Maryland Virtual High School
Instructional Activity

Stream Assimilation Capacity for Waste Material

Author: Tran Pham

Course: Chemistry - Grades 11-12 (target audience)

Duration: Two weeks for classes meeting two successive periods daily

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STREAM ASSIMILATION CAPACIY FOR WASTE MATERIAL

Almost all human activities change the balance of nature. These disturbances can be planned or unplanned to nature in an unnatural manner. This computer model will examine the response of nature in a quantitative understanding of natural processes and serve as an assessment tool for the response and recovery of nature.

Unit Purpose:
By using a computer model of a dynamic system, the students can assimilate the process of biodegradable processes in nature. The students will evaluate, analyze and control the relationships among the natural and man-made factors that affect these natural processes. With laboratory experiments, the students can use the computer model to design and implement a system to control the environmental processes. The students will explore the concepts of chemical reactions, chemical equilibria, reaction rates, reaction mechanisms, catalyses, orders of reactions, reaction kenetics and chemical kenetics.

Unit Objective:
The unit objective is to develop a model which will simulate the biodegradable process of man–made waste released into a stream. The students can design, experiment, collect data, build a computer model, evaluate the model, and redesign it to produce a working model applying appropriate mathematics and chemistry concepts. The model is derived from Chemodynamics by Louis J. Thibodeaux, copyright 1979, published by Wiley-Interscience Publication, New York, NY.

Unit Overview:
The stream simulation is a STELLA model that deals with oxygen levels in a stream as related to the amount of a given kind of waste dumped into the stream. A factory is located near a stream. Then, the stream flows into a larger body of water. The factory dumps waste into the stream in varying amounts, and the waste affects oxygen concentration in the water through the biodegradable processes. When the oxygen concentration gets below a given concentration, the fish in the stream begin to suffocate. The goal of the model is to find the maximum amount of waste that can be released, without killing the stream.

Material:

- STELLA II, a modeling language for Mac/Windows platforms
- Chemicals and laboratory equipment for dissolved oxygen:
  - Lamotte's Dissolved Oxygen Test kit

  or

  - UV/VIS spectrophotometer (recommended)
  - Maganous sulfate
  - Sodium hydroxide
  - Sodium iodide
  - Sodium azide
  - Sodium carbonate
  - Sulfuric acid
  - Starch
  - Sodium thiosulfate
  - Potassium bi-iodate
  - Potassium flouride
- Starch as pollutant
- Chemicals and laboratory equipment for pollutant determination
  - Potassium metabisulfate
  - Potassium Iodate
  - UV/VIS Spectrophotometers

Concepts:
The model can be used to introduce students to chemical reactions, chemical equilibria, reaction rates, reaction mechanisms, catalyses, order of reactions, reaction kenetics and chemical kenetics.

Links to State Outcome:
Learning Outcomes in Science for Maryland School Perfomance Assessment Program, Maryland State Department of Education (1994). Life Science Concept Indicators, K-12 Progression.

- humans have a major impact on the living and nonliving environment
- basic priciples of physical science apply to living organisms (classes of biochmical compounds, transformation of energy, movement using basic forces)
- basic functions of organisms are carried out at the cellular level

Learning Outcomes in Science for Maryland School Perfomance Assessment Program, Maryland State Department of Education (1994). Physical Science Concept Indicators, K-12 Progression.

- materials have different physical properties
- matter undergoes physical and chemical changes
- every substance can exist in different states depending on temperature and pressure

Student Outcomes:
Students will gain skills in

- collecting, organizing, interpreting, and evaluating information
- decision making for individual, society, and the environment
- applying the chemistry concepts in the new technology
- evaluating the model according to the individual, social, ethical, and legal impacts of the enivironmental issues

Student Assessments:
By adding new factors or changing the variables of the model, students will be able to form new hypothesis and contruct another model to adapt to the changes.

Acknowledgements:
The original idea and the STELLA II implementation for this Instructional Activity was conceived and constructed by Sanjit Mohapatra for his Modeling and Simulation course during the 1994-95 year at the Blair Magnet Program.

