Before the Illinois Pollution Control Board

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In the matter of:

Proposed Amendments to Dissolved Oxygen Standard 35 III. Adm. Code 302.206 R04-25 (Rulemaking – Water)

Comments on the Proposed Rule; First notice Thomas J. Murphy, Ph. D. September 17, 2007

Conclusion

The Board's proposed rule is based on the premise that water that is 24% saturated (3.5 mg oxygen/l at 0°C) will permit the full complement of indigenous aquatic organisms to thrive. Nonsense! The IEPA and the DNR have presented evidence that more than 4 mg/L of dissolved oxygen is necessary for many indigenous aquatic organisms. On the other hand, *no evidence has been presented in these proceedings to demonstrate that 3.5 mg/L oxygen at cold temperatures is protective of indigenous aquatic life.* The Board is putting all of the oxygen sensitive aquatic organisms in the general use waters at risk when the temperatures get cold with *no evidence from studies at cold temperatures* to support this rule.

The Opinion and Order of the Board related to this rulemaking states (OOB p. 48), "When setting water quality standards, the Board places *significant weight* on adopting a standard that *fully protects aquatic life*, . . .". By ignoring the temperature effects on the availability of dissolved oxygen to organisms, the Board has clearly *not* met its goal with these proposed rules.

Discussion

This rulemaking has been a long and arduous process. The stakeholders and the state agencies have put considerable time and effort into updating the dissolved oxygen standards for general use waters in Illinois, which have been in place for 35 years. A successful outcome of these deliberations is critical to the future of all of the indigenous aquatic organisms that expect to be able to thrive in the natural waters of the state.

The new evidence that been incorporated into these proposed rules give additionaland necessary, protection in those months of the year when early-life stages of aquatic organisms tend to be present. Unfortunately, the proposed rule does not address in any way the fact that the availability to an organism of a given amount of dissolved oxygen in water (in mg/L) decreases as the water temperature gets colder. The evidence presented in this Opinion and Order of the Board (OOB) related to this rulemaking by the IEPA and DNR indicate that the proposed rules-that cover both warm and cold times of the year, put indigenous aquatic organisms at significant risk during the cold months.

An assumption related to oxygen uptake by organisms in these draft rules imply that if there is any oxygen present in the water, then organisms can take it up. This is demonstrated in the first line of the Introduction (OOB p. 1) where it is stated: "Dissolved oxygen ... occurs between water molecules as microscopic bubbles of oxygen that fish "breathe" through their gills." This statement is *not* correct. The oxygen is *dissolved* in the water. (A glass of freshly drawn Guinness stout has millions of microscopic bubbles of gas suspended in it. They are a separate phase–a gas (the stout is cloudy), and they slowly rise to the surface, leaving the clear–though colored, liquid *solution* of stout in the glass.) Being in solution in the water phase, oxygen can partition across membranes (gills), between phases (air/water), *etc.* Transport is always from the region with higher concentration to the one of lower concentration. For instance, a can of cold pop placed in a warm room always warms up. The heat goes from the higher temperature room to the colder can. The cold can *never* loses heat to the warmer room.

Because transport is always from the higher concentration to the lower, an organism can **only** obtain oxygen from water if the percent saturation in the water is higher than that in the organism. And the situation, of course, is even more complicated. The complication is that oxygen is only utilized in the mitochondria of the cells, a separate enclosed region within cells. To get oxygen into the mitochondria where it is used to release energy for the cells, the percent oxygen must be higher in the cells than in the mitochondria; to get oxygen into the cells, the percent oxygen into the blood must be higher than that in the cells; and finally, to get oxygen into the blood, the percent oxygen must be higher in the water than in the blood. Thus the percent saturation of the oxygen in the water has to be sufficiently higher than that in the mitochondria to drive the three transport processes to get sufficient oxygen to the mitochondria.

