

Canadian Water Quality Guidelines for the Protection of Aquatic Life

DISSOLVED OXYGEN (Marine)

issolved oxygen (DO) is the amount of oxygen, usually measured in milligrams or millilitres, dissolved in one litre of water. The solubility of oxygen in water is inversely correlated with temperature and salinity. For example, the solubility of oxygen in estuarine water with a salinity of 27‰ (i.e., 27 parts per thousand) exposed to water-saturated air at atmospheric pressure is 10.656 mg·L⁴ at 5°C, but only 8.54 mg·L⁴ at 15°C (APHA 1992). In comparison, the solubility of oxygen in freshwater (salinity of 0‰) at a temperature of 5°C and atmospheric pressure is 12.770 mg L^4 . Seawater may be over-saturated or under-saturated with oxygen, depending on the physical, chemical, and biological processes that produce or consume oxygen. Dissolved oxygen concentrations are usually measured using the Winkler (or iodometric) method, which is a titrimetric procedure, or the electrometric method, which uses membrane electrodes (APHA 1992). Davis (1975a) provides methods and references for calculating oxygen tension, oxygen concentration, and percent saturation of oxygen in water, which consider the major factors that influence these variables.

Oxygen is essential for the respiration of almost all life, including most marine and estuarine organisms. The amount of oxygen available for aquatic life depends on a number of factors that affect the solubility of oxygen in seawater. These factors include salinity, temperature, atmospheric exchange, barometric pressure, currents, upwellings, tides, ice cover, and biological processes (e.g., respiration and photosynthesis). Oxygen-consuming chemical processes may also be important factors in certain areas (Colinvaux 1973; Davis 1975b).

Oxygen levels are highest in surface waters, particularly coastal waters. The surface of marine and estuarine waters readily permits oxygen enrichment through atmospheric exchange, and sufficient light can penetrate surface waters to allow the oxygen-releasing processes of photosynthesis to occur (Davis 1975b). In the euphotic zone (i.e., the portion of the water column where light intensity is allow sufficient to photosynthetic processes). photosynthesis may exceed respiration and there is a net production of oxygen; below the euphotic zone, a net consumption of oxygen occurs (Davis 1975a). When conditions permit, oxygen supersaturation is possible and can reach 130‰ (Davis 1975a; Topping 1976). Values as high as 165% saturation have been measured in some areas (Birtwell et al. 1987). Under normal conditions (i.e., a sample of air-equilibrated seawater with a salinity of 35‰ at 10°C), the concentration of DO in seawater would be 8.6 mg·L⁴ (Davis 1975a). Values of 130% and 165% saturation would correspond to concentrations of 11.1 mg·L⁴ and 14.2 mg·L⁴, respectively.

In deeper waters, especially where light is scarce, oxygen is consumed by bacteria during decomposition of organic matter. In these cases, oxygen concentrations can be reduced to negligible levels and conditions can become anoxic (Topping 1976). The areas with the greatest DO depletion are those with restricted circulation and an abundant supply of organic matter from the accumulation of any combination of natural sources, sewage, foodrelated industries, agricultural runoff, pulp mills, or other human activities (Topping 1976). Colodey et al. (1990), in a review of the effects of pulp and paper mill effluent on the marine environment in Canada, reported considerable variability in DO conditions in the vicinity of 10 coastal mills in British Columbia and 16 coastal mills in the Atlantic provinces. Where effluent was rapidly mixed and dispersed, there was little or no effect on DO levels near the outfall. Where effluent was discharged into areas of restricted circulation, low DO levels were common. Extremely low DO levels were observed when flushing rates in estuarine inlets were reduced due to low river runoff. Such conditions were reported near three mills in

Table 1. Water quality guidelines for dissolved oxygen in marine and estuarine waters for the protection of aquatic life (CCME 1996).

