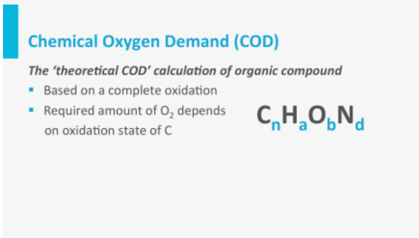
In organic matter, the carbon is partly reduced.
The level of reduction depends on the nature of the organic compound: sugars, protein, fats, etc.
Fats are most reduced.
Therefore, more oxygen is required for the complete oxidation of fats and fat-type compounds.

The complete oxidation of organic matter, can be accomplished in an analytical test, using bi-chromate as strong oxidizing agent.
In this test, carried out at 150°C and at low pH using sulphuric acid, all available carbon will be oxidized to CO_2.

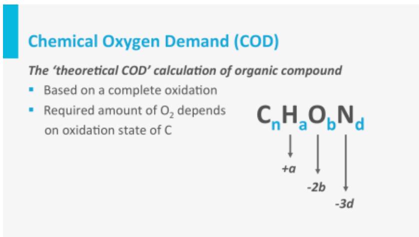
The consumed amount of bi-chromate, is measured and recalculated to oxygen equivalents. Remember that 1 molecule of oxygen can accept 4 electrons. In the COD test, we assess the Chemical Oxygen Demand of organic matter, being fully oxidized to CO_2.In fact, we express the concentration of organic pollutants in g oxygen, or g COD, that is required for the full oxidation. A very reduced organic compound, such as fat, is therefore characterized by a higher COD per gram weight, than for instance sugar.



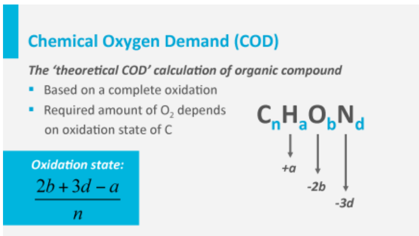
The oxygen requirement for this pure chemical oxidation, can also be calculated.
For this, the exact composition of the compound and thus the average carbon oxidation state must be known.



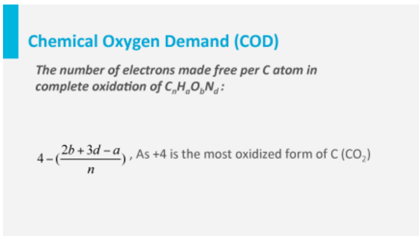
Imagine a hypothetical organic compound consisting of:
n Carbon atoms, a Hydrogen atoms, b Oxygen atoms, and d Nitrogen atoms.



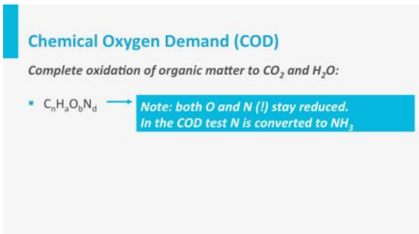
In an organic compound, O and N are fully reduced and have taken up 2 and 3 electrons, respectively, from the Carbon atom.
Hydrogen is fully oxidized and has delivered 1 electron. So the valence of H, O, and N in an organic compound is +1, -2 and -3, respectively.



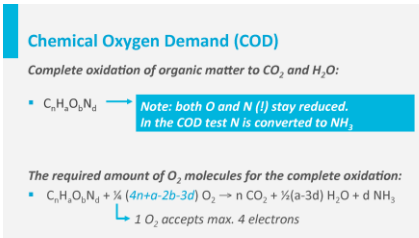
The average oxidation state of the carbon can then be calculated, taking the number of H, O, and N atoms into account, divided by the number of carbon atoms.
The lower the oxidation state of the carbon, the lower the number of O and N atoms in the compound.



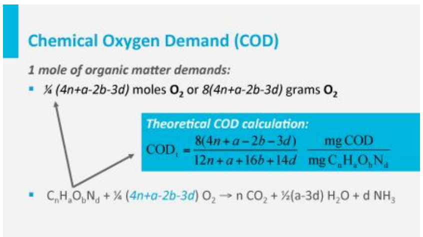
Based on the composition of this hypothetical compound, one can calculate the number of electrons that are made free per carbon atom, which is given in this formula.
It must be recalled that the valence of Carbon in CO_2 is +4, which is the most oxidized form of carbon.
The O and N present in the compound, already have accepted electrons from carbon.
So, this amount of electrons must be lowered from the total amount required for full oxidation of the carbon.
In contrast, H has donated an electron to the carbon.



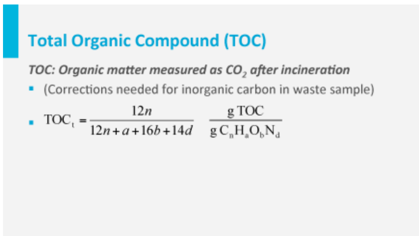
In the complete chemical oxidation of the organic compound to CO_2 and water, the O and N stay reduced - like in the original imaginary organic compound - and will not be oxidized during the COD test.
The H will stay oxidized during the test.
This means that only the C will transfer its remaining electrons to oxygen, and thus will be fully oxidized.