In addition, the amount and the *rate* of oxygen transferred is *not* proportional to the percent saturation of the water (or to its concentration in mg/L), rather they are proportional to the *difference* in percent saturation across the membrane (you lose heat much more rapidly when outside on a cold winter day, than on a cool fall day). For example, if an organism has a blood oxygen saturation of 30%, it can gain no oxygen if the water oxygen saturation is also 30%; if the water oxygen saturation is 35% the difference is 5% and some oxygen will be transferred. *Now, if the water oxygen saturation is 50%, the difference in saturation across the membrane is 20% and four times as much oxygen—and at four times the rate, will be transferred than when the saturation was 35%.* An important implication of this is that a fish with a blood oxygen saturation of 30% has to move at least four times as much water over its gills if the water is 35% saturated than if the water is 50% saturated. Besides experiencing a slower oxygen uptake, the fish has to expend considerable more energy to acquire oxygen at low percent saturations and is exposed to four times the amount of the other chemicals also in the water. Of course, if an organism finds itself in an environment with an oxygen saturation less than its blood saturation, it will lose oxygen to the water.

In this rulemaking procedure, the IAWA and its supporters claim that the oxygen standards should be based only on the mass concentration of DO (mg/L), and this *Opinion and Order of the Board* has adopted that method. However, in previous testimony (PC #83,

PC #105) I have discussed that, based on the science of gas partitioning, that the availability of oxygen to an aquatic organism is solely dependant on the *percent saturation* of the oxygen in the water, which should serve as the rule-making criteria. The difference in these two methods is that the one based on mass does not factor in the temperature dependence of oxygen solubility. However that saturation is represented (3.5 mg/L DO at 25°C (43% sat.) is much more available to an organism than 3.5 mg/L at 0°C (24% sat.)).

The Board needs to understand that a standard of 24% saturation–which is being proposed (represented as 3.5 mg/L of DO at 0°C), is equivalent in oxygen availability to an organism of 2 mg/L of DO at 25°C. Does the Board feel confident in proposing a 2 mg/L standard for the March-July or August-February time periods? If not, why then is 3.5 mg/L being proposed for a standard to be in effect in February and March?

The scientific problems with the proposed rules are only at low temperatures, and independent of the units in the standard. The proposed rules are easily modified to prevent irreparable harm—as documented by the IEPA and DNR (OOB pp. 50-59), that could befall many organisms in the general use waters of Illinois, should these rules be adopted.

The proposed rules–ignoring the temperature dependence of the oxygen solubility, do not create problems for waters that are warm, because these are the temperatures at which the large majority of the studies have been performed, and where the errors are small due to the limited temperature range.

On the other hand, there are *major differences* in the two methods at low temperatures (see the example above for 3.5 mg oxygen/L) because the partitioning is driven by the difference in percent saturation. To an organism, 3.5 mg/L of oxygen at 25° C is much less available than 3.5 mg/L at 0° C (43% vs 24% saturation). As discussed by the Illinois DNR in these rule making proceedings, (OOB pp. 50-59; 64-68), the DNR and IEPA:

- Identified many organisms, including small-mouth bass, that require higher DO saturations than 24%, which is 3.5 mg/L at 0°C.
- Identified native mussels that have an 82% mortality rate at DO concentrations less than 5 mg/L;
- Identified 374 stream reaches that have a meaningful number of oxygen sensitive organisms (OOB pp. 56-7); The Illinois Chapter of the American Fisheries Society states that it has reviewed the record and believes that the DNR/IEPA procedures for "earmarking 'Category I' stream segments are sound and scientifically based." (PC 100 at 1; OOB p 62);
- Reported sub-lethal effects on mayflies when the DO is in the 25-35% sat. range;
- Identified 31 stream-fish species that require DO minima higher than the NCD's warmwater criteria;
- Found that many stream macro invertebrates-the forage for many of the fish, are more sensitive to low DO than are the fish.

(Because of the thin hypolimnion that forms when the central basin of Lake Erie stratifies in the spring, this region of the lake goes anoxic before the lake overturns in the

fall, killing all the aerobic organisms present. In the terms of Earthday 1970, Lake Erie was a "dead lake". This annual phenomenon in Lake Erie has been intensively studied for the past 40 years or so. When the dissolved oxygen concentration falls below 2 mg/L at 10°C the waters are lethal to all the aerobic organisms in the lake, and the lake is said to be hypoxic. *Water with 2 mg/l of oxygen at 10°C is 18% saturated and it is not able to sustain aerobic aquatic life.*) ¹

The Board's proposed rule is based on the premise that water that is 24% saturated (3.5 mg oxygen/l at 0°C) will permit the full complement of indigenous aquatic organisms to thrive. **Nonsense**! The IEPA and the DNR have presented evidence that more than 4 mg/L of dissolved oxygen is necessary for many indigenous aquatic organisms. On the other hand, *no evidence has been presented in these proceedings to demonstrate that 3.5 mg/L oxygen at cold temperatures is protective of indigenous aquatic life.* The Board is putting all of the oxygen sensitive aquatic organisms in the general use waters at risk when the temperatures get cold with *no evidence from studies at cold temperatures* to support this rule.

