

Canadian Water Quality Guidelines for the Protection of Aquatic Life

DISSOLVED OXYGEN (Freshwater)

Dissolved oxygen (DO) is the most fundamental parameter in water. This double-bonded, twoatom molecule is essential to the metabolism of all aerobic aquatic organisms. Air contains approximately 20.9% oxygen gas by volume. The proportion of oxygen in air that dissolves in water is about 35%. This solubility is governed by atmospheric and hydrostatic pressure, turbulence, temperature, salinity, currents, upwellings, ice cover, and biological processes (Wetzel 1983). At any given barometric pressure and temperature (and the corresponding water vapour pressure), the oxygen partial pressures can be calculated; the solubility of oxygen in freshwater at 5°C and 101.3 kPa (i.e., standard atmospheric pressure) is 12.77 mg·L⁻¹.

Major sources of DO in water are the atmosphere and photosynthesis by aquatic vegetation. The amount of oxygen available for aquatic life, however, depends on the factors that affect its solubility. The saturation concentration of DO is quickly achieved at the air–water interface, and in shallow moving water, will be relatively consistent throughout the water column.

In large and deep freshwater systems, oxygenation depends on circulation by winds, currents, and inflows to move aerated water away from the surface. At spring turnover, the water column is near 100% saturation for both oligotrophic (i.e., low nutrient level) and eutrophic (i.e., high nutrient level) lakes. With increased summer temperatures, the DO concentration and solubility in the circulating epilimnion (warm upper water layer) decreases. Conversely, a temperature decline in the metalimnion (mixing water layer) and hypolimnion (cold lower water layer) causes the oxygen concentration to increase, and the level of saturation will be close to 100% with increasing depth. In most situations, however, the settling of organic matter into the deeper areas from the productive zones could result in undersaturation as a result of oxidation processes.

In shallower waters, the bulk of oxygen loss that is attributable to oxidation occurs at the sediment–water interface, where bacterial activity and organic matter are concentrated. A considerable amount of oxygen is also lost in the water column by bacterial, plant, and animal respiration, particularly in deep lakes. Oxygen depletion also occurs by direct chemical oxidation of dissolved

organic matter. In eutrophic lakes, hypolimnion depletion may progress to complete anaerobic conditions shortly after summer stratification, resulting in a shift to anaerobic bacterial metabolism and slower decomposition. Fall cooling of epilimnial waters breaks down the density barrier at the thermocline (layer at which water temperature changes drastically), resulting in a turnover. In the winter, ice formation prevents the exchange of atmospheric oxygen, and the concentration profile for an idealized oligotrophic lake is constant at saturation relative to depth. Again, biotic influences of respiration and oxidation are normally present and there is a reduction in oxygen concentration with depth. In eutrophic lakes, the photic zone is reduced, but can remain active where sufficient light penetration through ice continues and the normal consumptive demands are lessened by cooler temperatures. The resultant oxygen profile showing depletion at depth is similar to, but more gradual than, that for summer stratification (Wetzel 1983).

There are other important mechanisms that control oxygen levels in the littoral zone (shallow area close to shoreline), which can be quite different from those of the pelagic zone (open, deep water). For example, well-developed stands of aquatic macrophytes and associated periphytons will substantially raise oxygen levels during photosynthesis and consume oxygen during respiration at night. This diurnal event also gives rise to a diel cycle due to the net production of oxygen during the growth seasons. Late in the year, much of the macrophyte standing crop dies back to the root crown, and the concomitant decomposition can cause a prolonged oxygen demand extending beyond the littoral areas.

Table 1. Water quality guidelines for dissolved oxygen in
freshwater for the protection of aquatic life (based on
CCREM 1987, AEP 1997, and Truelson 1997).

	Guideline value $(\mathbf{mg} \cdot \mathbf{L}^{1})^{*}$	
Ecosystem	Early life stages	Other life stages
Warm water	6	5.5
Cold water	9.5	6.5

Lowest acceptable dissolved oxygen concentration.

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The DO content in water is largely controlled by the balance between input of oxygen and consumptive metabolism of oxidizable matter received. Anthropogenic (industrial, including deforestation, influences agricultural, and municipal wastes) tend to load the latter scale by the addition of organic effluents. The depletion of DO in receiving waters is often a ready indicator of wastewater treatment requirements. Specific empirical procedures have been devised to measure oxygen demand. Biochemical oxygen demand (BOD) is a standard microbial incubation procedure that measures the oxygen required to oxidize organic material and certain inorganic materials over a given period of time. Alternatively, the measure for the amount of oxygen required to chemically oxidize reduced minerals and organic matter of a sample is termed chemical oxygen demand (COD). Both terms are applied to the level of reducing material present from a combination of natural and anthropogenic sources. They have particular usefulness in assessing the potential effects of effluents. Wastes that are primarily nutrient-related and/or high in carbon may enhance or deplete DO levels. They commonly do both, depending on the location in the water column. Additional oxygen is usually produced in the photic zone by increased primary production following enhancement by inorganic nitrogen and phosphorus. A subsequent drop in the nutrient supply, however, can be accompanied by algal die-off, decomposition, and oxygen depletion (Wetzel 1983).

