Contribution of Organic Contaminations and Nutrient level on Dynamic Equilibrium of Dissolved Oxygen in Water Bodies of Costal Belt of Ampara District

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Abstract

The dissolved oxygen (DO) of a water body (WB) is dynamically equilibrated between the two films such as gas and liquid phases. Domestic and other related waste materials may alter this equilibrium as a result aquatic organism can suffocate. Therefore, an investigation is necessary to analyse the Contribution of Organic Contaminations and Nutrient level on its related WBs. The selected parameters such as chemical oxygen demand (COD), dissolved sulphide (DS), salinity, nutrient level, and DO were used to analysis above contribution. Randomly selected three different WBs namely Ninthavur (S1), Kalmunai (S2) and Sammanthurai (S3) were used for this study over a period of six month. The correlations studies were carried out among parameters and measured data were also utilized in estimating the oxygen transfer efficiency (OTE), Eh, α and β values. Contribution of domestic and other related waste materials on dynamic equilibrium of dissolved oxygen (DEDO) were studied based on the OTE, α and β values. The DO has negatively correlated with COD, DS and nutrient level and these implies a strong contribution of domestic and other related waste materials on the DEDO on these WBs. A poor negative correlation ($r2 < 0.5$) was observed for DO with salinity and it has demonstrated that impact of salinity on DEDO is very less.

Keywords: Dissolved oxygen, oxygen transfer efficiency, chemical oxygen demand, nutrient level, dynamic equilibrium of DO

Introduction

The domestic and other waste materials of developed and developing countries are much contributed to wash off the public and private waste disposal. The problem come across, during the period of summer usual washing activities lead to degrade the quality of the water bodies which are connected to waste materials. In this study, the qualities of such water bodies are considering to analyze the environmental impact to the public who were living around these water bodies. The pollution of these water bodies is significant enough to contribute to the numerous environmental issues.

In aquatic systems, rate of oxygen transfer (ROT) is an essential factor in determining the availability of DO levels. Thus, an investigation on the parameters governing the DO levels is essential in understanding the fate of aquatic life. The mechanism of gas transfer to a liquid is given by the two film theory. It is the presence of two films, one liquid and one gas, at the gas-liquid interface which provides the resistance to the passage of gas molecules from the bulk of the gas phase to that of the liquid phase. The higher and lower solubility of the gases such as SO_2 and O_2 in the liquid phase is restricted by gas film relative to liquid film.

Three processes are involved in ROT including saturation of the liquid surface between the two phases, the passage of oxygen molecules through liquid interface film by molecular diffusion and transfer of oxygen to bulk of the liquid by diffusion and convection. Lewis and Whitman (1924) argue that the combination of resistance in the water and air film affects on an overall mass-transfer rate of the oxygen based on the two-film theory. "The level of dissolved oxygen is presumably controlled by the water film during the air-water transfer mechanism" (Liss and Slater, 1974,).The wastewater constituents impact on the above mechanisms and it is the common practice to facilitate mass-transfer models through the use of correction factors for the overall mass-transfer coefficient and saturation concentration for transfer of O_2. The impurities of wastewater components such as organic substances (especially surface active substances) and inorganic dissolved solids effect on the O_2 transfer rate (Eckenfelder *et al*., 1956, Downing *et al*., 1960 and Chern*et al*., 2001).

The factor effecting coefficient (FAC) of the DO, ROT and the OTE are subjected to this study in three different water bodies namely Ninthavur (S1), Kalmunai (S2) and Sammanthurai (S3). These distributions are compared to better understand the exchange of salt, organic matters and nutrients in these systems, and to evaluate their effects on the DEDO. The pH, temperature, concentration of saturated and dissolved DO, nutrient level, COD, OTE, α and β values are considered to evaluate

the impact of urban drainage on DEDO. Hence, to assess whether DEDO in S1, S2 and S3 are affected by COD and nutrient level.