Mathematical Model: The Material Balance - Deoxygenation and Reoxygenation of a Stream

Material Balance:

The law of conservation of mass is a general form of material balance. Consider a system with constant volume V, the concentration of the chemical B varies within the system V. One can determine the concentration of B as:

> [Rate of mass B flow into V]=[Rate of mass B flow out of V] + [Rate of mass B loss due to mass transfer from V] + [Rate of mass B loss due to chemical reaction within V] + [Rate of accumulation of mass B in V] (eq. 1)

Natural Reoxygenation of a Stream:

The natural processing of oxygen from air into the water of a stream is the first chemodynamic problem that students encounter in studying environmental pollution. The discharge of organic impurities, such as municipal sewage and industrial waste, into streams presents a common problem in the field of environmental engineering. Some organic impurities are removed by waterborne organisms using dissolved oxygen in the water to break them down to simpler compounds:

$$C_xH_yO_z + n\ O_2 \text{ ---microbial/enzymes----> products of } CO_2,\ H_2O, \text{ etc.} \qquad \text{(eq. 2)}$$

This equation simplifies the biological removal processes of organic pollutants, $C_xH_yO_z$, in streams. The organic impurities require an amount of of oxygen, O_2, measured as an "oxygen demand". The biochemical conversion of 1 g of "oxygen demand" organic matter requires 1 g of molecular oxygen. The removed oxygen must be replaced by reoxygenation which occurs through the contact between the water's surface and the atmosphere. The concentration of oxygen in the stream water is called dissolved oxygen. Factors which affect it include temperature, concentration of all organic wastes, and water's surface areas. However, the concentration of the organic impurities can be so great that it will reduce the concentration of dissolved oxygen. When the oxygen concentration falls below the minimum requirements of marine life, the diversity of organisms in the stream will be reduced. Therefore, some discharge of organic waste into streams is acceptable, but it must be limited to the stream's capacity to assimilate.

Deoxygenation and Reoxygenation Mathematical Theory:

The classical work of Streeter Phelps in 1925 presented a mathematical analysis of the organic waste and oxygen content in water known as the oxygen sag. Consider an idealized stream: has a volume V of water, moves at the average velocity v, contains an oxygen concentration ρA and organic chemical B of concentration ρ_B. This volume V is located a distance L downstream from the single organic waste point of entry. Only two mechanisms, biochemical oxydation and interphase mass transfer of oxygen are occurring within the water. According to eq. 1, the organic material B can be written as:

$$0 = 0 + 0 + V(-r_B) + d(V\rho_B)/dt \qquad \text{(eq. 3)}$$

The rate disappearance of B is assumed to be a first order rate equation:

$$-r_B = k'''_B\ \rho_B \qquad \text{(eq. 4)}$$

where k'''_B is the rate constant. The negative sign in front of the rate symbol denotes the disappearance of B.

Combining eq. 3 and eq. 4, we can have:

$$d(\rho_B)/dt = -k'''_B\rho_B \qquad \text{(eq. 5)}$$

Oxygen, component A, enters the water through water's surface area A_{ZX}. The interphrase flux rate is:

$$n_A = {}^1k'_A(\rho^*_A - \rho_A) \qquad \text{(eq. 6)}$$

where: ${}^1k'_A$ is mass transfer coefficient of oxygen
ρ^*_A is the concentration of oxygen upstream from the organic waste point of entry
$(\rho^*_A - \rho_A)$ is the oxygen deficit

$$\Delta_A = (\rho^*_A - \rho_A) \qquad \text{(eq. 7)}$$

According to eq. 1, the material balance of oxygen can be written as:

$$0 = 0 - n_A A_{ZX} + V(-r_B) + d(V\rho_A)/dt \qquad \text{(eq. 8)}$$

Where A_{ZX} is the interface area of air and water contact for a constant volume V.

