

## Environmental Transport and Fate

### Chapter 4

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### Rivers & Streams

### Dissolved Oxygen

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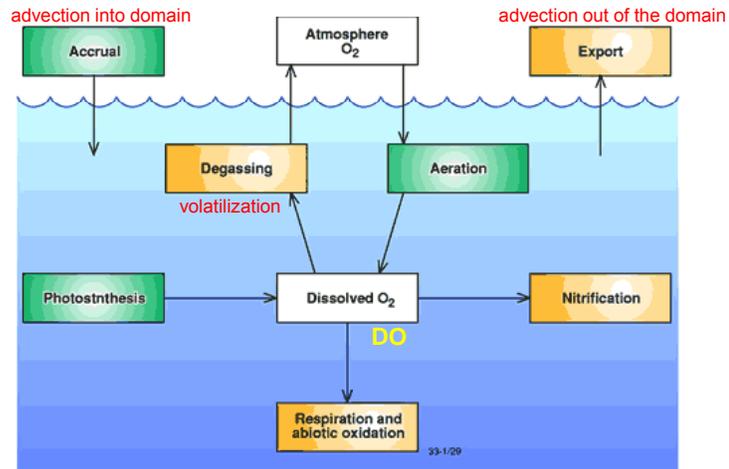
#### Dissolved Oxygen (DO)

By far the most important characteristic determining the quality of a river or stream is its dissolved oxygen, DO (measured in mg/L).

While the saturated value  $DO_s$  is rarely achieved, a stream can nonetheless be considered healthy as long as its dissolved oxygen DO exceeds 5 mg/L.

Below 5 mg/L, most fish, especially the more desirable species such as trout, do not survive. Actually, trout and salmon need at least 8 mg/L during their embryonic and larval stages and the first 30 days after hatching.

Processes adding and subtracting dissolved oxygen in open water



At equilibrium

Henry's Law:

$$[\text{dissolved gas}]_{\text{in water}} = K_H P_{\text{gas in air}}$$



Temperature (in °C)	Oxygen (M/atm)	Carbon dioxide (M/atm)
0	0.0021812	0.076425
5	0.0019126	0.063532
10	0.0016963	0.053270
15	0.0015236	0.045463
20	0.0013840	0.039172
25	0.0012630	0.033363

$$P_{\text{O}_2} = 0.21 \text{ atm}$$

$$P_{\text{CO}_2} = 390 \times 10^{-6} \text{ atm} \quad (390 \text{ ppm})$$

Values of saturated dissolved oxygen,  $DO_s$ , as function of ambient temperature

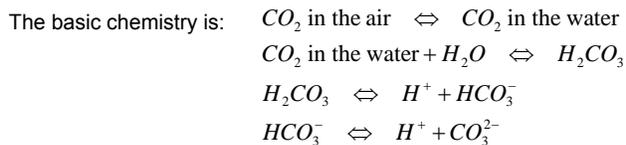
Temperature (°C)	Oxygen (mg/L)	Temperature (°C)	Oxygen (mg/L)
0	14.6	13	10.6
1	14.2	14	10.4
2	13.8	15	10.2
3	13.5	16	10.0
4	13.1	17	9.7
5	12.8	18	9.5
6	12.5	19	9.4
7	12.2	20	9.2
8	11.9	21	9.0
9	11.6	22	8.8
10	11.3	23	8.7
11	11.1	24	8.5
12	10.8	25	8.4

U.S. EPA recommendation for a healthy fish population:  $DO \geq 5$  mg/L.

For the better fish, such as trout and salmon:  $DO \geq 8$  mg/L.

### Acidity of pristine water

Open water, that is, water in contact with the atmosphere, exchanges  $CO_2$  with the air. Ditto of rain droplets.



with 1<sup>st</sup> equilibrium governed by Henry's Law  $[CO_2] = K_H P_{CO_2}$

with  $K_H = 0.045463 \text{ M / atm}$

2<sup>nd</sup> equilibrium governed by  $K_1 = \frac{[H_2CO_3]}{[CO_2]} = 1.58 \times 10^{-3}$  @ 15°C

3<sup>rd</sup> equilibrium governed by  $K_2 = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} = 2.83 \times 10^{-4} \text{ M}$

4<sup>th</sup> equilibrium governed by  $K_3 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 4.68 \times 10^{-11} \text{ M}$

While these reactions occurs, water always dissociates a little:



with  $K_w = [H^+][OH^-] = 10^{-14} M^2$

To complete the set of equations, we express the fact that no electron is left behind:  
(statement also known as *electroneutrality*)