Material and methods

Water samples were collected from selected WBs in the region. Sampling station S1 (latitude N 7° 21' 25.0767", longitude E 81° 50' 88.0947", 0.5 m above sea level) is of water column depth of 1.5 m and 100 m away from the shoreline of Ninthavur local government building, Sampling staion2 (latitude N 7° 24' 13.252", longitude E 81° 49' 57.3641" 1 m above sea level), which is 1000 m offshore from the Kalmunai shoreline, and having an open water column depth of 2.5 m and Sampling station S3 (Latitude N 7° 22' 23.7985", Longitude 81° 48' 47.4067", 3 m above sea level) is 12000 m offshore from the Karaitivu shoreline having the water column depth of 2 m and widely open to urban drainage.

The water samples were collected once a month, between January to June 2013 between 09:00 am and 12:00 noon, the pH, DO, salinity and temperature (T) values of the water samples were determined in situ using portable meters on side. The spectroscopic method (Hach, DR/2800) was used to measure the phosphate (PO_4^{3-}), and nitrate (NO_3^-); COD was measured at the laboratory using traditional titration method after digesting the samples using Eco 6 thermoreactor (VelpScientifica, Europe). Significance of the concentration of organic contaminations and nutrient level among the WBs were evaluated using MINITAB (statistical software version 14); based on that p value was calculated using general linear model analysis of variance (ANOVA).

Results and Discussion

The mean values of the parameters such as pH, temperature, and TDS are summarized in Table 1. The pH change was within the acidic range having 5.48 ± 0.48 for S1 and 5.83 ± 0.26 for S3. However, it doesn't exceed preferred pH range of 6.0 to 10.0 for fish production (Matthews, 1998) and they did not exhibit significant variation among the stations ($p<0.05$). During this study DO level was varied significantly ($p< 0.05$) among the locations, this could be attributed to nutrient loading, decomposition and mineralization of microbes (Dibia, 2006) Inorganic and organic dissolved solids.

Table 1: Summary of the measured physical properties of the selected water bodies

Sampling Station	pH mean ± SD	Temperature ^{o}C mean ± SD	TDS mean ± SD
S1	5.48 ± 0.48	29.74 ± 0.44	323 ± 55
S2	5.74 ± 0.52	28.82 ± 0.97	318 ± 51
S3	5.83 ± 0.26	29.13 ± 0.29	310 ± 34

Mean ± SD = mean ± standard deviation for 36 measurements for S1 and 18 measurement for S2 and S3, TDS = total dissolved solid.

The equilibrium between oxygen gas and dissolved oxygen in water is such that the concentration of a solute gas in a solution is directly proportional to the partial pressure of that gas above to solutions described by Henry's law as,

$$O_{2\,(aq)} \rightleftharpoons O_{2\,(g)} \tag{1}$$

The equilibrium constant for this equilibrium is,

$$K_H = \frac{[O_2]_{(aq)}}{p_{O_2}} \tag{2}$$

Where, p_{O_2} is the partial pressure of the oxygen in the gas phase, $[O_2]$ is molar concentration of dissolved gas concentration in aqueous medium and K_H is the Henry's law constant and it is a temperature dependent thermodynamic constant.

The partial pressure of the oxygen molecules was calculated using the Henry's law and the higher value of 49.02 ppm was obtained at S2 compared to the other stations. It has exhibited that the higher level of oxygen molecules may lead to enhance the p_{O_2} at low temperature. The concentrations of saturated dissolved oxygen of these WBs were calculated using empirical equation (3). This is representing the solubility of oxygen (Truesdale*et al.*, 1955,) based on the more corrected values as

determined by a modification of the standard Winkler method (ALPHA 1971). The Water Pollution Research Laboratory in England has published this equation as.

$$C_s = 14.161 - 0.3943t + 0.007714t^2 - 0.0000646t^3 \qquad (3)$$

where C_s is the saturated concentration of oxygen in ppm and t is the temperature in ^oC.

The concentration of saturated oxygen levels were ranged between 7.56 ± 0.15 mg/l and 7.35 ± 0.29 mg/l with the temperature range of 28.82 ± 0.97^oC to 29.74 ± 0.44^oC for theses WBs (Table 2).

It exhibited the saturation level of oxygen significant to the temperature (Davies *et al.*, 2008). Similar trend of higher DO value of 4.20 ± 0.77 mg/l was observed with the lowest temperature of 28.82 ± 0.97^oC at S2. The lowest mean DO value of 2.47 ± 0.69 mg/l was shown with highest temperature of 29.74 ± 0.44^oC at S1.

