# Faster dissolved oxygen test kit

The purpose of my project is to determine if there is any significant difference in dissolved oxygen (DO) levels as measured by the traditional HACH method or the newly developed CHEMets test kit under typical field conditions.

Hypothesis My hypothesis is that there is no significant difference in dissolved oxygen (DO) levels as measured by the traditional HACH method or the newly developed CHEMets test kit under typical field conditions. Review of Literature “ Ours is a watery world, and we, its dominant species, are walking sacks of sea water. The presence of large amounts of liquid water on Earth make our planet unique in the solar system.” (Hill, 1992 p. 477) People have recently become more concerned with preserving our earth for future generations. Even the government pitches in to help save our earth by enacting laws to help preserve our natural resources.

There is local evidence that improved sewage treatment means improvement in water quality. Monitoring on a national level showed that large investments in point-source pollution control have yielded no statistically significant pattern of improvement in dissolved oxygen levels in water in the last 15 years. It may be that we are only keeping up with the amount of pollution we are producing. (Knopman, 1993) The early biosphere was not pleasant for life because the atmosphere had low levels of oxygen. Photosynthetic bacteria consumed carbon dioxide and produced simple sugars and oxygen which created the oxygen abundant atmosphere in which more advanced life forms could develop. (Brown, 1994) The mystery of how Earth’s oxygen levels rose is very complex.

Scientists don’t agree when or how the oxygen on earth got here, but we know we could not live without it. (Pendick, 1993) Oxygen is crucial for humans to survive. Dissolved oxygen is also crucial for most fish and aquatic organisms to survive.

Dissolved oxygen is for them what atmospheric oxygen is for humans. If humans have no oxygen to breathe, they die.

The same goes for fish. However, fish get their oxygen from the water, and humans get theirs from the atmosphere. (Mitchell and Stapp, 1992) Different aquatic organisms need different levels of dissolved oxygen to thrive. For example, pike and trout need medium to high levels of dissolved oxygen. Carp and catfish are the exact opposite, needing only low levels of dissolved oxygen.

(Mitchell and Stapp, 1992 ) Low levels of dissolved oxygen inhibit the growth of Asiatic clams. ( Belanger, 1991) In the American River, too much dissolved oxygen resulted in mortality of salmonoid fishes. (Colt, Orwicz and Brooks, 1991) Brood catfish, or catfish raised on fish farms, are especially susceptible to low dissolved oxygen.

Since catfish are a major food source for many people, their production is important.

(Avault, 1993) There are two main sources of dissolved oxygen: (1) the atmosphere – waves on lakes, rapidly moving rivers, and tumbling rivers all act to mix oxygen from the atmosphere with water; (2) aquatic plants – algae and benthic plants (bottom-rooted plants) deliver oxygen into the

water through photosynthesis. The solubility of all gases, including oxygen, is inversely proportional to temperature which means that the solubility of gases goes down as the temperature goes up, and vice versa. The concentration of dissolved oxygen also varies directly with atmospheric pressure and atmospheric oxygen concentration. When the atmospheric pressure or atmospheric oxygen concentration goes up, the level of dissolved oxygen goes up. (Roskowski & Marshall, 1993)

D. H.

Farmer studied the fluctuation of dissolved oxygen content in a body of water before, during, and after a storm. During the storm, the increased wave activity increased the dissolved oxygen content. (Farmer and McNeil, 1993) Turbulent flow in streams has caused most of the biocenogenesis (the environmentally determined characteristics of an organisms) to be represented by attached or benthic organisms. For this reason, a method of evaluating the role of benthic organisms in the total dissolved oxygen balance was created. Benthic plants play an important role in providing dissolved oxygen.

These plants respire oxygen through photosynthesis. Benthic plants are plants such as cattail, bulrush, arrowhead, water lily, pond weeds, and muskgrass. (Nebel, 1990)

Many things can change the level of dissolved oxygen in a body of water. Dissolved oxygen levels rise from morning through afternoon as a result of photosynthesis. Photosynthesis stops at night, but animals and plants continue to respire and consume oxygen.

Water temperature and volume of water also affect dissolved oxygen levels. Dry weather causes dissolved oxygen levels to decrease and wet weather causes dissolved oxygen levels to increase. (Mitchell and Stapp, 1990) The breakdown of organic matter by bacteria decreases dissolved oxygen in the water and yet enriches the water with plant nutrients. A reasonable amount of breakdown is good, so the water won't become oligotrophic or nutrient poor. But too much organic breakdown will decrease dissolved oxygen and leave an excess of nutrients. Eutrophication is a term used to describe a body of water in which the organic nutrients reduce the level of dissolved oxygen to such a point that plant life is favored over animal life.