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$


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We have a set of 6 equations for 6 unknowns,

$$[CO_2], [H_2CO_3], [HCO_3^-], [CO_3^{2-}], [H^+], [OH^-]$$

### Solution

For a concentration  $CO_2$  in the atmosphere of 390 ppm, the partial pressure is

$$P_{CO_2} = 390 \times 10^{-6} \text{ atm}$$

$$\rightarrow [CO_2] = (0.045463 \text{ M / atm})(390 \times 10^{-6} \text{ atm}) = 1.773 \times 10^{-5} \text{ M}$$

We then get in succession

$$[H_2CO_3] = K_1 [CO_2] = 2.801 \times 10^{-8} \text{ M}$$

$$[HCO_3^-] = \frac{K_2 [H_2CO_3]}{[H^+]} = \frac{7.928 \times 10^{-12} \text{ M}^2}{[H^+]}$$

$$[CO_3^{2-}] = \frac{K_3 [HCO_3^-]}{[H^+]} = \frac{3.710 \times 10^{-22} \text{ M}^3}{[H^+]^2}$$

From the equilibrium of water, we have

$$[OH^-] = \frac{10^{-14} \text{ M}^2}{[H^+]}$$

Having expressed all concentrations in terms of  $[H^+]$ , we can substitute in the equation of electroneutrality, which becomes an algebraic equation for  $[H^+]$  :

$$[H^+] = \frac{10^{-14} M^2}{[H^+]} + \frac{7.928 \times 10^{-12} M^2}{[H^+]} + 2 \frac{3.710 \times 10^{-22} M^3}{[H^+]^2}$$

of which the only physically acceptable solution is:

$$[H^+] = 2.82 \times 10^{-6} M = 10^{-5.55} M$$

$$\rightarrow pH = -\log_{10}[H^+] = 5.55$$

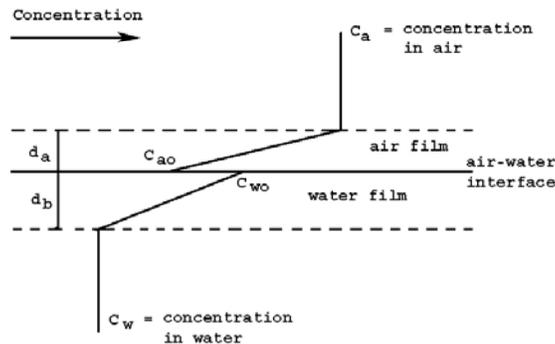
Note that this  $pH$  value is less than 7 (neutral water). Thus, water in contact with the atmosphere is slightly acidic because of the carbonic acid resulting from the  $CO_2$  taken from the atmosphere.

For a normal level of  $CO_2$  in the atmosphere, the resulting, weakly acidic water is said to be pristine.

For abnormally high levels of  $CO_2$ , the water became abnormally acidic ( $pH < 5.55$ ).

### Away from equilibrium

Thin-film model of re-aeration



$$j = k_r (DO_s - DO) \quad \leftarrow \text{Replenishment flux is proportional to the amount lacking, called deficit.}$$

$$\text{with } k_r(T, ^\circ C) = k_r(20^\circ C) 1.024^{T-20}$$

Re-aeration coefficient

$$K_r = \frac{k_r}{H}$$

with

$$k_r(T, \text{ in } ^\circ\text{C}) = k_r(20^\circ\text{C}) \times 1.024^{T-20} \quad (\text{in which } T \text{ is expressed in } ^\circ\text{C})$$

and

$$k_r(20^\circ\text{C}) = 3.9 \left( \frac{\bar{u}}{H} \right)^{1/2} \quad \text{with } \bar{u} \text{ in m/s and } H \text{ in m to get } k_r \text{ in m/day}$$

Typical values of the re-aeration coefficient,  $K_r$ :

Stream type	$K_r$ at 20°C (in 1/day)
Sluggish river	0.23 – 0.35
Large river of low velocity	0.35 – 0.46
Large stream of normal velocity	0.46 – 0.49
Swift stream	0.69 – 1.15
Rapids and waterfalls	>1.15

(Values from Peavy, Rowe & Tchobanoglous, 1985, page 87)

## Biochemical Oxygen Demand (BOD)

Except for pathogens, organic matter in water is generally not harmful in and of itself but may be considered as a pollutant because its bacterial decomposition generates a simultaneous oxygen depletion. Indeed, bacteria that feed on organic matter consume oxygen as part of their metabolism, just as we humans need to both eat and breathe.

