ORIGINAL

Before the Illinois Pollution Control Board

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STATE OF ILLINOIS
Pollution Control Board

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

PC#105

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 Environmental Science Program at DePaul. My research was principally related to the atmospheric transport and deposition of toxic substances to bodies of water. I was the first to determine that the atmosphere was an important source of toxic organics to bodies of water. I served as editor of the Journal of Great Lakes Research 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– including one from the McCormick Place Exposition Center, and spurred the MWRDGC to revamp its Lake Michigan water quality monitoring programs.

My comments here relate to the physical chemistry of the exchange of gases between air and water phases, and the driving force for their distribution within these phases. Chemists claim that chemistry is the fundamental science because *everything* is composed of atoms and molecules, *and all exchanges and 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), R04-025. Their request is for a *scientifically defensible* standard to update the current regulations, which were adopted in 1972. Testimony before this Board in subsequent hearings, supports the need to update the DO standards as requested by the IAWA.

I agree with the statement in the March 31, 2006, Recommended Revisions to the Illinois General Use Water Quality Standards for Dissolved Oxygen," report (IEPA 2006; Exhibit 23) by the Illinois DNR and Illinois EPA that, "...the current standard for Illinois General Use waters is too simplistic; it inadequately accounts for the varied DO requirements of aquatic life in these waters." I also agree with their recommendation of replacing the current standards with additional levels of standards that will apply in specific situations. Their recommendation, however, is not based on the science of gas exchange, and is deficient in not requiring additional protection during times when General Use waters are cold, and higher oxygen saturation levels of DO are required to provide sufficient DO availability to indigenous aquatic organisms

The recommendation of the IDNR and the IEPA for amendments to the DO standards is described and supported in 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."*, and cite it 48 times in the document. But USEPA (1986) suffers from major deficiencies which include:

• Very few of the studies discussed were on warm water fish, most were on cold water fish.

• Almost all of the studies were done in the laboratory which this study and all other relevant studies admit often have little relevance to the natural world.

• The science in the document is 20 years old.

• The temperature at which most of the studies referenced in the report were conducted is not reported, which prevents the determination of the percent saturation of the DO to be determined.

Further discussion of these deficiencies was in my testimony to this Board on April 25, 2006 [Exhibit 27] and is in Appendix A. *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 issues are 1) that the transfer of gases between phases (between air and water across the water surface; between water and a fish across a gill surface; etc.) is driven by the difference in partial pressure of the two phases; and 2) that the concentration of oxygen dissolved in the water is a function of the pressure of oxygen in the atmosphere *as well as* the temperature and salinity dof the water. The problem is that it takes considerably more oxygen (mg/L) to saturate water at 0°C than at 25°C. In other words a mg/l of DO is much more 'available' to an organism at 25°C than at 0°C. *A standard-including the proposed standard (IEPA 2006) that does not take the temperature dependence of the solubility of oxygen into account could lead to significant oxygen deficiencies for organisms at cold temperatures* (see discussion in Appendix B).

The significance of this temperature dependency of oxygen solubility with the proposed DO amendments (IEPA 2006) is that each of the different proposed time periods has months of the year when the water in Illinois rivers are zero degrees (Celcius) or close to it–March and February, and months of the year when the water is often above 25°C–July and August. IEPA (2006) gives no explanation or justification why they require a daily minimum of 53% saturation at 30°C (4 mg/L) but require only 27% saturation at 0° (4 mg/L). It could be noted that the oxygen pressure at the summit of Mt. Everest, often described as in the 'death zone', 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 silent* on a 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.* 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? Basing standards on assumption (mg/L will work; the organisms have evolved with low DO concentrations in the summer months; the availability of DO to aquatic organisms is independent of temperature; etc., are fine, but the standards then are only as good as the assumptions are valid.

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 (see Appendix C) is that the recommended criteria are in units of percent saturation NOT in mg O_2/L.*

Davis (1975) recommends a constant PO_2 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.*

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 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*. Considerable time and resources have been expended by state agencies to evaluate the large body 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 revise the proposed amendments to increase the dissolved oxygen concentrations at low temperatures. These revisions would look like the example above from Davis (1975, Appendix C). It would divide each of the tiers into two or more sections–each covering a limited temperature range, and would set separate, higher DO standards (mg O_2/L) for the low temperature range based on the percent saturation (the percent oxygen saturation would be similar at the different temperatures).

The current water quality standards for DO have been in place in Illinois for 34 years. Amending them is clearly a long 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 (IEPA 2006; Exhibit 23) are adopted, they will be obsolete before they go into effect, being bases on 1986 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. Adopting a DO tier for low temperatures described above, will be an important step in making the Illinois WQ Criteria for DO protective of aquatic organisms in the 21st century.

