# Before the Illinois Pollution Control Board

| In the matter of:         | ) |        |
|---------------------------|---|--------|
|                           | ) |        |
| Proposed Amendments to    | ) | R04-25 |
| Dissolved Oxygen Standard | ) |        |
| 35 III. Adm. Code 302.206 | ) |        |

Testimony of Thomas J. Murphy, Ph. D.

I am Thomas J. Murphy, an emeritus professor of chemistry at DePaul University. I founded and chaired the ESP at DePaul. My research was principally related to the atmospheric transport of toxic substances, the deposition of particulates containing these substances in wet and dry deposition, and the exchange of vapors of these substances with bodies of water. I served as editor of the JGLR for six years. I have been involved with water quality issues in Illinois for more than 35 years. As a board member and technical advisor for the lake Michigan Federation for 20 years or so, I participated in and commented on many water quality issues related to nutrients, dissolved oxygen and toxics in the rivers and lakes of Illinois and their sediments. I was the scientific advisor to and member of a citizen's task force, Operation Lakewatch, in the early 1980's. This group uncovered major illegal discharges to Lake Michigan and spurred the WRDGC to revamp its lake-monitoring programs. My comments here relate to the physical chemistry of the exchange of gases between phases, and the driving force for their distribution within phases. Chemists claim that chemistry is the fundamental science because everything is composed of atoms and molecules, and all of the transformations that occur in the universe, on the earth, in organisms, *etc.* obey the laws of chemistry.

The Illinois Association of Wastewater Agencies (IAWA) has proposed amendments to the Dissolved Oxygen (DO) Water Quality Standards for General Use waters in Illinois to the Illinois Pollution Control Board (Board), R 04-025. Their request is for a *scientifically defensible* standard to update the current regulations adopted in 1972. Testimony before this Board in subsequent hearings, supports the need to update the DO standards as requested by the IAWA.

The background papers (Joel Cross 2006; Roy Smoger 2006) submitted by the Illinois DNR and the Illinois EPA for these standard settings demonstrate that the agencies put in considerable effort and did a thorough job in evaluating the available data on Illinois streams and the indigenous aquatic organisms that inhabit them. These data should form a good basis for a science-based review of the WQ standards for DO in Illinois.

The recommendation of the IDNR and the IEPA for amendments to the DO standards is described and supported in the document, "Recommended Revisions to the Illinois General Use Water-Quality Standards for Dissolved Oxygen", March 31, 2006 (IEPA 2006). In this document (p. 2) they describe the 1986 Ambient Water Quality Criteria Document of the USEPA (USEPA 1986): "...a foundation from which to interpret...information applicable to the DO needs of aquatic life in Illinois."

This claim is echoed in other testimony presented to the Board in this standard-setting procedure. Let us review the usefulness of USEPA (1986) to the IEPA in making their recommendations:

- Most of the studies discussed in USEPA (1986) relate to *cold water* fishes. IEPA (2006) states: Because USEPA (1986) "warmwater" criteria are based on information for only a few tested "warmwater" fish species …"
- Most of the reports discussed in USEPA (1986) are based on laboratory studies. IEPA (2006) states (p. 22): "Moreover, particularly for non-toxic substances like dissolved oxygen, sole reliance in laboratory-based acute thresholds is not recommended;" and they quote Smale and Rabeni (1995), "Considerable difference have been found between laboratory tolerance values and lethal conditions in natural situations (Moore 1942; Davis 1975).
- Very few studies of stream macroinvertebrates are discussed in USEPA (1986). IEPA (2006) states (p. 15): "...USEPA (1986) ... relied primarily on only two studies of relatively few types of insects from streams in ..."
- The absence in USEPA (1986) of any information from the last 20 years.
- Most of the reports of DO concentrations in USEPA (1986) do not include the temperature of the measurement. This precludes the determination of the percent saturation of the oxygen in the sample.

These deficiencies demonstrate that USEPA (1986) is an outdated, limited and inadequate 'foundation', and preclude it from contributing meaningful help to a scientifically defensible standard-setting procedure. A house built on such a foundation can not be expected to stand. Why do the IDNR, the IEPA and the MWRDGC claim it as a 'foundation'? The answer may be in a consideration of the science of gas partitioning.

The partitioning of gases between different phases and their movement within phases are well understood physical phenomena discussed in all physical chemistry and even most intro chemistry texts. The partitioning and movement is driven by differences in pressure (activity; percent saturation). The occurrence of differences in pressure, within or between phases drive and control such processes as the exchange of oxygen, water vapor, carbon dioxide, nitrogen, *etc.* between the atmosphere, soils, and bodies of water, and the uptake and distribution of gases to and within all organisms.