Table 2: Summary of the measured and calculated concentration of oxygen for the selected water bodies

Sampling Station	Concentration of Oxygen (mg/l) mean $\pm$ SD		$p_{O_2} (ppm)$	E_h
	Dissolved	Saturated		
S1	3.38 ± 0.04	7.35 ± 0.29	42.67	0.90
S2	4.20 ± 0.77	7.56 ± 0.15	49.02	0.89
S3	2.47 ± 0.69	7.37 ± 0.05	40.97	0.88

Mean $\pm$ SD = mean $\pm$ standard deviation for 36 measurements for S1 and 18 measurement for S2 and S3, p_{O_2} partial pressure of oxygen

The reduction potential (E_h) value of these WBs was investigated based on Nernst equation and their stability was studied based on the upper and lower region of E-pH diagram. In the upper region, water can be oxidized to produce oxygen while in the lower region it can produce hydrogen gas. Water is therefore only thermodynamically stable between these regions.

Upper stability limit of water is given by

$$O_2(g) + 4e + 4H^+ \rightleftharpoons 2 H_2O \quad E^o{}_{O_2/H_2O} = 1.23v \qquad (4)$$
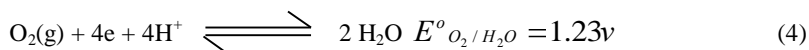
Applying Nernst equation for the reaction (4),

$$E_h = E^o{}_{O_2/H_2O} + \frac{RT}{nF} \ln \left(P_{O_2} \times \left[H^+ \right]^4 \right) \qquad (5)$$

where F = Faraday constant (96485 C mol^{-1}), n = electrical charge of the ion and T is temperature in ^oK.

The estimated E_h values were in the range of 0.88 to 0.90 indicating that the waste effluents were not disturbed the thermodynamic stability of WBs, since the values are less than the standard potential value (1.23 v) of the water (Allen *et al.,* 1985). The DO level of these WBs was compared with other parameters such as nutrient levels, salinity and COD.

The mean factor affecting coefficient (FAC), salinity, nutrient level, and COD are summarized in Table 3. The calculated partial pressure of O_2 reflects the equilibrium partial pressure of O_2 just above the water level. This partial pressure of oxygen gas may further reduced due to the aquatic plants and limiting to its solubility. Hence, the possible exposure of O_2 to solubility in water may be significantly lower than the calculated O_2 levels.

Table 3: Factor affecting coefficient and the calculated physico-chemical parameters of the WBs

Sampling Station	NL (mg/l) mean $\pm$ SD	COD (mg/l) mean $\pm$ SD	STY (‰) mean $\pm$ SD	FAC (mg/l) mean $\pm$ SD
S1	4.49 ± 0.38	399.72 ± 84	0.37 ± 0.26	4.186 ± 0.92
S2	2.10 ± 0.22	388.89 ± 34	0.25 ± 0.02	3.373 ± 0.67
S3	5.05 ± 0.24	422.89 ± 24	0.22 ± 0.10	5.063 ± 0.59

Mean ± SD = mean ± standard deviation for 36 measurements for S1 and 18 measurement for S2 and S3, FAC = Factor affecting coefficient, NL= nutrient level, STY = salinity.

The mean FAC was calculated based on the difference between the saturated concentration of the oxygen and the dissolved concentration. It was found to be within the range of 4.186 to 3.373 mg/l for all these three water bodies. Among the WBs, DO concentration was varied with NL and COD values. Lower DO concentration was observed with higher level of NL (5.05 ± 0.24 mg/l) and COD (422.89 mg/l) at S3. The low level of COD was found at S2 corresponding to higher level of DO and the opposite trend also true at S3 with respect to the nutrient level. During this study, saturation of the oxygen gas between gaseous and an aqueous phase is considered to analysis other than passage of the oxygen molecules through the liquid interface film by molecular diffusion and it is transferred to the bulk of the liquid by diffusion and convection.