Aquatic life—Marine and estuarine

The recommended minimum concentration of DO in marine and estuarine waters is 8.0 mg·L⁴.^{*} Depression of DO below the recommended value should only occur as a result of natural processes. When the natural DO level is less than the recommended interim guideline, the natural concentration should become the interim guideline at that site. When ambient DO concentrations are >8.0 mg·L⁴, human activities should not cause DO levels to decrease by more than 10% of the natural concentration expected in the receiving environment at that time.

^{*}Interim guideline.

British Columbia and one in New Brunswick. For example, levels of DO <3 mg·L⁴ (i.e., a level potentially lethal to salmon) extended for over 5 km from the local pulp mill throughout the Neroutsos Inlet near Port Alice, British Columbia. Similarly, lowered levels, 1.5–3.0 mg· L⁴, were measured in Muchalat Inlet, near the bleached kraft mill at Gold River, British Columbia (Colodey et al. 1990). Poor dispersal of pulp mill effluent in these locations may have contributed to fish kills that were observed in the area at that time.

In several Atlantic and Pacific Canadian coastal inlets, surface water is close to saturation at all times, but bottom water can have seasonally low oxygen levels, in some cases reaching 0% saturation (Davis 1975a). Oxygen depletion can occur in deep marine waters with thermal and/or salinity stratification (a warmer and/or less saline layer of water overlying a colder and/or more saline layer). Under these conditions, oxygen produced by photosynthesis near the surface is not likely to be transported to deeper waters, where oxygen consumption continues during this stratification period. Vertical stratification is often coupled with little or no horizontal mixing, which would otherwise bring oxygen to the deeper waters (Colinvaux 1973; Davis 1975b). In Howe Sound, for example, DO concentrations decreased from 3.0 to $0.5 \text{ mg} \cdot \text{L}^4$ at a depth of 250 m during a 3-month period of restricted bottom water renewal (Levings 1980).

Seasonal oxygen depressions have been observed in poorly flushed areas of estuaries. Birtwell et al. (1987) found considerable spatial and seasonal variability in DO content and percent saturation in Deas Slough and adjacent areas of the Fraser River estuary, British Columbia. Data on dissolved oxygen recorded over a year and a half ranged from 0 to 165% of air saturation. The highest DO levels tended to be observed in well-flushed shallow areas when photosynthesis was most active and stratification was minimal.

Biological Effects

Reduced oxygen levels have been shown to cause lethal and sublethal effects (physiological and behavioural) in a variety of organisms, especially in fish. Hughes and Ballintijn (1968) observed an increase in the ventilatory muscle activity of dragonets in oxygen-depleted marine water. A subsequent study on the same species noted an increase in heart rate at DO concentrations below $5.58-5.67 \text{ mg} \cdot \text{L}^4$ (Hughes and Umezawa 1968). Sockeye salmon showed signs of elevated blood and buccal pressure and an increased breathing rate at concentrations below 5.07 mg·L⁴ (Randall and Smith 1967). Physiological studies indicate that reduced DO levels restrict the ability of fish to maximize metabolic processes (Birtwell 1989). Consequently, the growth rates of fish are affected by reduced DO levels; reductions in the growth rate of salmon have been recorded at levels as high as 7 mg·L⁴ (USEPA 1986).

As oxygen availability is reduced in the aquatic environment, fish respond by attempting to maintain oxygen uptake through a series of modified behaviours, including avoidance, reduced feeding, and reduced swimming capacity. Under simulated estuarine conditions (similar to conditions at the head of the Neroutsos Inlet, British Columbia, near a pulp mill), juvenile chinook salmon avoided DO levels $<7 \text{ mg} \cdot \text{L}^4$ (Birtwell 1989). Scherer (1971) noted a drop in light avoidance (negative phototaxis) in walleye at levels ranging from 5.5 to 4.0 mg $\cdot L^4$. Largemouth bass showed some avoidance behaviour at 4.5 mg·L⁴, but at 1.5 mg·L⁴, this behaviour became quite distinct (Whitemore et al. 1960). For the coho salmon, DO concentrations lower than $4.5 \text{ mg} \cdot \text{L}^4$ caused erratic avoidance behaviour (Whitemore et al. 1960). Reduced maximum swimming speeds were observed in coho and sockeye salmon below the ranges of $11.3-9.17 \text{ mg} \cdot \text{L}^4$ and 9.17-8.53 mg·L⁴, respectively (Davis et al. 1963; Brett 1964).