A standard reference book on the principles of respiratory physiology by Pierre Dejours, 1981, *Principles of Comparative Respiratory Physiology*, discusses the science of gas exchange in many organisms, including fishes and other aquatic organisms. In the chapters relevant to aquatic organisms, I counted 88 equations that related in one way or another to gas exchange or transport in the functioning of organisms. In *all* of those equations the concentrations of the gas was given in units of pressure. In this text on the science of gas transport in organisms, I looked and did not find one reference to a concentration in mg/L as a driving force for molecular movement.

In contrast, IEPA (2006) uses units of mass mg  $O_2/L$  for the concentrations of oxygen in the proposed amendments and in the discussion supporting the changes. While there is a proportionality between pressure units and mass units, the proportionality factor differs depending on the temperature. The factor depends on the maximum solubility of the gas in water at that temperature,

and oxygen has a higher solubility in cold water than in warm water. For instance, its solubility in water is 14.6 mg O<sub>2</sub>/L at 0°C, and 7.5 mg O<sub>2</sub>/L at 30°. Thus water with 7.5 mg O<sub>2</sub>/L present at 30° is 100% saturated–the pressure of oxygen in the water is the same as in the atmosphere, while at 0° the water is only 51% saturated–the oxygen pressure in the water is only half of an atmosphere. *While the same mass of oxygen is present (7.5 mg O<sub>2</sub>/L) at both temperatures, its percent saturation–what an organism experiences, is only one-half as much at the lower temperature as it does at the higher temperature.* It could be mentioned here that water at 20°C in equilibrium with the atmosphere–the pressure of the oxygen in each phase is 0.21 atm, contains 9.1 mg O<sub>2</sub>/L while the air contains 284 mg O<sub>2</sub>/L.

The significance of this temperature dependency of oxygen solubility with the proposed DO amendments is that each of the different time periods has months of the year when the water in Illinois rivers are zero degrees or close to it–March and February, and months of the year when the water is often above  $25^{\circ}$ C–July and August. IEPA (2006) gives no explanation or justification why they require a daily minimum of 53% saturation at  $30^{\circ}$ C (4 mg/L) but require only 27% saturation at  $0^{\circ}$ . It could be noted that the oxygen pressure at the summit of Mt. Everest is 33% of the pressure at sea level.

Inexplicably and unaccountably, the IEPA is proposing DO standards for General Use waters in Illinois in mass units (mg  $O_2/L$ ). Perhaps there are scientific reasons for not basing the proposed standards on pressure (or not exclusively on pressure), but their *support documents are totally silent* on an explanation, rationalization or scientific justification for this choice, a choice that does *not* follow the established science of gas transport and partitioning, as demonstrated in Dejours (1981) and Davis (1975).

The only document cited that supports the use of a mass-based DO standard is USEPA (1986). IEPA (2006) states (p. 5): "Illinois DNR and Illinois EPA primarily base the recommended revisions to DO standards on information in USEPA (1986), which provides a sound, scientifically based foundation." USEPA (1986) states on its page 1: "Expressing the criteria in terms of the actual amount of dissolved oxygen available to organisms in mg/L is considered more direct and **easier to administer** compared to expressing the criteria in terms of percent saturation. DO criteria expressed as percent saturation, such as discussed by Davis (1975 a,b), are **more complex** and could often result in unnecessarily stringent criteria in the cold months and potentially unprotective criteria during times of high ambient temperature or at high elevations." (emphasis added)

*Clearly* **USEPA** (1986) does not provide a sound, scientifically based foundation for these proposed DO standards (see also comments above). Is 'ease to administer' the basis on which we should base water quality standards in Illinois? Do IDNR scientists find it 'complex' to convert mg/L at a particular temperature to percent saturation? Should we have standards that are not based on the actual availability of oxygen to aquatic organisms?

In a paper referenced several times in the IDNR and IEPA background documents, Davis (1975) arrives at recommended DO criteria essential for the protection of fish populations and lists them for six different groups. The results for the group of 'freshwater mixed fish populations with no salmonids' are shown in the abbreviated table 10 below. *The significance of Table 10 is that the recommended criteria are in units of percent saturation NOT in mg O*<sub>2</sub>/L.

Davis (1975) recommends a constant PO<sub>2</sub> until 25°, when he recommends a modest increase. The basis for these recommendations is (p. 2324): "It must be emphasized that ... fish require both the correct oxygen tension (pressure) gradient to move  $O_2$  into the blood and sufficient oxygen (per unit volume of water breathed) to fulfill the requirements of metabolism."