The Opinion and Order of the Board related to this rulemaking states (OOP p. 48), "When setting water quality standards, the Board places *significant weight* on adopting a standard that *fully protects aquatic life*, . . .". By ignoring the temperature effects on the availability of dissolved oxygen to organisms, the Board has clearly *not* met its goal with these proposed rules.

Proposal

The clear advance in these proposed rules is the recognition that early life stages require higher levels of dissolved oxygen than adults do in order to properly develop. The problem is that the proposed revisions to these Standards, in mg/L, each cover six month periods that include both warm and cold months. As previously discussed, while these concentrations of DO may be sufficient at warm temperatures, they are not protective at cold temperatures with percent saturations of less than 25%. All that needs to be done is to choose a standard (in mg/L, lbs/yd³, or whatever) that corresponds to a percent saturation of 33% or greater -5 mg/L at 0°C, or 4 mg/L at 5-10°C, as suggested by the IEPA and DNR evidence. Since oxygen is much more soluble in water at cold temperatures, this modification should cause minimal problems, as is demonstrated by the monitoring data presented in these proceedings.

I am not suggesting that the DO standard be written in terms of percent saturation, only that the standards as adopted be *based* on the science of gas partitioning in organisms, and reflect the temperature dependence of oxygen solubility. I am suggesting that a standard of 3.5 mg/L of oxygen at 0°C–equivalent in the availability of oxygen to fish of 2 mg/L at 25° C, is not a standard that, "*fully protects aquatic life*," and should **not** be adopted.

It should be noted that all continuous DO measurements and most discrete measurements (for BOD determinations, for instance) use electronic sensors that respond to the percent saturation of oxygen in the water being tested rather than the 119 year old Winkler chemical method² that yields DO in mass units.

Implementation Issues

On a different matter, I agree with the comments by Albert Ettinger of the Environmental law and Policy Center (PC 101) and by Mr. Kollias of the Metropolitan Water Reclamation District of Greater Chicago (PC 111) that implementation rules for these proposed standards are critical to their effectiveness and need to be part of the proposed new rules. Along with the practical issues discussed by Ettinger and Kollias, are measurement uncertainties and their implications on the effectiveness of the proposed rules. USGS data on continuous DO monitoring of several Illinois streams were presented early in the rule making process and proved very useful in defining and understanding the issues. While it has received little attention (see, however, April 25, 2005 Hearing Transcript, pp 88-9) the USGS qualified their data with the statement that the reported DO concentrations had an uncertainty of ± 2 mg/L.

Assume that the proposed standard for Level 1 streams, other life stages, August through February of 4 mg/L of DO is adopted. A monitoring value of 2.5 mg/L DO (17% Sat. at 0°C) could be deemed to be in compliance since—within the precision of the measurement, it is in accord with the standard. Likewise, a measured value of 5 mg/L would raise no alarms or concerns as it is above the standard. However, the actual DO—within the precision of the measurement, could be as low as 3 mg/L. *It needs to be understood that the actual DO concentration in a body of water has a 50% chance of being below the standard when a measurement indicates that the DO is at the standard value* (assuming that the data are normally distributed).

Measurement uncertainties can be reduced, but not eliminated. They are an issue with all actual determinations. The risk to the indigenous population of organisms of the actual value of DO being up to 2 mg/L less that the measured value need to be taken into account when setting standards. Such uncertainties are usually dealt with by including a margin of error–some additional protection, to the regulations to protect those organisms at risk due to these errors inherent in the measurement process. When the DO concentrations in these proposed standards are determined by the Board, the risks due to the measurement uncertainty could be taken into account by adding one or more mg/L to each of the proposed standards, depending on a valid determination of the measurement uncertainty for monitoring data.

References

- 1. Hawley, Nathan et al., EOS <u>87</u>, 313 (2006).
- 2. Winkler, Lajos, Chem. Ber., <u>21</u>, 2843 (1888).