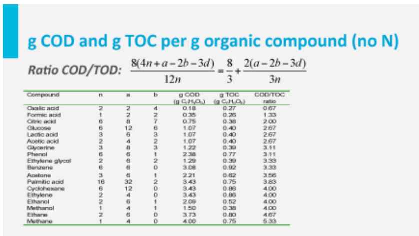
Now, we can calculate how much oxygen is required to oxidize all carbon to CO_2.
Note that 1 molecule oxygen will accept 4 electrons



The next step is to couple the COD molar ratio to the mass weight of the compound.
Note that the molar weight of oxygen is 32 g/mol.
With the obtained ratio, the COD of every organic compound can be calculated per gram weight of that compound.

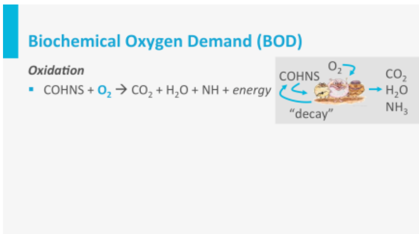


Don't mix up the COD assessment with TOC assessment.
TOC stands for Total Organic Carbon, which is the total weight of organic carbon atoms relative to the weight of the organic compound.
In this test, all carbon is incinerated after which it is measured as CO_2.
Test results must be corrected for inorganic carbon already present in the water sample.

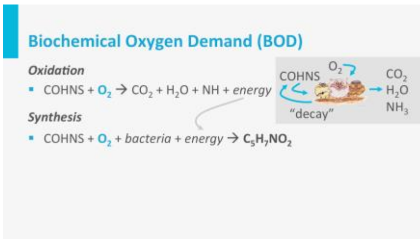


Compound	n	a	b	g COD ($g\ C_nH_aO_b$)	g TOC ($g\ C_nH_aO_b$)	COD/TOC ratio
Oxalic acid	2	2	4	0.18	0.27	0.67
Formic acid	1	2	2	0.35	0.26	1.33
Citric acid	6	8	7	0.75	0.38	2.00
Glucose	6	12	6	1.07	0.40	2.67
Lactic acid	3	6	3	1.07	0.40	2.67
Acetic acid	2	4	2	1.07	0.40	2.67
Glycerine	3	8	3	1.22	0.39	3.11
Phenol	6	6	1	2.38	0.77	3.11
Ethylene glycol	2	6	2	1.29	0.39	3.33
Benzene	6	6	0	3.08	0.92	3.33
Acetone	3	6	1	2.21	0.62	3.56
Palmitic acid	16	32	2	3.43	0.75	3.83
Cyclohexane	6	12	0	3.43	0.86	4.00
Ethylene	2	4	0	3.43	0.86	4.00
Ethanol	2	6	1	2.09	0.52	4.00
Methanol	1	4	1	1.50	0.38	4.00
Ethane	2	6	0	3.73	0.80	4.67
Methane	1	4	0	4.00	0.75	5.33

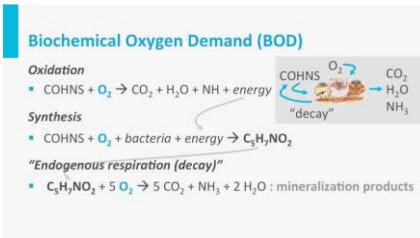
The COD/TOC ratio for all compounds ranges between 0 and 5.33, and is a direct measure of the average oxidation state of the carbon in a specific compound or waste sample.
The higher the COD/TOC ratio, the more impact the compound or waste sample will have on the surface water oxygen concentration.
Is the COD value, or the COD/TOC ratio, of an unknown organic waste sample a proper measure to assess its biological impact? Or to estimate its maximum degree of biological conversion?
The answer is no! As mentioned previously, the biodegradability of an organic compound depends on its exact composition.
Organic residues present in the sewer system consists of partly biodegradable compounds.
To assess the actual biodegradability of organic compounds, another test has been developed, which is based on microbial conversion of the organics, the so-called biochemical oxygen demand or BOD test.



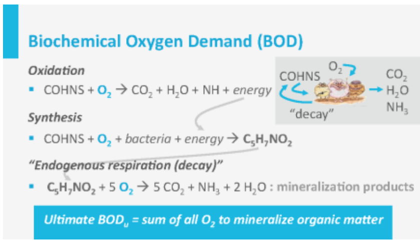
In the BOD test, the known or unknown organic compound or substrate, is also oxidized using oxygen as electron acceptor, but now the conversion is performed by bacteria, as schematically presented in this slide.
Why bacteria do that?
Well, similar to why we consume food, bacteria gain energy from this oxidation reaction, which they need for the subsequent process:



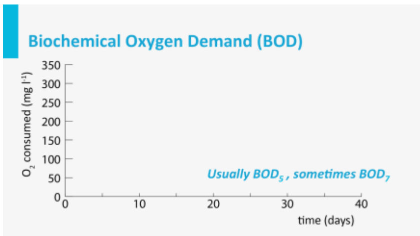
Synthesis of new cell material.
In both reactions, oxygen is required as electron acceptor.