Substitute eq. 6 and eq. 7 into eq. 8 to obtain:

$${}^1k'_A\,(A_{ZX}/V)(\rho^*_A - \rho_A) - k'''_B\,\rho_B = d\rho_A/dt \qquad \text{(eq. 9)}$$

With the definition of oxygen deficit in eq. 7, eq. 9 can be expressed as: (assuming a constant stream temperature)

$$d\Delta_A/dt = k'''_B\,\rho_B - {}^1k'_A\,(A_{ZX}/V)\Delta_A \qquad \text{(eq. 10)}$$

Note: k'''_B is the oxygenation coefficient (t^{-1})
${}^1k'_A\,(A_{ZX}/V)$ is the reaeration coefficient (t^{-1})

Here, the rate of reaeration of oxygen can be examined with equation 5 and 10. If the initial conditions are

$\Delta A = \Delta A^\circ$
$\rho_B = \rho_B^\circ$
$t = 0$
$h = A_{ZX}/V$ - the depth of river

One can integrate with the initial conditions and combine eq. 5 and eq. 10 to obtain the relationship of oxygen deficit:

$$\Delta A = \{\{[k'''_B\,\rho^\circ_B]/[\,({}^1k'_A/h) - k'''_B]\}*\{e\hat{}(-k'''_B t) - e\hat{}({}^1k'_A t/h)\}\} + \Delta_A^\circ e\hat{}(-{}^1k'_A t/h) \qquad \text{(eq. 11)}$$

Note: This Model came from Chemodynamics by Louis J. Thibodeaux.

One STELLA II Model of Deoxygenation and Reoxygenation:

The concentration of oxygen in water is a function of temperature, pressure, and other dissolved and undissolved materials. However, the temperature and pressure in this model are considered to be constant. The dissolved waste B is only the total waste entering into the stream, and there is no soil corrosion on the banks of the stream. This waste B can be studied to determine the WasteCoef (k'''_B) in the laboratory. The growth rate of a micro-organism is considered in the determination of the WasteCoef (see Suggested Exercises and Discussion Questions). In addition, the waste can be easily monitored, and there is not another entry point before or below the mixing point of waste B. At the mixing point, there is a complete mixing between waste B and water. There is also a constant velocity of the water flow in the stream. In general, the stream is an ideal stream.

This model will use eq. 5 to describe the rate of removal of organic waste by bacteria:

WasteEaten=WasteCoef*WastePPM*Time

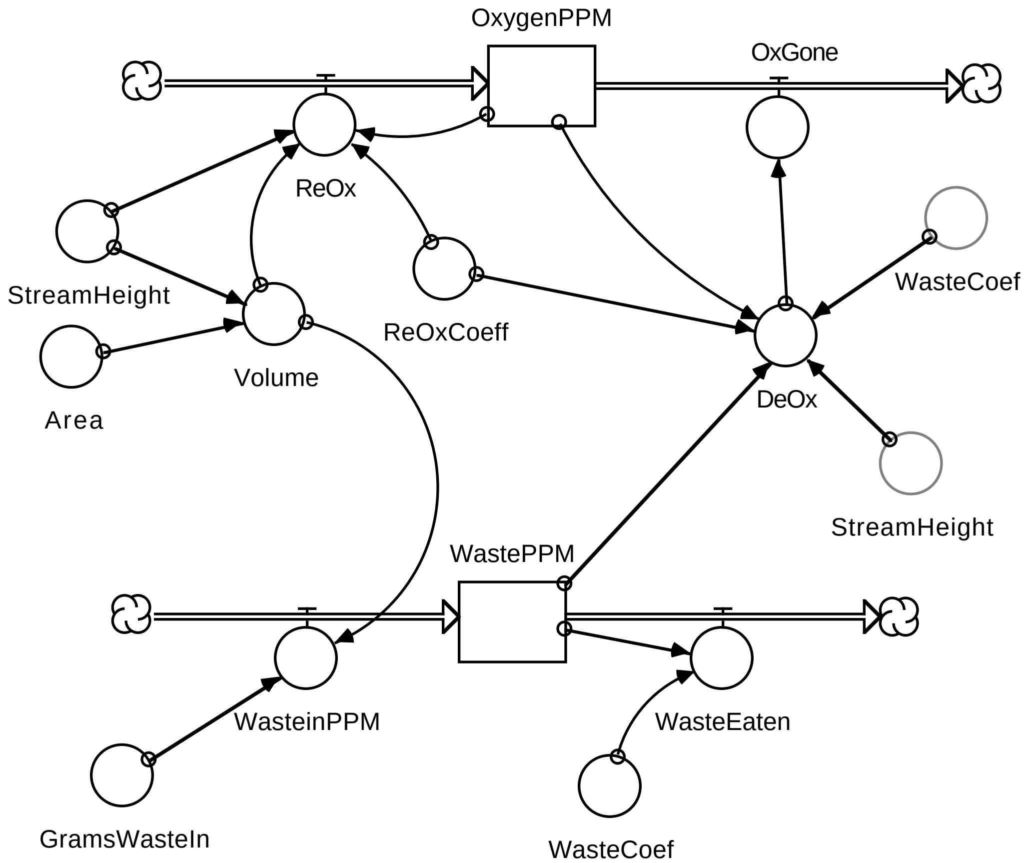
With eq. 10, the process of deoxygenation is:

DeOx = (wastecoef*WastePPM*time) -(ReOxCoeff/Streamheight*OxygenPPM*time)

The saturation value of oxygen in water is 9.8 ppm. Therefore, the rate of oxygen absorption is only the interphase of the water’s surface and air; there is no other mechanical or natural devices to increase the surface area of water. The rate of reoxygenation is:

ReOx = Area*(9.8-OxygenPPM)*ReOxCoeff*time

Figure 1: Deoxygenation and Reoxygenation Model



In this model, the test data are:

- Temperature = 17˚C
- Saturation value of oxygen = 9.8 ppm
- $k'''_B = 7.38 \times 10^{-5}$ ppm/sec (WasteCoef)
- $^1k'_A = 1.65 \times 10^{-3}$ ppm.ft/sec (ReOCoeff)
- Initial waste = 0 ppm in the water at time 0 sec
- Initial waste amount = 150,000*1000 g
- Stream height = 20 ft
- Stream volume = 200*20 ft^3
- Velocity of stream is 2ft/sec

Figure 2: System Equations for Deoxygenation and Reoxygenation

```
OxygenPPM(t) = OxygenPPM(t - dt) + (ReOx - OxGone) * dt
    INIT OxygenPPM = 9.8
    INFLOWS:
        ReOx = IF OxygenPPM=9.8 THEN 0 ELSE MIN((Volume/StreamHeight) * (9.8-
            OxygenPPM) * ReOxCoeff * (time-dt),9.8-OxygenPPM)
    OUTFLOWS:
        OxGone = DeOx

WastePPM(t) = WastePPM(t - dt) + (WasteinPPM - WasteEaten) * dt
    INIT WastePPM = 0
    INFLOWS:
        WasteinPPM = GramsWasteIn*(time)/(Volume*1000)
    OUTFLOWS:
        WasteEaten = WasteCoef*WastePPM*(time+dt)

Area = 200
DeOx = (WasteCoef*WastePPM*(time))-(ReOxCoeff/StreamHeight*OxygenPPM*(time))
GramsWasteIn = IF TIME = 1 THEN 250000*1000 ELSE 0
ReOxCoeff = .0000738
StreamHeight = 20
Volume = Area*StreamHeight
WasteCoef = .00165
```

By setting running the time options, the students can observe the relationship between the oxygen concentration and waste B concentration (in PPM) (see figure 3).