DO in surface waters may range from nondetectable to $18.4 \text{ mg} \cdot \text{L}^4$ (NAQUADAT 1985). In lakes it may be influenced by climatic conditions (e.g., ice cover), morphometry (e.g., depth), productivity, and watershed characteristics (e.g., oxygen sources and nonpoint source loading of organic material). These characteristics can vary tremendously, both temporally and spatially. Generally, variations in oxygen levels are not a result of point source discharges.

Interstitial and sediment oxygen concentrations are highly variable. They can markedly differ from the overlying water due to a number of independent variables that include surface and interstitial water velocity/discharge, hydraulic gradient, sediment texture and porosity, bottom morphology, daily water temperature fluctuation, and the consumptive oxygen demand of the substrate. In standing water environments, interactions between the diverse sediment biota and the concentration of the particulate organic material are the major cause of oxygen depletion (both through respiration and release of decomposition byproducts in reduced form). Oxygen itself, however, will regulate important redox reactions at the sediment–

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water interface. Oxygen penetration into the substrate from the water column is governed by the rate of turbulence of superficial sediments and by the oxygen demand per unit volume. Typically, diffusion from even well-aerated water will supply only the top few centimetres (Wetzel 1983). In some cases, filter-feeding organisms can introduce oxygen to greater depths by physically reworking compacted, oxygen-deficient mud and extending the habitat range. Similarly, in riverine environments, the act of redd construction by salmonids through excavation and backfilling results in localized dispersal of fine sediments and increased interstitial flows for improved oxygen delivery to buried eggs.

Water Quality Guideline Derivation

Toxicological methods for measuring the effects of chemicals on aquatic life have been standardized for many years. Basically, these methodologies involve the addition of a chemical in varying concentrations to determine the concentration at which the chemical has an effect or no effect. In contrast, for DO it is the lack of oxygen rather than an excess of oxygen that causes adverse effects. Also, the types of toxicity endpoints vary; for acute exposure, they include mortality, loss of equilibrium, and lack of opercular movement. The exposure times for these shortterm tests also vary widely (Chapman 1986). For chronic exposure, endpoints include the traditional growth and reproduction impairment parameters, oxygen uptake/consumption, and swimming capacity. The low oxygen threshold at which some reaction first becomes apparent is usually referred to as the incipient or critical level. At this level, the organism must extend or adjust its available energies to counteract the influence of hypoxia (oxygen starvation). When this stress is a chronic occurrence, it could have a detrimental effect on longterm survival. This, or any departure from a "no-effect" level, can be considered an undesirable risk (Davis 1975). The variability in toxicity endpoints and exposure times challenges the derivation of water quality guidelines for DO, and as a result, the guideline derivation does not follow the standard CCME protocol (CCME 1991). Two supporting documents (AEP 1997 and Truelson 1997) were used to develop these guidelines.

Freshwater Life

Reduced oxygen levels have been shown to cause lethal and sublethal (physiological and behavioural) effects in various organisms, especially fish. Younger fish tended to be more sensitive than older fish (Doudoroff and Shumway 1970; Alabaster and Lloyd 1982). A more recent study on yellow perch supported this general finding (Johnson and Evans 1991). In contrast, adult graylings were more sensitive to low DO levels than fry. At the same water temperature, adults lost equilibrium at DO concentrations $0.4 \text{ mg} \cdot \text{L}^4$ higher than fry (Feldmeth and Eriksen 1978). Furthermore, weight and size had no significant effect on the critical DO concentration of several species (Smale and Rabeni 1995). Acclimation to low DO concentration decreased the lethal concentration (Doudoroff and Shumway 1970). The incipient lethal concentration was determined in situ in three lakes in Ontario. For northern pike, the incipient lethal limit was $<0.75 \text{ mg} \cdot \text{L}^{1}$ DO for all three lakes. Northern pike were extremely tolerant to low DO winter concentrations; some were found alive at $0.04 \text{ mg} \text{ L}^{4}$ (Casselman 1978). Observed lethal oxygen levels generally increased at higher water temperatures (Doudoroff and Shumway 1970; EIFAC 1973; USEPA 1986). Mortality and/or loss of equilibrium occurred between 1 and 3 mg \cdot L⁴.