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Table 10. Oxygen criteria based on percentage saturation values derived with three levels of protection in the text. PO<sub>2</sub>'s and values of mg O<sub>2</sub>/L were extracted from Table 9 and rounded off for use here. The values shown for mg O<sub>2</sub>/L were calculated from the values of mg O<sub>2</sub>/L in this table.

The criteria essential for protection of aquatic fish populations are expressed as percentage saturation values at various temperatures. They were derived from both PO<sub>2</sub> and mg O<sub>2</sub>/L values, as both oxygen tension and oxygen content are critical factors. At the lower temperatures, the percentage saturation value was determined using the PO<sub>2</sub> values essential for maintaining the necessary oxygen tension gradient between water and blood for proper gas exchange. Higher percentage saturation values are necessary at the higher temperatures to provide sufficient oxygen content to meet the requirement of respiration as defined by the mg  $O_2/L$  values.

Percentage saturation values are defined as "oxygen minima" at each level of protection. Graphical presentation of the results is found in Fig. 19. The temperatures corresponding to the percent saturation criteria are defined as "seasonal temperature maxima."

| Freshwater Mixed Fish Populations with no Salmonids |                                    |                      |    |    |     |     |        |     |  |
|---|------------------------------------|----------------------|----|----|-----|-----|--------|-----|--|
| Protection  | Protection % Saturation for Criter |                      |    |    |     |     | iteria |     |  |
| Level   | PO <sub>2</sub>                    | mg O <sub>2</sub> /L | 0° | 5° | 10° | 15° | 20°    | 25° |  |
| Α   | 95                                 | 5.5                  | 60 | 60 | 60  | 60  | 60     | 66  |  |
| В   | 75                                 | 4.0                  | 47 | 47 | 47  | 47  | 47     | 48  |  |
| С   | 55                                 | 2.5                  | 35 | 35 | 35  | 35  | 35     | 36  |  |

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Based on the petition from the IAWA and the stated objectives of the IDNR and the IEPA that the new standards be based on science, the proposed amendments to the DO standards now before the Board are fatally deficient and should not be approved by the Board. They are not based on the science of gas partitioning and they put organisms with high oxygen requirements at risk in cold waters.

The IAWA has invested considerable resources in consultants, legal expertise, and staff time to have the DO standards for the General Use waters in the state amended based on *defensible science*. Major time and resources have been expended by state agencies to evaluate the considerable amount of information on the physical and chemical characteristics of the general use water bodies in the state and their indigenous aquatic organisms. Perhaps the best remedy at this point is to reëvaluate the DO data now in hand in terms of percent saturation and revise the proposed amendments accordingly in order to protect the most sensitive types and life stages of aquatic life that require

relatively higher dissolved oxygen concentrations. These revisions could look like the example above from Davis (1975) and would keep the current two-tiered set of standards intact.

A more complex and less satisfactory way to base the standards on good science, while keeping the obtuse method of setting standards based on mass (mg/L), could be to divide each of the tiers into three or more sections–each covering a limited temperature range, and set separate DO standards for each temperature range. For example, have ranges of 0-10°, 10-20° and 20-30°. Then using the percent saturation required for each range, determine the mass of oxygen present at the midpoint of each (5°, 15° and 25° in this case), and use that as a proxy for a pressure-based standard.

The current water quality standards for DO have been in place in Illinois for 34 years. Amending them is clearly an involved and complex process. The Board should not allow this one-in-34-year opportunity to be only 'tweaking the numbers'. While the scientific base of the proposed amendments is appreciably better than that of the current standards, the changes are only evolutionary. The IAWA petition has presented the Board the opportunity to 'get it right'. Dennis Streicher, the president of the IAWA has testified in these hearings, "... good science should not be negotiated." If the proposed amendments are adopted, they will be obsolete before they go into effect, being bases on 1972 science. But they may well remain in effect for many years. Thus, *it is important to get them right*. Neither the current standards nor the proposed amendments are based on the science of gas partitioning. Therefore there needs to be revolutionary changes in the proposed amendments if they are to be based on current science.

I urge the Board to delay approving amendments to the DO Water Quality Standards for General Use waters in Illinois until the amendments are based on current science. *I urge the Board to require the Agencies to develop amended standards based on the percent saturation of oxygen*, and on the stream and biology data they have already developed. Such amended standards would satisfy the request for science-based standards from the IAWA, and should serve to protect the indigenous aquatic organisms in Illinois waters until climate change necessitates their revision, hopefully well into the future.