Reduced disease resistance and fecundity have also been reported for fish living under depressed DO conditions (Davis 1975a, 1975b; Sprague 1985). Brungs (1971) observed a reduction in the number of eggs produced per female of the fathead minnow when DO levels dropped to 4 mg·L⁴. In this study, spawning ceased at 1 mg·L⁴ of DO. While very little information exists on the larval and egg DO demands of marine fish, studies on the early stages of freshwater and anadromous fish development have also revealed responses to reduced DO levels. Reduced growth, retarded development, deformities, and mortality are among the most extreme responses to hypoxia (Davis 1975b). Atlantic salmon alevins reared in 4.5-5.0 mg·L⁺ did not absorb their yolk sacs effectively and weighed one-half the weight of those larvae reared in $6.8-7.5 \text{ mg} \cdot \text{L}^4$ (Nikiforov 1952).

Various similar effects have been shown for marine and estuarine invertebrates (Davis 1975a, 1975b). Invertebrate dependency on oxygen is determined by numerous factors, including the existence of a circulatory system, diffusion distances, temperature, degree of locomotor activity, ability to regulate external respiration, and the existence of respiratory pigments (Davis 1975b). Unlike fish, invertebrates vary dramatically in their need for DO. For instance, the marine intertidal lugworm (*Arenicola marina*) cannot withstand DO above 4 mg·L⁴ (Nicol 1967), while Pacific sea urchins are often stranded on rocks at low tide and have evolved to withstand up to 15 h of exposure to moist air (i.e., approximately 20% oxygen) before perishing (Johansen and Vadas 1967).

If prolonged changes in DO occur, modifications can also be expected in the local biotic community structure. Species intolerant of depressed oxygen will either die or try to avoid such environments, while the more tolerant species, originating from either within the habitat or colonized from elsewhere, will survive (Davis 1975b). Levings (1980) reported dramatic changes in benthic communities during and following a period of severe oxygen depletion ($<0.5 \text{ mg} \cdot \text{L}^{-1}$) in Howe Sound. These changes appeared to be the result of the death of sessile species as well as emigration of more mobile species. A study on the fluctuations of the benthic community of Petpeswick Inlet, Nova Scotia, illustrates the impact of naturally or anthropogenically altered DO regimes (Hoos 1973). During spring and part of the summer, when sufficient DO conditions prevail, the bivalves Mytilus edulis and Mya arenaria, the polychaetes Nephtys incisa and Capitella capitata, and copepods were the dominant organisms. In late summer and fall, the waters became anoxic, causing species diversity to drop to zero before anoxia-tolerant species such as the bivalve Yoldia limatuloides, the polychaetes Polydora quadrilobata and phyllodocid sp., the amphipod Corophium sp., and nematodes recolonized the area (Hoos 1973).

Dissolved oxygen has been observed to modify the susceptibility of aquatic organisms to environmental stresses such as the presence of toxic substances (Alabaster and Lloyd 1980; Hutcheson et al. 1985; McLeay and Associates 1987; Birtwell 1989). The toxicity of kraft pulp mill effluents and hypoxia may act synergistically on aquatic organisms (Birtwell 1989). Hicks and DeWitt (1971) found that the median survival time for juvenile coho salmon exposed to kraft mill effluent dropped from 56 h when DO concentrations were maintained at 8.1 mg·L¹ to 11 h when levels fell to 3.4 mg $\cdot L^{4}$. A positive linear correlation was observed between the LC₅₀ of aqueous ammonia and DO levels for rainbow trout fingerlings; ammonia toxicity increased as DO levels decreased (Thurston et al. 1981). Chapman and Shumway (1978) exposed early stages of the rainbow trout to pentachlorophenol, a biocidal wood preservative used