The product of the decomposition is generally cellular material and carbon dioxide. The more organic matter is present, the more bacteria feed on it, and the greater the oxygen depletion. For this reason, the amount of organic matter is directly related to oxygen depletion, and it is useful to measure the quantity of organic matter not in terms of its own mass but in terms of the mass of oxygen it will have removed by the time it is completely decomposed by bacteria.

This quantity is called the **Biochemical Oxygen Demand** and noted BOD. Like dissolved oxygen DO, it is expressed in mg/L.

BOD values can be extremely large in comparison to levels of dissolved oxygen. For example, BOD of untreated domestic sewage generally exceeds 200 mg/L and drops to 20–30 mg/L after treatment in a conventional wastewater treatment facility. Still, a value of 20 mg/L is high in comparison to the maximum, saturated value of dissolved oxygen (no more than 8 to 12 mg/L). This implies that even treated sewage must be diluted, lest it completely depletes the receiving stream from its oxygen.

BOD decay rate:  $K_d$

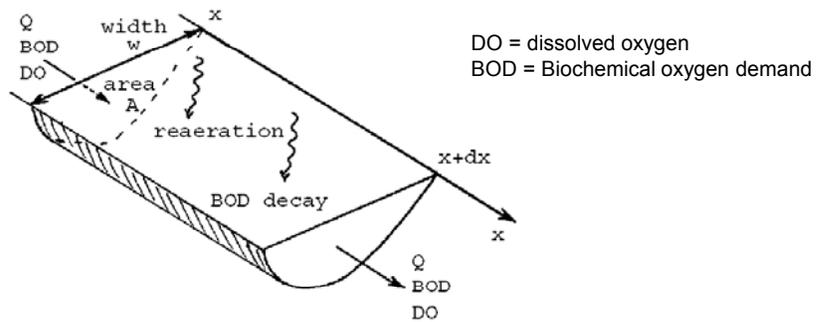
$$K_d(T, \text{ in } ^\circ\text{C}) = K_d(20^\circ\text{C}) \times 1.047^{T-20}$$

in which  $T$  is temperature in  $^\circ\text{C}$ .

Waste type	$K_d$ at 20°C (in 1/day)
Raw domestic sewage	0.35 – 0.70
Treated domestic sewage	0.12 – 0.23
Polluted river water	0.12 – 0.23

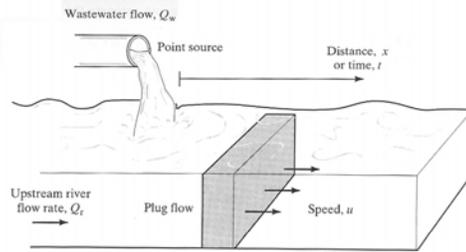
(Values from Davis & Cornwell, 1991)

### Dissolved Oxygen distribution along a river



Active processes are:

- Downstream advection of both dissolved oxygen (DO) and polluting substances (BOD)
- Decay of BOD, entraining an equal removal of DO
- Replenishment of dissolved oxygen in the stream through surface by exposure to atmosphere, by re-aeration.



(Diagram from Masters, 1997)

BOD budget:

$$\bar{u} \frac{dBOD}{dx} = -K_d BOD \rightarrow BOD = BOD_0 \exp\left(-\frac{K_d}{\bar{u}} x\right)$$

DO budget:

$$\bar{u} \frac{dDO}{dx} = K_r (DO_s - DO) - K_d BOD$$

Downstream advection

Surface re-aeration

Biochemical consumption

Assuming a highly advective situation

Mathematically, the solution is

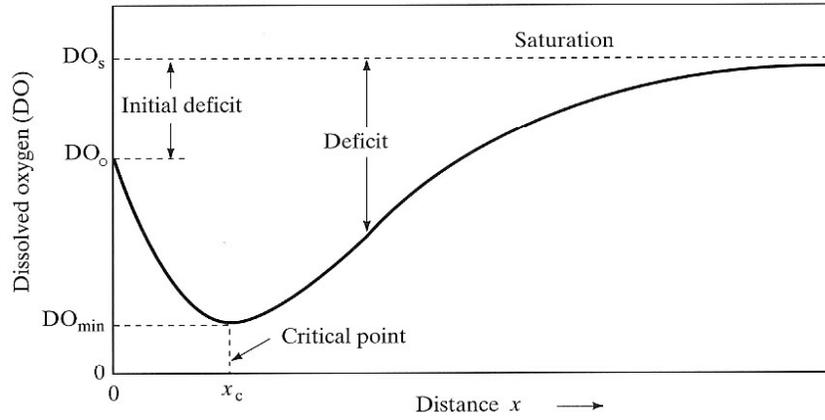
$$DO(x) = DO_s - \frac{K_d BOD_0}{K_d - K_r} \left[ \exp\left(-\frac{K_r x}{\bar{u}}\right) - \exp\left(-\frac{K_d x}{\bar{u}}\right) \right] - (DO_s - DO_0) \exp\left(-\frac{K_r x}{\bar{u}}\right)$$