For chronic exposures, low DO reduced the growth of coho salmon (Mason 1969), mountain whitefish (Siefert et al. 1974), smallmouth bass (Siefert et al. 1974), lake trout (Carlson and Siefert 1974), and lake herring (Brooke and Colby 1980). Alabaster and Lloyd (1982) concluded from reviewing the information available at that time that a minimum value of 5 mg \cdot L⁴ would be satisfactory for most stages and activities in the life cycle of fish. Processes such as juvenile growth, fecundity, hatch of eggs, larval morphology and survival, upstream movement of migratory salmon, and schooling behaviour of some species were not particularly susceptible to DO levels above $5 \text{ mg} \text{ L}^4$. However, the authors stated that the $5 \text{ mg} \cdot \text{L}^{-1}$ value might be necessarily high merely to ensure satisfactory survival of fish and adequate survival of juveniles.

Doudoroff and Shumway's (1970) review indicated that low DO during embryonic development resulted in delayed development and increased mortality as embryos aged. In fish species other than salmonids, low DO in some instances resulted in mortality and delayed development. Alabaster and Lloyd (1982) concluded that any reduction of DO from air saturation value could slow development and embryonic growth, or delay hatching in salmonids. Most salmonid embryos will hatch successfully between 2 and 3 mg·L⁴ DO to produce relatively small and underdeveloped larvae that are viable and not deformed. Reduction of hatching success, however, can even occur at concentrations >3 mg·L⁴. At low DO concentrations, hatching of fathead minnows (Brungs 1971), walleye (Oseid and Smith 1971), mountain whitefish (Siefert et al. 1974), white suckers (Siefert and Spoor 1974), lake trout (Carlson and Siefert 1974), scale carp (Kaur and Toor 1978), lake herring (Brooke and Colby 1980), and burbot (Giles et al. 1996) was delayed.

Fish compensate for hypoxia by several behavioural responses: increased use of air breathing or aquatic surface respiration (ASR), changes in activity level or habitat, and avoidance behaviour. Birtwell (1989) reported that much of a chum salmon run was prevented as a result of low DO. Migrating salmon avoided DO levels of $3.5-5 \text{ mg}\cdot\text{L}^4$ (Birtwell and Kruzynski 1989). McGreer and Vigers (1983) found avoidance reaction in juvenile chum salmon up to 10 km from a pulp mill, partially as a result of severely depleted DO conditions in an inlet. Walleye in their second summer remained in the shade at DO >5.5 mg·L⁴ (Scherer 1971). However, at DO levels <5.5 mg·L⁴, walleye increased mobility into higher light intensities. Below 2 mg·L⁴, walleye remained longer in higher light conditions.

Low DO during embryonic development could result in structural deformities (Doudoroff and Shumway 1970). Exposure of chum salmon embryos to $0.3 \text{ mg} \cdot \text{L}^4$ DO resulted in shortening of the vertebral column and abnormal alevins (Alderdice et al. 1958). A level of 1 mg $\cdot \text{L}^4$ resulted in irreversible locked lower jaw of largemouth bass larvae, making the fish unable to swim up and feed (Spoor 1977). Exposure of steelhead trout eggs to 2.6 mg $\cdot \text{L}^4$ DO resulted in significant abnormal development, such as deformed tails and spines, and abnormal nervous systems and brain development (Silver et al. 1963). At 1–2 mg $\cdot \text{L}^4$, high numbers of lake herring fry had deformed heads, jaws that did not articulate, and irregular-shaped eyes (Brooke and Colby 1980).

The specific oxygen requirements of aquatic invertebrates have been studied extensively. The great range of tolerances identified is predictable for such a diverse group. Organisms that can endure low oxygen conditions are capable of some form of anaerobic metabolism (Davis 1975). Some invertebrates may have developed physiological and behavioural adaptations: chironomid larvae and leeches have the ability to acclimate by regulating oxygen uptake; *Daphnia* can produce hemoglobin and turn red; *Gammarus* can increase activity and leave the low oxygen environment; and freshwater snails usually lift themselves to the surface. The acute toxicity data included data on seven invertebrate species. The 2- to 5-h LC_{50} values (expressed as percentage saturation) varied from 5.2% for the mayfly *Siphlonurus aestivalis* to 49.5% for the mayfly *Rhithrogena iridina* (0.5–5.3 mg·L⁴ at an assumed atmospheric pressure of 101.3 kPa) (Jacob and Walther 1981). For 22 species, the 2- to 5-h LC_{50} values (expressed as percent saturation) varied from 0.3% for the mayfly *Ephemera vulgata* to 96.5% for the mayfly *Epeorus sylvicola* (0.03–8.77 mg·L⁴ at an assumed atmospheric pressure of 101.3 kPa) (Jacob et al. 1984).