The basic equation for oxygen-transfer rate is

$$\left(\frac{dC_L}{dt} \right) = N = K_L a \, (C_S - C_L) \tag{6}$$

Where N is mass of oxygen transferred per unit time, K_L is liquid film coefficient, a is interfacial area per unit volume, $K_L a$ is overall transfer coefficient (OTC) and $(C_S - C_L)$ is difference between saturated (Cs) and actual concentration of oxygen (C_L).Separating variables, integrating, and assuming $K_L a$ to be independent of the time of sampling

$$\ln(C_S - C_L) = -K_L \, at + \text{constant}. \tag{7}$$

The standard oxygen transfer efficiency (OTE) for waste water is,

$$N = N_o \left[\frac{C_s - C_L}{8.86} \times 1.024^{(T-28)} \alpha \right] \tag{8}$$

Where N is OTE under filed conditions (temperature and pressure); N_o OTE is 2.65 at zero turbulence, 8.86 is the oxygen saturation value at 28°C in mg/l.

The oxygen uptake capability, solubility and its transferring ability between the phases were analysed based on the calculated parameters such as OTE, OTC ($K_L a$), α, and β factor are summarized in the Table 4. The OTE did not sufficiently changed by the viscosity in an aerated system (DeMoyer *et al*., 200). Nevertheless, during this study OTE has shown that the lowest value 8.90 at the S2 with significant level of organic and inorganic substances.

Organic and inorganic substances are significantly impact on the characteristic of the aqueous phase. Mostly concentrated organic substances alter the surface tension and the clean water have approximately 72.8 mN m^{-1} surface tension while domestic waste water is 50.0 mN m^{-1} at 20 $^{\circ}$C (Henze *et al*., 1995).The change in the surface tension is known to the affect on the oxygen uptake rate in the water bodies.

The ratio, α factor is between the rate of oxygen uptake in wastewater and tap water respectively.

$$\alpha = \frac{K_L a(wastewater)}{K_L a(tap \, water)}$$

The surface active substances of WBs are altering the surface tension and it cause turns the oxygen uptake rate of the WBs (O'Connor., 1963). Furthermore, the surface tensions of these WBs were studied through α factor.

Table 4: Mean values of the oxygen uptake and solubility determining factors and oxygen transfer efficiency of the WBs

Sampling Station	OTE mean	$K_L a$	α Factor mean	β Factor mean
S1	21.91	0.083	16.88	0.99
S2	8.90	0.135	8.67	1.02
S3	18.40	0.052	11.86	1.00

Mean = mean values for 36 measurements for S1 and 18 measurements each for S2and S3. $K_L a$ = overall transfer coefficient

During this study low level of OTE (8.90) was observed at S2 with respect to lowest level of α factor (8.67) exhibiting the impact of surface active substances on oxygen transfer efficiency at this station. On the other hand, the highest level of OTE (21.91) relative to highest level of α factor (16.88) was observed at S1. Since the O_2 molecules do not need to possess enough kinetic energy to break the surface tension and pass through air-water interface result in more oxygen being up taken by the WBs through week surface tension. However oxygen uptake rate varied significantly (P < 0.05) among the stations.

The β factor is used to correct the reduction of the solubility of DO in wastewater caused by the organic and inorganic dissolved solids concentration. The concentration relation for the β factor is,

$$\beta = \frac{C_s(wastewater)}{C_s(tap\ water)} \tag{10}$$

Organic and inorganic dissolved solid concentrations of these water stations were investigated based on the total dissolved solid (TDS) values. The solubility of the DO was significantly reduced by the hug level of TDS (323 ± 55 mg/l) at the stations S1 rather than other stations. However, β factor does not exhibit significant variation (p> 0.05) between the stations.

Moreover Inorganic substances are increasing the viscosity of the water phase (O'Connor., 1963) and the molecular diffusion process of a gas in liquid is significant to the viscosity that is lowering the viscosity increases the molecular diffusion process. During this study, the lowering the OTE (8.90) exhibited increasing β factor at the station S1. However, the OTE did not sufficiently changed by the viscosity in an aerated system (Stukenberg *et al.*, 1977).The impact of salinity on the concentration of DO inS2 was significantly deviated from S1 and S3 with negative correlation. The analysis of the COD with the concentration of the DO exhibit the higher organic content (422.89 mg/l) had low DO (2.47 ± 0.69 mg/l) concentration at S3 whereas it was lower at S2 (388.89 mg/l) and higher DO (4.20 ± 0.77 mg/l) concentration. The above variation clearly proved by the significant negative correlations of DO *vs* COD with higher r^2 values of the WBs ($r^2 > 0.7$) Table 5.

