Manual for Marine Monitoring in the

COMBINE

Programme of HELCOM

Part B

General guidelines on quality assurance for monitoring in the Baltic Sea

Annex B-8

Technical note on the determination of hydrographic parameters

Appendix 3

Recommended equations for the calculation of solubility and saturation of dissolved oxygen in sea water

ANNEX B-8: TECHNICAL NOTE ON THE DETERMINATION OF HYDROGRAPHIC PARAMETERS

ANNEX B-8 APPENDIX 3: RECOMMENDED EQUATIONS FOR THE CALCULATION OF SOLUBILITY AND SATURATION OF DISSOLVED OXYGEN IN SEA WATER

1. INTRODUCTION

When only physical processes are involved, the dissolved oxygen (DO) concentration in water is governed by the laws of solubility, i.e., it is a function of atmospheric pressure, water temperature, and salinity. The corresponding equilibrium concentration is generally called solubility. It is an essential reference for the interpretation of DO data. Precise solubility data, tables, and mathematical functions have been established (Carpenter, 1966; Murray and Riley, 1969; Weiss, 1970) and adopted by the international community (UNESCO, 1973). However, Weiss (1981) drew attention to an error in the international tables in which the values are low by 0.10 % since they are based on ideal gas molar volumeinstead of actual dioxygen molar volume. Later, the Joint Panel on Oceanographic Tables and Standards (JPOTS) recommended that the oxygen solubility equation of Benson and Krause (1984), which incorporated improved solubility measurements, be adopted and the tables updated (UNESCO, 1986). However, the UNESCO paper only referred to the equation that gives concentrations in the unit “micromole per kilogram”.

The present document repeats the equations that should be used for the computation of solubility values of dissolved oxygen, in various units, according to the UNESCO recommendation. These equations (so-called B & K equations) are directly taken from the paper of Benson and Krause (1984), who provided two equations for calculation either in “micromole per kilogram” or in “micromole per litre”, and the conversion factors for data in “milligram per litre” and “millilitre per litre”.

2. B & K SOLUBILITY EQUATIONS

Two equations of the same type have been established for DO solubility, to obtain concentrations either in “micromole per kilogram” or in “micromole per litre”.

Two points should be clear:

1. in these equations, the species under consideration is dioxygen (O2), therefore, “micromole” means “micromole of O2”;
2. 1 litre = 1 cubic decimetre, exactly.

The following symbols are used:

t : Celsius temperature (°C),

T : Kelvin temperature (K), T (K) = t (°C) + 273.15,

S : salinity on the Practical Salinity Scale 1978 (PSS78),

Cs : DO solubility concentration (the unit is mentioned using subscripts).

The equations can be expressed as follows:

$$\ln Cs_{(\mu\text{mol kg}^{-1})} = A + B/T + C/T^2 + D/T^3 + E/T^4 - S \times (F + G/T + H/T^2),$$

and

$$\ln Cs_{(\mu\text{mol l}^{-1})} = I + J/T + K/T^2 + L/T^3 + M/T^4 - S \times (N + P/T + Q/T^2).$$

The constants A to Q are the following:

Unit:

micromole per kilogram	micromole per litre
A = –135.29996	I = –135.90205
B = +1.572288 × 10^5	J = +1.575701 × 10^5

$\mathbf{C = -6.637149 \times 10^{7}}$ $K = -6.642308 \times 10^{7}$

$\mathbf{D = +1.243678 \times 10^{10}}$ $L = +1.243800 \times 10^{10}$

$\mathbf{E = -8.621061 \times 10^{11}}$ $M = -8.621949 \times 10^{11}$

$\mathbf{F = +0.020573}$ $N = +0.017674$

$\mathbf{G = -12.142}$ $P = -10.754$

$\mathbf{H = +2363.1}$ $Q = +2140.7$

Application domain: t = 0–40 °C; S = 0–40.

Cs is obtained as:

$Cs = \exp(\ln Cs)$,

i.e., when developing the equation:

$Cs_{(\mu mol\ kg^{-1})} = \exp[-135.29996 + (1.572288 \times 10^{5}) / (t + 273.15) - (6.637149 \times 107) / (t + 273.15)^{2} + (1.243678 \times 10^{10}) /$

$(t + 273.15)^{3} - (8.621061 \times 10^{11}) / (t + 273.15)^{4} - S \times (0.020573 - 12.142 / (t + 273.15) + 2363.1 / (t + 273.15)^{2})]$.

and

$Cs_{(\mu mol\ l^{-1})} = \exp[-35.90205 + (1.575701 \times 10^{5})/(t + 273.15) - (6.642308 \times 10^{7}) / (t + 273.15)^{2} + (1.243800 \times 10^{10})$

$/ (t + 273.15)^{3} - (8.621949 \times 10^{11}) / (t + 273.15)^{4} - \times (0.017674 - 10.754 / (t + 273.15) + 2140.7 / (t + 273.15)^{2})]$.

3. SOLUBILITY DATA IN "MILLIGRAM PER LITRE" AND "MILLILITRE PER LITRE"

Solubility in **milligram per litre** is obtained from the value in micromole per litre by multiplying by the molar mass of dioxygen (O_2) and 10−3 for unit consistency, that is:

$Cs_{(mg\ l^{-1})} = Cs_{(\mu mol\ l^{-1})} \times 0.0319988$.

Solubility in **millilitre per litre** is obtained from the value in micromole per litre by multiplying by the molar volume of the gas at standard temperature and pressure (STP; 0 °C, 1 atmosphere). For that conversion, some data previously published refer to the molar volume (STP) of dioxygen (O_2; 0.0223916 ml per micromole), like those of Weiss (1970), while others refer to that of an ideal gas (0.022414 ml µmol−1), like those of the UNESCO tables and Benson and Krause (1984). Referring to exact O_2 molar volume:

$Cs_{(\mathrm{ml\ l}^{-1})} = Cs_{(\mu\mathrm{mol\ l}^{-1})} \times 0.0223916$.

4. OXYGEN SATURATION

The percentage of oxygen saturation in the water is calculated from the following equation at temperatures between 0–40 ºC and salinity between 0–40:

$$\%\,O_2 = \frac{O_2}{O_2'} \times 100$$

where:
O_2 is the oxygen concentration in the sample,
O_2’ is the oxygen solubility in sea water at the same temperature and salinity, as the sample, calculated according to Section 2, above.

5. CHECKING THE CALCULATIONS

After programming the computer with the new equations, the calculations can be checked against the ICES oceanographic calculator, which uses the same equations. It is available on the ICES website at http://www.ices.dk/ocean.

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