← reference level  
 ← BOD consumption  
 ← trailing deficit

In the case of clean upstream water, there is no initial oxygen deficit ( $DO_0 = DO_s$ ):

$$DO(x) = DO_s - \frac{K_d BOD_0}{K_d - K_r} \left[ \exp\left(-\frac{K_r x}{\bar{u}}\right) - \exp\left(-\frac{K_d x}{\bar{u}}\right) \right]$$

Solution looks like:



This is called the "oxygen sag curve" or the "Streeter-Phelps oxygen sag curve".

Obviously, the place of greatest environmental concern is the DO minimum.

The minimum lies where  $dDO/dx = 0$ , which is found to be at:

$$x_c = \frac{\bar{u}}{K_r - K_d} \ln \left\{ \frac{K_r}{K_d} \left[ 1 - \frac{(K_r - K_d)(DO_s - DO_o)}{K_d BOD_0} \right] \right\}$$

This is the distance downstream from the discharge to the location where the lowest dissolved oxygen occurs. At that location, the BOD decay rate exactly balances the re-aeration rate, so that there is no local change in the amount of dissolved oxygen.

Note that an  $x_c$  value may not exist if the expression inside the logarithm is negative. This occurs when the upstream oxygen deficit  $DO_s - DO_o$  is relatively large compared to the  $BOD_0$  loading, in which case re-aeration dominates from the beginning, and the dissolved oxygen simply recovers from its initial deficit without passing through a minimum anywhere downstream.

When the stream has no oxygen deficit upstream of the BOD discharge:

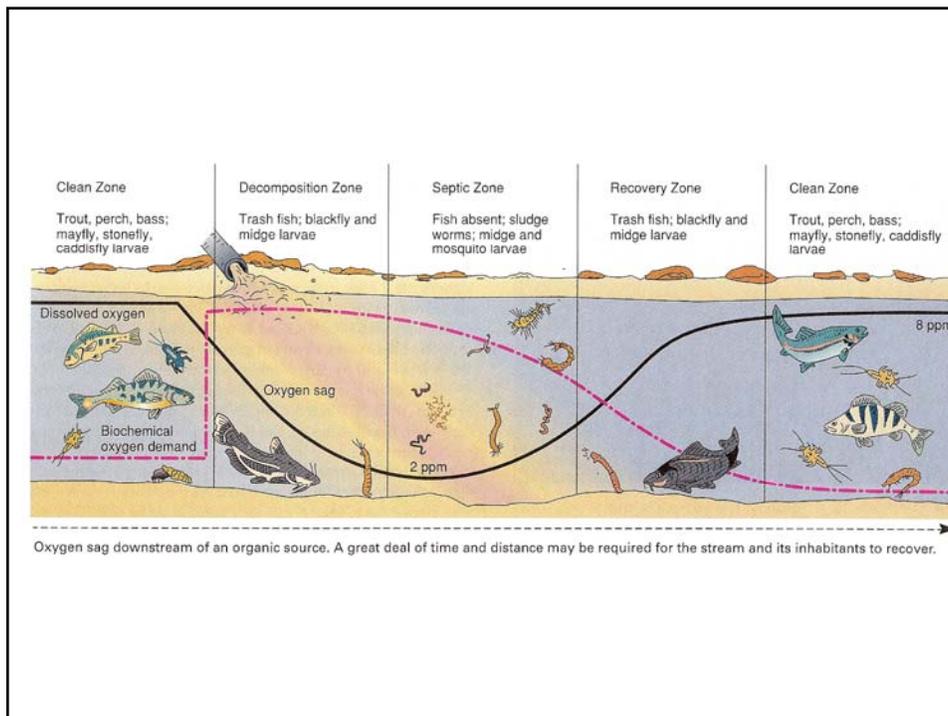
$$DO_o = DO_s \rightarrow x_c = \frac{\bar{u}}{K_r - K_d} \ln\left(\frac{K_r}{K_d}\right)$$

which is independent of the loading  $BOD_o$  and always exists.

