Pollutant Discharge Limits

- If pollutant discharge continues unabated, rivers and lakes will lose their acceptability for their intended beneficial use.

- Regulatory agencies’ primary responsibility is to impose restrictions on the quality of domestic or industrial effluents on water bodies on the basis of certain guidelines or standards of a particular country.

- In Bangladesh, DoE is the main regulatory agency which monitors effluent discharges by the industries and verify their compliance with the standards stated under the Environmental Conservation Rules 9ECR), 1997.
Surface Water Quality: Detection of Pollution

- Often pollution is first detected from visual observation. Visible signs of pollution include:
  - Floating debris
  - Occurrence of fish-kill
  - Bad taste and odor
  - Excessive growth of aquatic plants
  - Floating oil
  - Scum deposition
Principal Pollution Problems, affected uses and water quality variables

- Manifestation of problem
  - Fish kill, nuisance, odor, radical change in ecosystem

- Water use interference
  - Fishery, recreation, ecological health

- Water quality problem
  - Low dissolved oxygen

- Water quality variables
  - BOD, NH$_3$, TKN, Organic solids, phytoplankton, DO
Principal Pollution Problems, affected uses and water quality variables

- Manifestation of problem
  - Disease transmission, gastrointestinal disturbance, eye irritation

- Water use interference
  - Water supply, recreation

- Water quality problem
  - High bacterial levels

- Water quality variables
  - TC, FC, Fecal streptococci viruses
Principal Pollution Problems, affected uses and water quality variables

- Manifestation of problem
  - Taste and odor, excessive algae, unbalanced ecosystem

- Water use interference
  - Water supply, recreation, ecological health

- Water quality problem
  - Eutrophication

- Water quality variables
  - N, P, phytoplankton
Principal Pollution Problems, affected uses and water quality variables

- Manifestation of problem
  - Ecosystem upset – mortality, reproductive impairment (suspended carcinogen in water)

- Water use interference
  - Water supply, fishery, ecological health

- Water quality problem
  - High toxic chemical levels

- Water quality variables
  - Metals, pesticides, radioactive substances, other toxic chemicals
Water Quality Assessment Methods

- Chemical Assessment:
  - Well known and involve regular sampling of water in natural system, in the abstraction and treatment processes and of most effluents before being released.
  - Assessment involves regular testing for the presence and concentration of the major chemical parameters (Tables 11.2 and 11.3).
  - Test protocols are according to Standard Methods.
Table 11.2: Bangladesh Standards for sewage discharge into surface and in land water bodies.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>mg/l</td>
<td>40</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg/l</td>
<td>250</td>
</tr>
<tr>
<td>Phosphate</td>
<td>mg/l</td>
<td>35</td>
</tr>
<tr>
<td>Suspended Solids (SS)</td>
<td>mg/l</td>
<td>100</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>30</td>
</tr>
<tr>
<td>Coliforms</td>
<td>number/100ml</td>
<td>1000</td>
</tr>
</tbody>
</table>

*Source: Schedule- 9, Rule-13, Environment Conservation Rules, 1997.*
Table 11.3: Bangladesh Standards for industrial effluent discharge