Algae blooms cause excessive organic material also. When algae die, they become a part of the organic wastes. (Nebel, 1990) Most organic material can be broken down by microorganisms. Microorganic biodegradation can be either aerobic or anaerobic. Aerobic oxidation results in the further depletion of dissolved oxygen. When dissolved oxygen in water is decreased by excessive organic matter and ongoing degradation, the process then shifts to an anaerobic process.

Anaerobic bacteria actually flourish in the absence of oxygen. Animal life can be permanently suppressed in this environment. (Hill, 1992) When dissolved oxygen decreases, major shifts occur in the kinds of aquatic organisms found in a body of water . The insects that need high levels of dissolved oxygen are replaced by anaerobic organisms.

Mayfly nymphs, stonefly nymphs, caddisfly nymphs, and beetle larvae (all need high levels of dissolved oxygen) are replaced by pollution tolerant

worms, fly larvae, nuisance algae, and other anaerobic organisms. (Mitchell and Stapp, 1992)

So what is a good level of dissolved oxygen? Under 4 ppm is not good. But what about too much dissolved oxygen? ( Hidaka, Shimazu, Kumanda, Takeda and Aramaki, 1991) “ A nonlinear relationship was found between oxygen concentration and median lethal concentrations values, with significantly increased toxicity at the middle oxygen concentration. It was concluded that dissolved oxygen concentration was an important environmental factor in the assessment of photo-induced toxicity of anthracene to fish.

” (McCloskey and Oris, 1991 p. 145) We have present day examples of the effects of pollution on dissolved oxygen, which then in turn effects the ecosystem. Following are two clear examples of the devastating effects of neglect of our ecosystem. (1) The Chesapeake Bay. Chesapeake Bay is the largest estuary in North America. Before the 1970s the bay was also the most productive, yielding millions of pounds of fish and shellfish and a home for a variety of waterfowl.

Most of the food chains started with the sea grasses.

Over half a million acres of this underwater “ grass” was present only a few feet beneath the surface. The sea grass provided food, a place for spawning, shelter for young fish, and dissolved oxygen for the fish to breath. In the early 1970s, the sea grasses started to die. By 1980 the grasses were gone, except in the lower bay.

All animals that had depended on the grasses died accordingly. Even worse, the bottom water did not have enough dissolved oxygen and caused large numbers of lobsters, oysters, and fish to be suffocated. The water of the Chesapeake Bay was very murky and cloudy. The cloudiness persisted over extended periods of time. The reduced light was decreasing photosynthesis and the sea grass began to die as a result. Without the photosynthesis of the sea grass, dissolved oxygen was no longer being adequately supplied.

In addition, bacterial decomposition was consuming dissolved oxygen, thus making it unavailable to fish and shellfish. Chesapeake Bay has been overcome by the process called eutrophication. This is not unusual. In the past 40 years, many other ponds and small lakes have also suffered this fate.

(Nebel, 1990) (2) The Black Sea. The polluting of the Black Sea is causing the Black Sea to die. Over 300 rivers dump into the Black Sea a deadly mix of nitrates, phosphorous, and oil. A local joke in Varna, Bulgaria, tells suicide cases not to worry about drowning, since the sea’s poisons will kill them first.

The worst offenders are the Danube, Dniester, and Dnieper Rivers. Waste from the Danube River has increased at least tenfold over the past decade. Johann Strauss Jr.’s “ Blue Danube” would hardly be recognizable to the composer. Its never blue now, instead it’s always a color of pea-green or black.

When the sun hits puddles of oil, it forms rainbows on its ripples. The biggest problem is not the poisons but the nutrients – the phosphorous and nitrogen. The entry of more nutrients into the sea means more harmful surface algae

to keep sunlight from the seabeds, killing them and halting the production of dissolved oxygen. (Pomfret, 1994) Other rivers are polluted also, such as the River Borovniscica (Yugoslavia), which is polluted with organic substances and the River Bistra, which is polluted with inorganic substances. Also the death of the Cuyahoga River, which burst into flames on June 22, 1969.

( Gordon and Steele, 1993) Dissolved oxygen levels can vary even within the same stream, river, or body of water. Outside the main current of a stream, dissolved oxygen levels can be low. This point was graphically illustrated by biologist E. P.

Pister as he attempted to rescue an endangered species of pupfish.

In his hurry to collect more pupfish, he had placed the cages containing previous captures in eddies away from the main current. By the time he noticed his error, a number of these fragile creatures were already dead. (Pister, 1993) Sometimes it’s not lack of dissolved oxygen that kills the fish. Rather it can be too much dissolved oxygen, as in the case of the American River.