Figure 3: The Graphical Relationship Between the Oxygen Concentration and Waste B Concentration

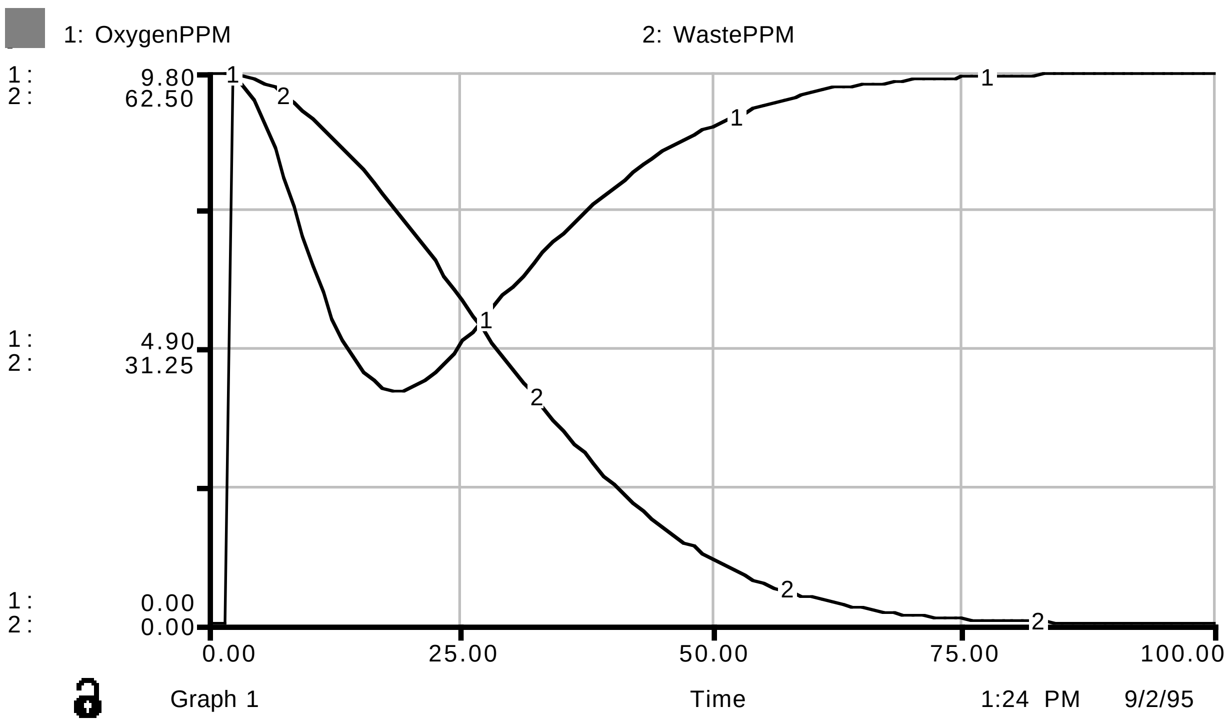


Figure 4: The Numeric Relationship Between the Oxygen Concentration and Waste B Concentration

Time	OxygenPPM	WastePPM	OxGone	ReOx	WasteEaten	GramsWasteIn
14	4.73	52.75	1.22	0.97	1.31	0
15	4.49	51.44	1.27	1.1	1.36	0
16	4.31	50.08	1.32	1.21	1.4	0
17	4.21	48.68	1.37	1.32	1.45	0
18	4.16	47.23	1.4	1.41	1.48	0
19	4.17	45.75	1.43	1.49	1.51	0
20	4.23	44.24	1.46	1.56	1.53	0
21	4.34	42.71	1.48	1.61	1.55	0
22	4.47	41.16	1.49	1.65	1.56	0
23	4.63	39.6	1.5	1.68	1.57	0

Teachers: Dissolved oxygen (DO) and $^{1}k'_{A}$ can be found in the CRC Chemical and Physical Handbook or Perry's Chemical Engineering Handbook. k'''_{B} for a specific chemical can also be found in Perry's or CRC's, but they can also be easily determined in the laboratory.

Suggested Exercises and Discussion Questions:

1. From the equations, determine the lowest concentration of oxygen in the stream?

   This minimum can be obtained by substituting the test data into eq. 11, and the answer is 4.1 ppm.

2. From the graph (oxygen sag curve) and data table of the model, determine the lowest concentration of oxygen in the stream?

   The answer is 4.17 ppm.