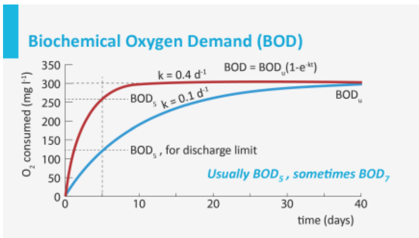
Finally, bacterial cells will dye-off, after which the cell material will be disintegrated in organic compounds.
This process is called decay.
The released bio-polymers are subsequently mineralized, using again oxygen as electron acceptor.
The oxygen requirement to oxidize these bacterial polymers, is called endogenous respiration.
The total amount of oxygen, used by the bacteria in all 3 processes, is a measure for the actual oxygen demand, of the organic compound that was discharged into the surface water.



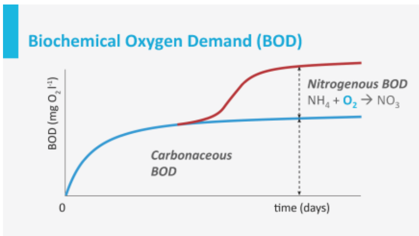
The ultimate BOD is the biochemical oxygen demand of the organic substrate, when the test is followed until infinite period of time.
Or, in other words, until all organic matter including the biomass produced during the test, is mineralized to inorganic compounds by the bacterial inoculum.
Non-biodegradable matter, for instance lignin, will remain untouched.
Since the BOD assessment is a biological test, the final result depends on a number of parameters: the test duration, the temperature, the presence of toxic compounds, the quality of the bacterial inoculum, the oxygen transfer, and of course the biodegradability of the sample.
The high number of variable parameters means that deviation in tests results will be much larger compared to the COD tests.



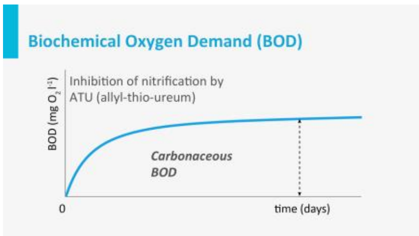
Since in general, there is no time to wait for such long periods of time, the BOD tests is standardized to a duration of 7, or most commonly, 5 days, indicated as BOD7 and BOD5, respectively.
The result of this standardization is that the 5-days test may underestimate the actual BOD values, when the conversion of the organic compound is more difficult… or when the inoculum is very poor.



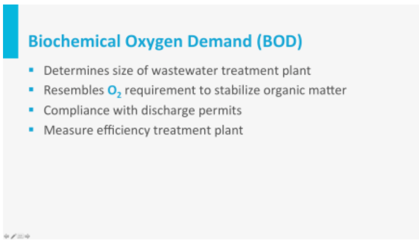
The red line in this graph shows a rapid bacterial conversion of the added compound, resulting in a more or less completion of the test after 5 days. The BOD5 is here a good estimate of the actual BOD value. However, the test results of the blue line at day 5 severely underestimates the actual BOD value.
Imagine what this means for a stagnant water body when we discharge this water? Proper assessment of the effluent BOD concentration is absolutely necessary to prevent possible oxygen depletion in the receiving surface water.
But also for estimating whether the biological capacity of an activated sludge plant is sufficient. Generally, these tests are done in triplicate.



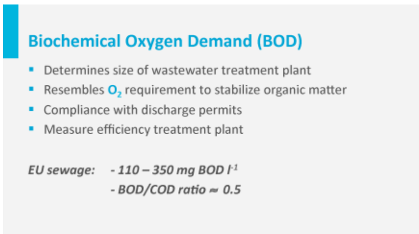
A major difference between the COD and the BOD test, is that in the BOD test ammonium is biologically oxidized to nitrate, whenever this nitrifying capacity is available.
Since these organisms grow slowly, it may take some time before the nitrification reaction starts.



While performing the BOD test, it is possible to deliberately prevent the nitrification reaction, by adding the inhibitor, allyl-thio-ureum or ATU, to the medium.



Irrespective the difficulties of the BOD tests, BOD is the prime parameter for the design of activated sludge plants, since it resembles the actual oxygen requirement, needed to stabilize the organic pollutants.
Therefore, it is also the most important standard in the effluent of STPs. Moreover, by comparing the influent and effluent BOD value, the operator can calculate the BOD removal efficiency, an important plant control parameter.



In European domestic sewage the average BOD value is between 110 and 350 mg BOD/l, whereas the BOD/COD ratio in the influent is about 0.5. What could be the reason why the COD value of sewage always exceeds the BOD value? And what happens with the BOD/COD ratio during biological treatment of the sewage?
Check out the questions and answers of our online course.