Dissolved oxygen levels were considerably higher in the American River than those reported to cause death in hatchery salmonoids due to gas bubble disease. The source of this gas bubble disease and supersaturation in the river was from air entrainment, solar heating, and photosynthesis. The impact of the high dissolved oxygen levels in the hatchery water supplies was decreased with the installation of degassing structures to remove excessive dissolved oxygen. (Colt and Orwicz and Brooks, 1991)

As people try to solve disasters like those cited above, they need to determine the source of the problem before they work on a solution.

Sometimes even while people are trying to clean up, there is no statistically discernible pattern of increases in the water’s dissolved oxygen content. Many companies offer test kits to measure water quality. Some tests take a long time to run, but people are always looking for a quicker way to run the tests especially under field conditions where response time is critical. Some companies have come up with a quicker way to run tests, but are they as accurate as we’d like to believe? One type of kit for measuring dissolved oxygen is put out by CHEMetrics. The CHEMets ampoules contain a solution of indigo carmine in reduced (near colorless) form.

When you snap the tip the ampoule fills with your water sample and any dissolved oxygen in that sample will cause the reagent to oxidize to a blue color. Then the ampoule is compared with the standard color bars.

A noticeable problem is that there is definitely a change in the shade of color from 0-4 ppm, but in the higher ranges it is hard to tell any difference. For example, 5-10 ppm seem to be the same shade of blue, and there is not even a specific color bar for 9 ppm. There is an 8 ppm and then a 10 ppm.

If you say that the shade of blue is darker than the 8 ppm color bar but less than the 10 ppm color bar, then you could declare it 9 ppm. There is no way of saying if something is 7. 5 ppm because there is no shade of blue halfway between 7 ppm and 8 ppm. The HACH method takes longer, but it is easier to determine the amount of dissolved oxygen in the water. The way you determine the amount of dissolved oxygen in the water is by how many

drops of Sodium Thiosulfate Standard Solution you add until the sample changes from yellow to colorless. Each drop equals one ppm of dissolved oxygen.

We need to think about accuracy, but what about safety?

The HACH method uses chemicals that are labeled with “ Keep Out Of Reach Of Children. For Laboratory Use Only. Causes Eye Burns. Do Not Ingest. May Cause Skin Irritation.

” along with direction what to do if you inhale, ingest, or come into contact with the chemical. The directions indicate the need to be very cautious with the chemical, particularly because it isn’t safe without proper use. By contrast the CHEMets kit has no warnings like this. The obvious hazard is that you would squeeze the glass ampoule too hard and it would break. There are many things to take into consideration when you are selecting a test kit , not just which one is faster. Such as quality, time, safety, expense, accuracy and much more.

MaterialsHACH TESTING KIT-Dissolved Oxygen 1 Reagent Powder Pillows-Dissolved Oxygen 2 Reagent Powder Pillows-Dissolved Oxygen 3 Reagent Powder Pillows-Sodium Thiosulfate, Stabilized, Standard Solution, 0. 0109N-Bottle, Dissolved Oxygen, glass stoppered-Bottle, square, mixing-Clippers-Stopper, for dissolved oxygen bottle-Tube, measuring 5. 83 mLCHEMets TESTING KIT-Self filling ampoules for colorometric analysis-Chart with color bars for comparison to self filling ampoulesTABLE-Covered with newpaper and/or paper towelsWATER-Kankakee River-Melted snow-Tap water-Tap water stirred for one minute-Roof runoff-Fish aquariumEQUIPMENT TO

RECORD RESULTS-Paper-Pencil-ClipboardSAFETY EQUIPMENT-Rubber gloves-Goggles-Rubber apronsProcedureHACH TESTING KIT

1) Fill Dissolved Oxygen bottle (round bottle with glass stopper) with the water to be tested by allowing water to overflow the bottle for 2 or 3 minutes. To avoid trapping air bubbles in the bottle, incline the bottle slightly and insert the stopper with a quick thrust. This will force the air bubbles out.

If bubbles become trapped in the bottle in Steps 2 or 4 the sample should be discarded before repeating the test.

2) Use the clippers to open one Dissolved Oxygen 1 Regent Powder Pillow and one Dissolved Oxygen 2 Reagent Powder Pillow. Add the contents of each pillow to the bottle. Stopper the bottle carefully to exclude air bubbles. Grip the bottle and stopper firmly, shake vigorously to mix.

A flocculent (floc) precipitate will be formed. If oxygen is present in the sample, the precipitate will be brownish orange in color. A small amount of powdered reagent may remain stuck to the bottom of the bottle. This will not affect the test results.

3) Allow the sample to stand until the floc has settled halfway in the bottle, leaving the upper half of the sample clear. Shake the bottle again. Again let it stand until the upper half of the sample is clear. Note the floc will not settle in samples with high concentrations of chloride, such as sea water.