3. Determine the time and location of the lowest oxygen concentration. (Thibodeau)

   By setting the first derivative of eq. 11 to zero, the critical time is

$$t_c = \{1/[({}^1k'_A /h) - k'''_B]\}*\ln\{({}^1k'_A/hk'''_B)*[1 - \Delta_A{}^{\circ}([({}^1k'_A/h)-k'''_B]/k'''_B\rho_B{}^{\circ})]\}$$

$$t_c = 18 \text{ sec}$$

$$L_c = v*t_c$$

4. What is the importance of the lowest concentration of oxygen in the stream?

   This minimum should not be less than the oxygen concentration to sustain aquatic life in the stream. The students can determine the types and levels of higher life forms in a stream with the minimum concentration of oxygen. For example, catfish needs about 3.8 ppm or trout needs about 6 ppm.

5. How can you increase the minimum point of oxygen concentration on the oxygen sag curve of the model?

   By changing such elements as the amount of pollutants, season, flow of stream, mechanical mixing, and/or surface area of water.

6. Experiment: Design and build an aeration system to increase the transfer of oxygen from air to water. Optimize the size-cost-power by calculating the size of aeration system, the best type of equipments and cost.

   Teachers: Oxygen can be transferred:
   - from bubbles to liquid water (aspirators)
   - from atmosphere to water droplets (water falls)
   - from atmosphere to water interphase (quiet turbulent, sheets films, etc.)

7. Problem: (This problem is taken from class work developed by Dr. Craig Myler, Professor of Chemical Engineering, University of Maryland Baltimore County.)

   This morning, the headlines of local news paper read: "ACME chemicals kills catfish!" As a head engineer for the ACME company, it is going to be up to you to talk to the press this evening. You phone the plant and are told that no upsets have occured and nothing but non-toxics have been discharged. The sampling data from the previous day show the following:
   - Water saturated with oxygen above the plant (9.37 ppm)
   - Average depth = 20 ft

- Width = 10 ft
- Velocity = 2 ft/sec
- Temperature = 17˚C
- Distance to catfish kill is 0.5 mile
- $^{1}k'_A = 1.65 \times 10^{-3}$ ppm.ft/sec
- $k'''_B = 7.38 \times 10^{-5}$ ppm/sec
- Catfish need 3.8 ppm of DO to survive

What are you going to tell your boss? the press? and the public?

ACME did not kill the fish. The minimum dissolved oxygen is 4.10 ppm.

8. <u>Experiment</u>:
Determine k'''_B in laboratory with Lamotte's Dissolved Oxygen Test Kit or DO Standardized Methods for starch simulation.

<u>Procedure</u>:
The purpose of this section is to provide a general guide to the teachers. The teachers must supervise students and provide detailed procedures to each section of the experiment. In this experiment, starch is the organic pollutant.

- Make a 4% sollution of starch.
- Let the starch solution cool to room temperature.
- Install a pump to circulate the solution as an aeration system to change flow rate, surface area of water, etc.
- Determine the DO with Lamotte's Dissolved Oxygen Test Kit or DO Standarized Methods in time interval. DO Standardized Methods can be found in Standard Methods for the Examination of Water and Waste Water by Greenberg, Clesceri, and Eaton (Page 4–98 - 4–103). Lamotte's Test Kit can be purchased by calling (800) 344-3100 or (410) 778-3100.
- Determine the concentration of starch in the solution with UV/VIS spectrophotometric methods and potassium iodate.
- Calculate and interpretate the data according to DO Standardized Methods can be found in Standard Methods for the Examination of Water and Waste Water by Greenberg, Clesceri, and Eaton (Page 10-31 to 10-40).

9. What are the assumptions used by this model?

Constant biosphere
Constant chemical reactions
Constant rate of absorption
Constant surface area
Constant velocity
Constant volume
Homogenous system
Neglect of other absorptions
Neglect of other O_2 usage such as fish and plants
O_2 input by other means
Solubility or other equilibrium

This model can be extended by expanding any one of the above assumptions.

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