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia-nitrogen (as elementary N)</td>
<td>mg/l</td>
<td>50</td>
</tr>
<tr>
<td>Ammonia (as free ammonia)</td>
<td>mg/l</td>
<td>5</td>
</tr>
<tr>
<td>Arsenic (as As)</td>
<td>mg/l</td>
<td>0.2</td>
</tr>
<tr>
<td>BOD₅ at 20°C</td>
<td>mg/l</td>
<td>50</td>
</tr>
<tr>
<td>Boron</td>
<td>mg/l</td>
<td>2</td>
</tr>
<tr>
<td>Cadmium (as Cd)</td>
<td>mg/l</td>
<td>0.05</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/l</td>
<td>600</td>
</tr>
<tr>
<td>Chromium (as total Cr)</td>
<td>mg/l</td>
<td>0.5</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>200</td>
</tr>
<tr>
<td>Chromium (as hexavalent Cr)</td>
<td>mg/l</td>
<td>0.1</td>
</tr>
<tr>
<td>Copper (as Cu)</td>
<td>mg/l</td>
<td>0.5</td>
</tr>
<tr>
<td>Dissolved oxygen (DO)</td>
<td>mg/l</td>
<td>4.5-8</td>
</tr>
<tr>
<td>Electro-conductivity (EC)</td>
<td>µSiemens/cm</td>
<td>1200</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>mg/l</td>
<td>2100</td>
</tr>
<tr>
<td>Fluoride (as F)</td>
<td>mg/l</td>
<td>2</td>
</tr>
<tr>
<td>Sulfide (as S)</td>
<td>mg/l</td>
<td>1</td>
</tr>
<tr>
<td>Iron (as Fe)</td>
<td>mg/l</td>
<td>2</td>
</tr>
<tr>
<td>Total kjeldahl nitrogen (as N)</td>
<td>mg/l</td>
<td>100</td>
</tr>
<tr>
<td>Lead (as Pb)</td>
<td>mg/l</td>
<td>0.1</td>
</tr>
<tr>
<td>Manganese (as Mn)</td>
<td>mg/l</td>
<td>5</td>
</tr>
<tr>
<td>Mercury (as Hg)</td>
<td>mg/l</td>
<td>0.01</td>
</tr>
<tr>
<td>Nickel (as Ni)</td>
<td>mg/l</td>
<td>1.0</td>
</tr>
<tr>
<td>Nitrate (as elementary N)</td>
<td>mg/l</td>
<td>10.0</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>mg/l</td>
<td>10</td>
</tr>
<tr>
<td>Phenolic compounds (as C₆H₅OH)</td>
<td>mg/l</td>
<td>1.0</td>
</tr>
<tr>
<td>Dissolved phosphorus (as P)</td>
<td>mg/l</td>
<td>8</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>6.9</td>
</tr>
<tr>
<td>Selenium (as Se)</td>
<td>mg/l</td>
<td>0.05</td>
</tr>
<tr>
<td>Zinc (as Zn)</td>
<td>mg/l</td>
<td>5</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>mg/l</td>
<td>2100</td>
</tr>
<tr>
<td>Temperature (thermal effluent)</td>
<td></td>
<td>°C (summer) 40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>°C (winter) 45</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>mg/l</td>
<td>150</td>
</tr>
<tr>
<td>Cyanide</td>
<td>mg/l</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Source: Schedule –10, Rule-13, Environment Conservation Rules, 1997*
Water Quality Assessment Methods

- Biological Assessment
  - By measuring the extent of the ecological upset, the severity of the impact can be assessed
  - Severity or tolerance to pollution varies from species to species
  - Overall effects of altered physico-chemical environment can be monitored through changes in
    - Species composition
    - Dominant groups within species
    - Behavior
    - High mortality of sensitive life stages (e.g. eggs)
    - Physiology
    - Metabolism
    - Morphological deformities
## Advantages and disadvantages of different water quality monitoring techniques

<table>
<thead>
<tr>
<th>Realm</th>
<th>Performances of chemical monitoring</th>
<th>Performance of biological monitoring</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precision (i.e. pollutant concentration assessment)</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Discrimination (i.e. what kind of pollution)</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Reliability (how representative is a single or limited number of samples)</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Measure of ecological effects</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Cost</td>
<td>Relatively high</td>
<td>Relatively low</td>
</tr>
</tbody>
</table>

Sayeed et al 2015
Oxygen Demanding Wastes

- Most common surface water pollutant
- Measured by
  - Biochemical Oxygen Demand (BOD)
    The amount of oxygen required by microorganisms to oxidize organic wastes aerobically is called “biochemical oxygen demand” (BOD). Usually expressed as mg/L
  - Chemical Oxygen Demand (COD)
    The amount of oxygen required for chemical oxidation of organic wastes is called “chemical oxygen demand” (COD). Usually expressed as mg/L
Aerobic vs Anaerobic decomposition

- **Aerobic decomposition:**
  
  \[
  \text{Organic matter} + O_2 \xrightarrow{\text{bacteria}} CO_2 + H_2O + \text{New cells} + \text{stable product}
  \]

- **Anaerobic decomposition:**
  
  \[
  \text{Organic matter} \xrightarrow{\text{bacteria}} CO_2 + CH_4 + \text{New cells} + \text{unstable products}
  \]

This produces highly objectionable end products e.g. $H_2S$, $NH_3$, $CH_4$ when emitted from water bodies.