Nutrient concentration of the WBs was varied with DO concentration such that, the sampling station S3 exhibit higher level (5.05 mg/l) of nutrient content with lowering the DO concentration. On the other hand, the opposite is true at S2. However, significant negative correlation was observed for DO *vs* NL at Sl. Nutrient enrichment in water bodies through the agricultural runoffs containing fertilizer stuff and other improper waste disposal lead to growth excess level of phytoplanktons (Khan & Ansari, 2005) as a result DO concentration may deplete or it may be the barrier to dissolve more oxygen in the water system. The impact of the Nutrient level and the COD on the DEDO of the sampling station S2 is illustrated in the Figure 1.

Table 5: Linear regression analysis for the parameters having good Pearson product moment correlation coefficients

Station	Parameters		Linear regression	r^2 value
	X	Y		
S1	DO	DS	Y = -0.002X + 0.018	0.65
	DO	COD	Y = -110.2X + 795.1	0.79
	DO	NL	Y = -0.808X + 7.775	0.54
	DO	STY	Y = -6.959X + 6.083	0.49
S2	DO	DS	Y = -0.002X + 0.019	0.74
	DO	STY	Y = -0.064X + 0.022	0.61
	DO	NL	Y = -0.435X + 3.864	0.49
	DO	COD	Y = -100.8X + 823.0	0.84
S3	DO	DS	Y = -0.003X + 0.006	0.59
	DO	STY	Y = -10.08X + 4.687	0.48
	DO	NL	Y = -1.109X + 7.305	0.51
	DO	COD	Y = -93.18X + 619.4	0.73

DO = dissolved oxygen in mg/l, DS = dissolved sulfide mg/l, COD = chemical oxygen demand, NL = nutrient level STY = salinity.

During the huge level of nutrient concentration, DO level gradually decreasing with increasing COD level. The impact of COD and nutrient level on DO concentration show a similar trend as shown in Figure 1for the other WBs, too. However, the actual values of the COD and nutrient concentration are differing from the below graphed values. DO, Nutrient level and COD are the variables of the above 3D graph of the sampling station S2 and it clearly exhibits the trend of one variable with respect to other. In order to consider the DO level has increased when the value of nutrient level lies between 7.5 - 6.0 mg/l. However,

the gradient of this graph suddenly decreases when the nutrient value below 6.0 mg/l. Nutrient enrichment led to growth excess level of phytoplanktons (Khan and Ansari, 2005) as a result DO concentration may deplete.
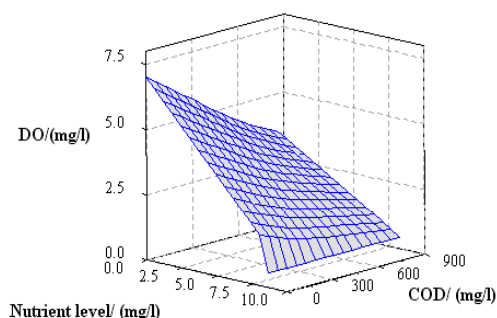

Figure 1: Variation of DO in (mg/l) with nutrient level (mg/l) and COD (mg/l) for S2

Conclusion

The domestic and other waste materials including surface active substances, significantly impact on dynamic equilibrium of dissolved oxygen (DEDO) through the contribution of organic contaminations and nutrient level. From the OTE analysis, viscosity of the stations altered by the significant level of Organic and Inorganic substances. Excess level of the domestic and other improper waste disposal lead to alter the characteristic of the WBs in such that Nutrient level and COD were impact on DO of these WBs. The COD significantly contributes to the variation of DO as like nutrient level and its level significantly reduce the DO concentration with increasing nutrient concentration. Not only the nutrient enrichment and organic content may remove the feasible space for the dissolution of the oxygen gas but DO consumers also may take more oxygen from the system. DEDO of these WBs is altered by the urban drainage system containing waste materials, which led to enhance the malodorous environment to the mosquitoes and other insects.

Acknowledgment

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