The ratio  $K_r/K_d$  has been called the **self-purification ratio**.

Once the critical distance  $x_c$  is determined, the minimum value  $DO_{\min}$  of the dissolved oxygen is found by substitution of the  $x_c$  value in the solution for  $DO(x)$ .

No mathematical expression is written down here because it is extremely cumbersome. In practice, numerical values are used before the substitution.



Mathematically, it may happen that  $DO_{\min}$  falls below zero, which is physically impossible.

Should this be the case, the dissolved oxygen reaches zero before a minimum is reached [at an  $x$  location found by setting the expression for  $DO$  to zero], and  $DO = 0$  persists further downstream. Over this stretch of the stream, the previously stated BOD budget no longer holds. Instead, the re-aeration rate, then equal to  $K_r DO_s$ , limits the BOD consumption, and if anaerobic degradation may be neglected (usually necessarily a good assumption!), we may write that the BOD decay is exactly the rate of re-aeration:

$$\bar{u} \frac{dBOD}{dx} = -K_r DO_s$$

$$\rightarrow BOD(x) = BOD(x_1) - \frac{K_r DO_s}{\bar{u}} (x - x_1)$$



where  $x_1$  is the value where  $DO$  first falls to zero.

The dissolved oxygen remains at zero to the point  $x_2$  where the BOD falls to a value where the aerobic decay  $K_d BOD$  can resume:

$$-K_r DO_s = -K_d BOD(x_2)$$

$$= -K_d \left[ BOD(x_1) - \frac{K_r DO_s}{\bar{u}} (x_2 - x_1) \right] \longrightarrow x_2 = x_1 + \frac{\bar{u}}{K_d} \left[ \frac{K_d BOD(x_1)}{K_r DO_s} - 1 \right]$$

The previous model tacitly assumed that the only oxygen demands on the river are the BOD of the discharge and any prior oxygen deficit.

In actual rivers, sediments may cause a significant additional oxygen demand, because many forms of river pollution contain suspended solids (SS) that gradually settle along the river bed, spreading over a long distance and subsequently decay.

In heavily polluted rivers, this sediment oxygen demand (SOD) may be in the range of 5 – 10 mg/(m<sup>2</sup>.day) along the surface of the channel bed.

In the  $DO$  budget, the sediment oxygen demand appears as a sink term on the left-hand side equal to  $-SOD/H$ , and the solution for  $DO(x)$  needs to be amended.

## Environmental Transport and Fate

### Chapter 4

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## Rivers & Streams Erosion & Sedimentation

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Rivers and stream carry material in the form of solid particles that may alternatively be deposited on the river bed (sedimentation) and entrained back into the moving water (erosion). Such material may be contaminated, and therefore one pollution transport mechanism in a river is by sedimentation and erosion.

Studies have shown that the entrainment of a solid particle lying on the bed into the flow depends primarily on the size of the particle and the stress exerted by the moving water onto the bed. A particle of diameter  $d$  is entrained into the flow when the bottom stress  $\tau_b$  exceeds a critical value. The greater the particle diameter, the stronger the stress must be.

We saw earlier that in a river the bottom stress is given by:

$$\tau_b = \rho g R_h S \approx \rho g H S$$

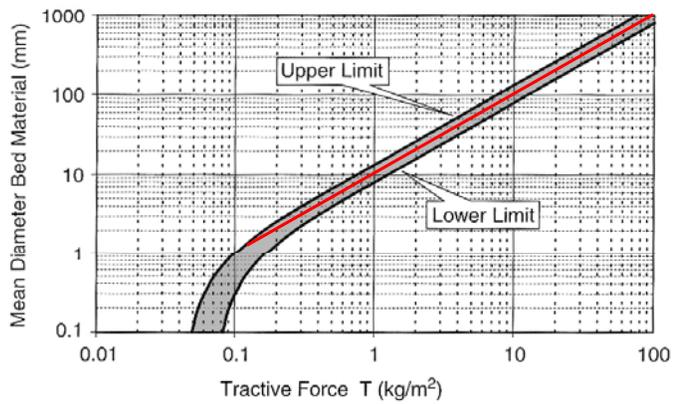
In erosion/sedimentation studies, the following reduced expression is often used:

$$T = \frac{\tau_b}{g} = \rho H S$$

which is called the *Tractive Force* (with units not of a force, but those of mass per area!).

There is a relation between the value of the tractive force  $F$  and the diameter of the largest particles being entrained.