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, a revolutionary change in the criteria. *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.

References

Cross, Joel (2006). Pre-Filed Testimony. Hearing on IL PCB Rule Making R 04-25, Amendments to Dissolved Oxygen Standard 35 Ill. Admin. Code 302.206; Springfield, IL. April 25.

Davis, John C. (1975). Minimal DO Requirements of Aquatic Life with Emphasis on Canadian Species: A Review. Canadian Journal of Fisheries and Aquatic Sciences, **32**, 2295-2332.

Dejours, Pierre (1981), *Principles of Comparative Respiratory Physiology*, 2nd Ed., Elsevier.

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Smoger, Roy (2006). Pre-Filed Testimony. Hearing on IL PCB Rule Making R 04-25, Amendments to Dissolved Oxygen Standard 35 Ill. Admin. Code 302.206; Springfield, IL. April 25.

Truelson (1997). Ambient Water Quality Criteria For Dissolved Oxygen. Ministry of Environment, Lands and Parks, Water Quality Branch, Victoria, BC.; February.

USEPA (1986). Ambient Water Quality Criteria for Dissolved Oxygen.

Appendix A

- Most of the studies discussed in USEPA (1986) relate to *cold water* fishes. IEPA (2006) states (p. 10): "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.

Appendix B

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 through the entire book and did not find one reference to a concentration in mg/L as a driving force for molecular movement.

Truelson (1997) states that, "fish physiology specialists commissioned by the IJC (1980) concluded that the rate of oxygen transfer across fish gills is governed by diffusion down a concentration gradient and is dependent on the mean difference in oxygen partial pressure across the gills."

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_2/L at 0°C, and 7.5 mg O_2/L at 30°. Thus water with 7.5 mg O_2/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_2/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_2/L while the air contains 284 mg O_2/L.

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In discussions with IDNR and IEPA personnel, they indicated that one of the other documents they relied on for justification of their use of mass units rather than percent saturation for DO, was the Ambient Water Quality Criteria for Dissolved Oxygen (Truelson 1997). This document considers the use of percent saturation but also ultimately rejects it in favor of mass units. In their rational for this choice in Section 4.7.2, they make several errors and several assumptions.

The first error is to assume that regardless of the percent saturation of the water, that the mass transfer coefficient is sufficiently high that the mass concentration limits the oxygen transfer regardless of the pressure difference. This is not true, of course if the saturation in the water is lower than the concentration in the organism, a condition that can arise in cold waters with little oxygen in them, the condition I am concerned with and am addressing in this testimony.

They also claim that the partial pressure of oxygen in saline waters would "unacceptably decrease" as the salinity increases. This is *not* correct. It is true that the saturation concentration of oxygen (mg/L) will decrease as the salinity increases, but the partial pressure (the activity; the percent saturation; the availability of oxygen to an organism) will be *unchanged* as the salinity changes. Saturation is saturation; 100% is 100%. This is just another reason for using percent saturation in place of mg/L to measure oxygen availability to an organism. It is independent of salinity as well as being independent of temperature.

Truelson (1997) claims that a plot in Davis (1975; Fig 16) of oxygen response data (mg/L) for freshwater fish plotted against test temperature showed the absence of any relationship. It's true that the line is flat, no change in response with temperature. *However*, the correlation coefficient for the correlation was less than 0.01, meaning that the absence of a relationship was without *any* significance, that a direct positive or negative relationship was equally as likely.

Truelson (1997) also uses the "added complexity" of percent saturation based standards as a justification for mass-based standards, also disregarding the fact that with most measurements today being made with electronic sensors, the percent saturation, the activity of the oxygen is the response produced by the sensor.

Both USEPA (1986) and Truelson (1997) reference other studies that show a temperature effect on the availability of DO to aquatic organisms, results in accord with gas exchange science. However, they continue to base their conclusions of the large majority of studies that did not measure temperature effects.

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USEPA (1986) implicitly acknowledges the decreased availability of DO at low temperatures when it states, "Many states have more stringent DO standards for cooler waters."

Appendix C

Table 10. Oxygen criteria based on percentage saturation values derived with three levels of protection in the text. PO_2's and values of mg O_2/L were extracted from Table 9 and rounded off for use here. The values shown for mg O_2/L were calculated from the values of mg O_2/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_2 and mg O_2/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_2 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 Level	PO_2	mg O_2/L	% Saturation for Criteria					
			0°	5°	10°	15°	20°	25°
A	**95**	**5.5**	**60**	**60**	**60**	**60**	**60**	**66**
B	**75**	**4.0**	**47**	**47**	**47**	**47**	**47**	**48**
C	**55**	**2.5**	**35**	**35**	**35**	**35**	**35**	**36**

Davis (1975)