$CH_4$ is often called “swamp gas”
Categories of Biochemical Oxygen Demand

- Carbonaceous BOD (CBOD)
- Nitrogenous BOD (NBOD)

- Carbonaceous organic material can be readily used by bacteria
- Decomposition of nitrogenous organic matter takes some time to start. There is a time lag in the growth of nitrifying bacteria necessary for oxidation of nitrogenous material
5 Day BOD Test

- Long time required for determining total $O_2$ required for decomposition of a particular waste sample (several weeks).

- It has become a standard practice to measure and report BOD over a period of 5-days (realizing that the ultimate demand is considerably higher).

Q. What kind of BOD would you expect to measure from 5-day BOD test? CBOD or NBOD?
5 Day BOD Test

- 300 mL BOD bottle used
- Stopper used to keep air from replenishing DO
- Light must be kept out of the bottle to keep algae from adding DO by photosynthesis
- Standard Temp is 20 degree C

\[ \text{BOD}_5 = (\text{DO}_0 - \text{DO}_5) \text{ mg/L} \]

- Oxygen demand of typical waste is often several hundred mg/L
- Saturated value of DO in water at 20°C is only 9.1 mg/L
- Wastewater samples, therefore are diluted to keep final DO (after 5 days above zero.)
BOD Test – 1 (without dilution)

BOD_5 = (DO_0 - DO_5) mg/L
BOD Test – 2 (with dilution)

Sample

Aeration

Well Mixed Reactor

Mixture

inlet

outlet

Dilution water (free from organic matter)

Dilution Factor = Volume of mix/Volume of sample

Measure DO_0

Measure DO_5

\[ \text{BOD}_5 = (\text{DO}_0 - \text{DO}_5) \times \text{Dilution Factor} \]

(mg/L)
In some cases, it becomes necessary to “seed” dilution water with microorganisms in order to ensure adequate bacterial population to carry out biodegradation.

In such cases, it is necessary to subtract oxygen demand caused by the seed from the demand in the mixed sample of waste and dilution water, in order to determine BOD of waste.
BOD Test – 3 (Seeded BOD Test)

BOD\textsubscript{m} = (DO\textsubscript{0} – DO\textsubscript{5}) \text{ mg/L}

BOD\textsubscript{d} = (DO\textsubscript{0} – DO\textsubscript{5}) \text{ mg/L}

BOD\textsubscript{m} \cdot V\textsubscript{m} = BOD\textsubscript{w} \cdot V\textsubscript{w} + BOD\textsubscript{d} \cdot V\textsubscript{d} \rightarrow \text{Find } BOD\textsubscript{w}
Chemical Oxygen Demand

- Measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in an acid solution where

\[
\begin{align*}
\text{CH}_n\text{O}_a\text{N}_b + d\text{CrO}_4^{-2} + (8d+c)\text{H}^+ & \rightarrow n\text{CO}_2 + \frac{a+8d-3c}{2}\text{H}_2\text{O} + c\text{NH}_4^+ + 2d\text{Cr}^{3+} \\
\text{where } \quad d &= \frac{2n}{3} + \frac{a}{6} - \frac{b}{3} - \frac{c}{2}
\end{align*}
\]
Why not cBOD is equal to COD?

1. Many organic substances which are difficult to oxidize biologically (e.g. lignin) can be oxidized chemically.

2. Inorganic substances that are oxidized by dichromate (e.g. sulfide, sulfite, ferrous ion)

3. Certain organic substances may be toxic to microorganisms used in the BOD test.
BOD vs COD

Typical BOD/COD of untreated domestic wastewater: 0.5-0.8

- **If BOD/COD ratio is 0.5:**
  → Waste is considered to be easily treatable by biological means

- **If BOD/COD ratio is 0.3:**
  → Organics in wastewater may be refractory
  → Organics in wastewater are degradable. However, another substance in wastewater leads to inhibition of bacteria that uses organic matter
  → Bacteria is not acclimated to wastewater
Problems

- A 15-mL sample of sewage is mixed with enough dilution water to fill a 300 mL BOD bottle. The bottle has an initial DO of 8.5 mg/L. At the end of 5 days, measured DO is 2.8 mg/L. Calculate BOD$_5$ of the sewage.

- Consider the previous example. 15 mL sewage has been mixed with dilution water to fill 300 mL BOD bottle. Initial DO is 8.5 mg/L and DO after 5 days is 2.8 mg/L. For a BOD bottle filled with only dilution water, initial DO is 8.7 mg/L and after 5 days DO is 7.7 mg/L. Calculate BOD of sewage.