This relationship is not unique, however, because there is considerable scatter in the data. This is due to underlying factors, such as particle shape and density.



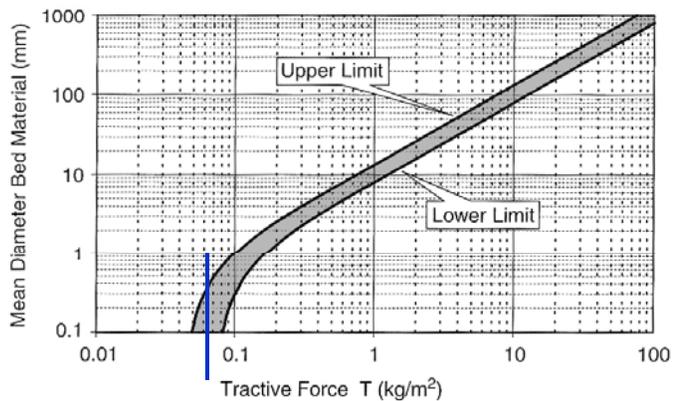
If one adopts the line that bisects the gray zone of scatter, one obtains the diameter  $d$  of the particle that has a 50% chance of being entrained into the stream.

For a tractive force exceeding  $0.1 \text{ kg/m}^2$ , the relationship is very nearly linear, and we can use the simple proportionality

$$d = 12.9 \frac{u_*^2}{g}$$

For smaller particle, with diameter  $d < 0.5 \text{ mm}$ , use the following criterion:

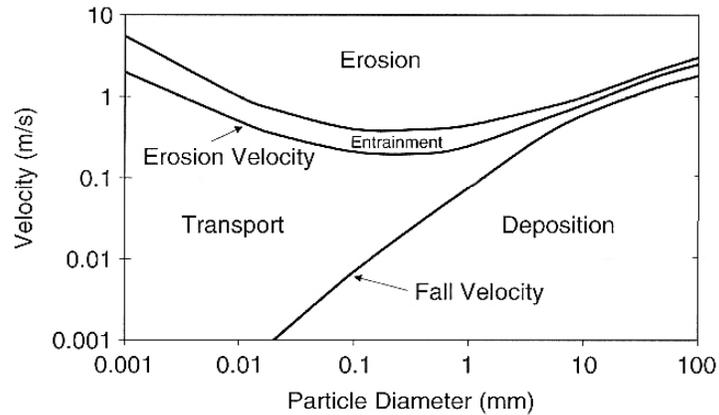
- If  $T < 0.065 \text{ kg/m}^2$ , there is no erosion of any particle of diameter less than  $0.5 \text{ mm}$
- If  $T > 0.065 \text{ kg/m}^2$ , all particles of diameter smaller than  $0.5 \text{ mm}$  are eroded.



Because the mean stream velocity  $\bar{u}$  is intimately related to the bottom stress, via

$$\bar{u} = Cu_* = C \sqrt{\frac{\tau_b}{\rho}}$$

and hence also to the tractive force, one can recast the preceding plot in terms of particle diameter and stream velocity. The result is the so-called Hjulstrom diagram, which also shows the settling (fall) velocity.



The amount of sediment transported by the stream, if any, is called the *wash load*, *suspended load*, or simply *bedload*. The load is carried downstream by a combination of sliding, rolling and bouncing (called *saltation*).

The volumetric bedload discharge  $q_s$  can be determined by the Meyer-Peter-Muller equation:

$$\frac{q_s}{\sqrt{g' d_{50}^3}} = \left( \frac{4u_*^2}{g' d_{50}} - 0.188 \right)^{3/2}$$

where  $q_s$  is expressed in  $m^3/s$  per m of channel width (hence in  $m^2/s$ ),

$d_{50}$  is the median particle size (in m),

$u_*$  is the friction velocity (in m/s), and

$g'$  is the gravitational acceleration experienced by the particles, defined as

$$g' = \frac{\rho_{solid} - \rho_{water}}{\rho_{water}} g$$

A typical particle density is

$$\rho_{solid} = 2650 \text{ kg} / \text{m}^3$$

$$\rightarrow g' = 16.19 \text{ m} / \text{s}^2$$

Entrained mass of sediments:

$$\dot{m} = \rho_{solid} q_s W$$

giving  $\dot{m}$  in kg/s from  $\rho_{solid}$  in kg/m<sup>3</sup>,  
 $q_s$  in m<sup>2</sup>/s  
channel width  $W$  in m.