extensively by the forest industry. At DO levels of 5 mg· L^4 , a concentration of 20 µg· L^4 of its salt, pentachlorophenate, resulted in 100% fish mortality. However, at a depressed DO concentration of 3 mg· L^4 , 10 µg· L^4 of this chemical was lethal. Lloyd (1961) believed that low DO levels caused aquatic organisms to increase the volume of water passing over the gill epithelium and, thus, magnified the amount of pollutant absorbed. Some substances, such as the kraft pulp mill effluent constituents, dehydroabietic acid (DHAA), and zinc, may damage gill tissue and exacerbate effects of reduced DO concentrations (Tuurula and Soivio 1982).

Dissolved oxygen levels in aquatic environments can affect the persistence and bioavailability of some chemicals. For example, the persistence in water of pentachlorophenol and pentachlorophenate is determined by a number of environmental factors, including DO concentration (Boyle et al. 1980). In addition, the DO concentration in the water column directly influences the flux of oxygen to sediments and, therefore, the depth of oxygen penetration in sediments. In sediments, the presence or absence of oxygen (or the redox potential) results in chemical transformations of trace metals, which can significantly affect their bioavailability to aquatic and benthic organisms (Landrum and Robbins 1990).

Interim Guideline

The recommended minimum concentration of DO in marine and estuarine waters is $8.0 \text{ mg} \cdot \text{L}^4$ (interim guideline). Depression of DO below the recommended value should only occur as a result of natural processes. When the natural DO level is less than the recommended interim guideline, the natural concentration should become the interim guideline at that site. When ambient DO concentrations are >8.0 mg \cdot \text{L}^4, human activities should not cause DO levels to decrease by more than 10% of the natural concentration expected in the receiving environment at that time (CCME 1996).

Rationale

The recommended guideline, which is adopted from that proposed by the USEPA (1986), ensures no level of production impairment for salmonid-inhabited (the most sensitive fish species) fresh waters. Although DO levels tend naturally to be somewhat lower in marine waters than in fresh waters (APHA 1992), no provision has been made for this difference, since this interim guideline applies to estuarine as well as marine waters. Evidence suggests that, although a range of adverse biological effects may occur in marine and estuarine organisms exposed to DO concentrations below 8.0 mg·L⁴ (e.g., Davis 1975a, 1975b; Levings 1980; USEPA 1986; Birtwell 1989), such effects would not be expected to occur in association with higher levels (USEPA 1986; Birtwell 1989).

This interim guideline represents an absolute minimum for DO concentrations that may be altered as a result of human activities. Dissolved oxygen should drop below the interim guideline only as a result of natural processes. Such a clause in the interim guideline is required because natural DO levels are known to vary extensively, from depletion to over-saturation. Because some species may be adapted to naturally lower DO levels, where they occur, such levels should be maintained. Marine and estuarine guidelines for Australia and for the United States jurisdictions of Alabama, Alaska, Delaware, Louisiana, Washington, Guam, American Samoa, Northern Mariana Islands, Puerto Rico, Trust Territory, and the Virgin Islands contain similar clauses.

The recommendation that DO concentrations above this guideline not be depressed by more than 10% from those that occur naturally is also included in guidelines of the State of California (1990). It implies that quantifiable DO cycles naturally above the guideline may occur and that the frequency of sampling is sufficient to record patterns of ambient diurnal and/or seasonal variability. Marine and estuarine DO regimes are often extremely variable and depend on such factors as location, season, depth, photosynthetic activity, respiration, organic decay processes, and atmospheric changes (Davis 1975a). For this reason, the Canadian interim marine and estuarine DO guideline observes a 10% permissible reduction in DO levels that are naturally above the established minimum guideline.

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Canadian Water Quality Guidelines for the Protection of Aquatic Life

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