No interference with the test results will occur as long as the sample is allowed to stand for 4 or 5 minutes.

4) Use the clippers to open one Dissolved Oxygen 3 Reagent Powder Pillow. Remove the stopper from the bottle and add the contents of the pillow. Carefully restopper the bottle and shake to mix. The floc will dissolve and a yellow color will develop if oxygen is present.

5) Fill the plastic measuring tube level full of the sample prepared in Steps 1 through 4. Pour the sample into the square mixing bottle.

6) Add the Sodium Thiosulfate Standard Solution drop by drop to the mixing bottle, swirling to mix after each drop. Hold the dropper vertically above the bottle and count each drop as it is added.

Continue to add drops until the sample changes from yellow to colorless.

7) Each drop used to bring about the color change in Step 6 is equal 1 mg/L of dissolved oxygen.

CHEMets TESTING KIT

1) Immerse the snapper into the sample.

2) Place a CHEMet ampoule, tapered end first into the snapper.

3) Press down on the ampoule to snap the tip.

4) Remove the ampoule from the snapper, and invert it several times, allowing the bubble to travel from end to end to mix the contents.

5) Wait 2 minutes for a full color development.

6) Use the color chart (inside box) to determine the dissolved oxygen content by matching the filled CHEMet ampoule with the color bars on the chart. The chart should be illuminated from above by a strong white light. Be sure to place the ampoule on both sides of the color bar before concluding that it gives the best match. ResultsLocation Chem Hach Temp CdifferenceKankakee River (near our dock) 10 12 2.

2 -2Kankakee River (near our dock) 10 11 3. 3 -1Kankakee River ( near our dock) 9 13 4. 4 -4Kankakee River (near our dock) 10 12 5. 0 -2Roof Runoff 4 5 5. 6 -1Kankakee River (near our dock) 10 11 5. 6 -1Tap Water 7 7 18.

9 0Snow (melted) 8 8 21. 1 0Tap Water (stirred for 1 minute) 7 8 21. 1 -1Fish Aquarium 7 7 23. 3 0Fish Aquarium 7 8 23.

3 -1Fish Aquarium 7 8 23. 3 -1Tap Water 3 1 23.

3 2GraphsConclusions

My conclusion is that there is a significant difference in dissolved oxygen (DO) levels as measured by the traditional HACH method or the newly developed CHEMets test kit under typical field conditions. CHEMets test kits are very hard to read, especially in the higher ranges. CHEMets does not compare well to HACH in areas where dissolved oxygen is higher than 8 ppm, and it does not measure above 10 ppm.

CHEMets would be fine for temperatures of about 150C or warmer. The HACH test kit is the method of choice for field analysis because it is more

reliable at all levels in providing accurate measures of dissolved oxygen. The HACH method requires more caution in use, but actually produces significant differences in measures of dissolved oxygen. Statistics Wilcoxson Matched Pairs Signed Rank Test Data gathered in the course of performing analysis is subject to certain random fluctuations.

These fluctuations may vary in size and in many cases make it difficult to decide whether the observed differences are due to real differences in the sample or to simple chance.

The discipline of statistics allows one to assess the probability (the odds) that measured differences arise from chance alone. Once one has a feel for the odds that the differences arise from chance, one can decide to reject or conditionally accept a hypothesis based on that data. The statistical test being used for this study (Wilcoxson – Matched Pairs Signed Ranks) was chosen for its computational ease and power. A nonparametric test was chosen because there was a question about the level of measurement (ordinal or interval) and whether or not the assumptions for a parametric test could be met. Procedure to apply Wilcoxson – Matched Pairs Signed Ranks test.

(see table)

1. Pair all data from each sample according to date.

2. Take the difference between each pair of measurements.

3. Rank the size of each difference paying no heed to sign (drop zero differences – split ranks on ties)

4. Compute the sum of the rank with the less frequent sign (T).

5.

Set alpha for 0. 05 with a two tailed test.

6. Look up the value for T in an appropriate statistical table.

(table G page 254 of Nonparametric Statistics by Sidney Sigel 1956 McGraw Hill)

7. Reject the null hypothesis (Ho) if T is equal to or less than the tabled value. Chem Hach Temp C Chem – Hach Rank7 7 23. 3 07 7 18. 9 08 8 21. 1 04 5 5.

6 -1 3. 57 8 21. 1 -1 3. 57 8 23.

3 -1 3. 57 8 23. 3 -1 3. 510 11 3. 3 -1 3.

510 11 5. 6 -1 3. 53 1 23. 3 2 810 12 5.

0 -2 810 12 2. 2 -2 89 13 4. 4 -4 10N= 10 (number of non zero differences) T= 8 (sum of ranks with less frequent sign) a = 0. 05 (significance level) Ho is rejected.

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