Chronic effects of low DO have been studied for various species of invertebrates. The 111-d LC_{50} for the stonefly *Acroneria pacifica* was 5.8 mg·L⁴, and the 90-d LC_{30} for the fly *Atherix variegata* was 1.7 mg·L⁴ (Gaufin 1973). Winter et al. (1996) found that for the mayfly *Hexagenia limbata*, the LOEC was 2.44 mg·L⁴ DO. They also noted that the mean growth (based on head width) decreased from 5.58 to 2.44 mg·L⁴.

As part of the Northern River Basins Study, Lowell and Culp (1996) found that at DO levels of $5 \text{ mg} \cdot \text{L}^4$, approximately 20% of mayfly larvae (*Baetis tricaudata*) moved from the bottom of the tanks to areas of increased current velocity, which may in turn have led to an increase in their predation. The authors also found a significant reduction in survival after 14 d, and noted that the mayflies were near the emergence life stage.

The effects of low DO levels in the presence of other stressors may also result in some adverse effects. Combined hypoxia and hypercapnia (high CO₂ levels) result in respiratory acidosis. Hyperventilation in this situation will not result in an increase in affinity of blood for DO (Jensen et al. 1993). Hydrogen sulfide liberates oxygen from oxygenated hemoglobin and forms sulfhemoglobin. More importantly, H₂S inhibits cytochrome(c) oxidase in mitochondria of tissue cells, which blocks the last step in the respiratory chain where oxygen is the final electron acceptor (Jensen et al. 1993). Some metals interfere with respiration. Zinc and nickel reduce the diffusing capacity of the gills, resulting in a fall of oxygen supply to fish tissue (Hughes 1981). Nickel also increases the diffusion distance. Ventilatory frequency and amplitude increased during hypoxia following zinc treatment. An increase in H⁺ and aluminum obstruct gill function through the precipitation of aluminum on the gill surface. Mucus production also increased and gill lamellae fused and thickened (McDonald and Wood 1993, as referenced in Jensen et al. 1993). The toxicity of zinc, lead, copper, and phenols to rainbow trout increased at lower DO concentrations (Lloyd and Herbert 1962).

During the winter months, DO concentrations in water systems are reduced by ice cover, which decreases reaeration, influxes of oxygen-depleted groundwater, and oxidation of organic material (Chambers 1996). It is important during winter, therefore, to ensure that no additional anthropogenic oxygen-depleting sources are discharged into these systems. For information concerning DO considerations during the winter months, see the Northern River Basins Study (Chambers 1996).

The Canadian water quality guidelines for the lowest acceptable DO concentrations are 6 and 5.5 mg·L⁴ for the early and other life stages, respectively, in warm-water ecosystems, and 9.5 and 6.5 mg·L⁴ for the early and other life stages, respectively, in cold-water ecosystems. The guidelines were derived from the U.S. Environmental Protection Agency's "slight production impairment" estimates (USEPA 1986), with an additional safety margin of 0.5 mg·L⁴ to estimate threshold DO concentrations.

Since intragravel DO concentrations are reduced due to sediment oxygen demand and respirating fish embryos, the water quality guideline value of $6.5 \text{ mg} \cdot \text{L}^{-1}$ should apply to conditions in the redds (gravel beds). CCREM (1987) adopted a differential of $3 \text{ mg} \cdot \text{L}^{-1}$ between the overlying water and the interstitial water to arrive at the guideline for the early life stage in cold-water ecosystems. This guideline was established to protect salmonid larvae in these redds. Survival during the emergence life stage of Leptophlebia and Ephemera invertebrates is decreased at DO concentrations $< 8.3 \text{ mg} \cdot \text{L}^4$ (Nebeker 1972), and occurs from mid-May to the end of June (Leonard and Leonard 1962; Edmunds et al. 1976; Clifford et al. 1979). Survival during this stage is also decreased at DO levels $<5 \text{ mg} \cdot \text{L}^{-1}$ for *Baetis* (Lowell and Culp 1996). Therefore, the early life stage guideline should be applied at those times and places where salmonid spawning and invertebrate emergence are known, or are likely, to occur.

During winter, lack of re-aeration can cause significant depletion of DO under natural conditions; during summer, the presence of aquatic macrophytes or benthic algae can result in significant oxygen fluctuations. Therefore, where natural conditions alone create DO concentrations <110% of the guideline, the minimum acceptable concentration is 90% of the natural concentrations.

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