THEORETICAL MODEL CALCULATION OF CONCENTRATION OF AMMONIA AND OXYGEN IN WATER POND

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TEORIJSKI MODEL IZRAČUNAVANJA KONCENTRACIJE AMONIJAKA I KISEONIKA U VODI RIBNJAKA

Abstrakt

Od kvaliteta vode u velikoj meri zavisi uspeh u proizvodnji riba. U gajenju pastrmki to znači da normalan rast, prirast, konverzija hrane, zdravstveni i reproduktivni status zavise osim od genetskih osobina i tehnologije proizvodnje i od ambijetalnih faktora, koji mogu direktno uticati na postizanje boljih ili slabijih rezultata u akvakulturnoj proizvodnji. U ovom radu su sa aspekta utvrđivanja koncentracija kiseonika i amonijaka u vodi istraživani teorijski modeli izračunavanja produkcije amonijaka i potrošnje kiseonika, kao jednih od najvažnijih parametara vode.

Utvrđeno je da potrošnja kiseonika i ekskrecija amonijaka neposredno zavise od mase riba, temperature i protoka vode, vrednosti pH, količine hrane i sadržaja proteina u njoj. Prosečna razlika između teorijski očekivane i utvrđene koncentracije kiseonika iznosila je 5,72%. Teorijski dobivene prosečne vrednosti produkcije amonijaka, razlikovale su se od laboratorijski utvrđenih za 7,66% (metod Piper-a i sar.), odnosno za 11,16% (metod Colt-a).

Ključne reči: *voda, riba, kiseonik, amonijak*

INTRODUCTION

Starting from the fact that intensive aquaculture inevitable burdens by toxicants the aquatic environment not only fisheries, but also the recipients of water from the pond, the knowledge and understanding of the physical and chemical properties of water for growing fish is critical to achieving cost-effective and successful production.

The content of individual fractions in water depends primarily on the total weight of fish, the technological process of growing, intensity of the biological autopurification, the quantity of the food and physical-chemical characteristics of the incoming water (Boaventura et al.,1997). Inadequate use of food for fish, creating a metabolic excretory products of the fish and the presence of organic fraction of nutrients that are subject to microbial oxidation, inevitably cause the reduction of dissolved oxygen and increased concentrations of harmful substances dissolved in water. This may call into question the sustainability of fish farming (Liao et al., 1974). According to Neor et al.,(1991) high protein diet food contributes to the body tissues of fish uses about 30% of the total nitrogen ingested by food, and up to 12% nitrogen of dry matter of food due to the water. Non-consumed nutrients, metabolic products, and faeces of fish in the aquatic environment are subject to intensive biochemical processes, resulting in reducing the concentration of dissolved oxygen and increases the concentration of ammonia, phosphate, carbon and suspended matter.

For successful aquacultural production of special importance are the amount of dissolved oxygen, temperature, concentration of nitrogen fractions and pH value of water, which affect the synergistic effect of certain toxic substances and gases dissolved in water. The intensity of the effects of chemical parameters of water in fish depends primarily on the density of plantation, age, nutritional state and condition factor of fish (Pillay, 1992).

Modern concepts of sustainable aquaculture are based on ecological principles of breeding and feeding fish, where emissions created by organic matter and gases have little effect on the capacity utilization of the water environment and the environment.

The aim of this study is a mathematical assessment of oxygen consumption and creation of ammonia in water to classic trout pond and a comparison of the calculated theoretical values and the values of laboratory results.

MATERIAL AND METHODS

The experiment was carried out on trout pond near Čačak, which is located at an altitude of 320 feet, for a period of 90 days during the summer period. The volume of experimental pool was 25,2 m^3 with a water flow rate of 41 changes of water for 24 hours. The pool is set on the 3370 rainbow trout individuals, aged 12 + months, average weight of 65,2 g and total body length of 17,92 cm. During the experiment, we used the extruded trout food, manufactured by "BioMar", that contained 45% crude protein. The amount and number of daily meals were determined according to table food manufacturers, which were adapted to water temperature and fish mass.

Water samples were taken twice a day every day for two control profiles, before entering the water in the pool and the release of water from the pool. For each studied parameter was found the average value for a period of seven days. Water parameters were determined using an automatic multiparametric photometer "MultiDirect", by Lovibond company.

In parallel with examining the characteristics of water, the growth of fish and feed conversion with a seven-day monitoring of health status and mortality were measured, which presents the average values on a monthly basis. Representative control sample of 50 individuals in the pool to determine the individual body weight and linear dimensions is taken by random sampling method. Individual weight of fish was determined by measuring with the decimal technical scale, and total body length was determined by using ichthyometer. Theoretical values of certain production parameters were determined using the formula:

Fulton's condition factor (Pravdin, 1966): **Fk = M(g) / L^3 (cm)**
Index density (Piper et al.,1982): **Ig = [M(kg) / L(mm)] x Q(m^3)**
Flow Index (Piper et al.,1982): **Ip = [M(kg) / L(mm)] x P(l/sec)**
Where: M - mass of fish, L - total length of fish, Q - the volume of pond; P - water flow
Specific growth rate (Brown, 1957): **G = [(MT-Mt) - (T-t)] x 100**
Where: G - specific growth rate,%; MT - final weight of fish, g; Mt - initial weight of fish, g, T - number of days at the end of the experiment, t - start of the experiment
Oxygen saturation of water, depending on altitude, temparature and partial pressure, was calculated using the following formulas (Boyd et al.,1998; Yin-Han, 2006).

$$Nv = \text{altitude (m)} \times 3{,}28 \qquad PP\ (\text{mm Hg}) = 10\wedge\ \frac{2{,}880814 - Nv}{64790{,}7}$$

$$Bk(L/L\text{-atm}) = 0{,}00099902 \times EXP\ \frac{9{,}7265 - 5268{,}95}{t^0C + 273{,}15} + \frac{1004170}{(t^0C + 273{,}15) \times (t^0C + 273{,}15)}$$

$$ZO_2\ (\text{mm Hg}) = 760 * EXP\ \frac{11{,}8571 - 3840{,}7}{t^0C + 273{,}15} - \frac{216961}{(t^0C + 273{,}15) \times (t^0C + 273{,}15)}$$

$$Pp\ O_2\ (\text{mm Hg}) = \frac{O_2}{Bk} \times 0{,}5318 \qquad O_2\ (\%) = \frac{Pp\ O_2}{0{,}20946 \times (PP - ZO_2)}$$

Where: Nv-altitude; PP-partial (barometric) pressure; Bk-Bunsen's coefficient; ZO_2-saturation O_2 in water (mm Hg); Pp O_2-partial pressure O_2 in water; O_2 -oxygen concentration (mg/l); O_2 (%) – saturation O_2 in water

The amount of oxygen consumed (Liao, 1971): **$PO_2 = K_2 \times T^a \times M^b$**
Where: PO_2 - oxygen consumption (Ib/100 Ib mass of fish/day); K_2 – the ratio of oxygen consumption and water temperature; T – water temperature ; T^a – numerical decline in oxygen consumption by reducing the temperature at the same weight of fish;M – mass of fish (g); M^b - numerical decline in oxygen consumption by the same temperature when increasing the mass of fish
The values of constant coefficients at different temparatures of water, according to Liao (1971), are: water temperature is less than or equal to 50 ^{0}F: K_2=1,9 x 10^{-6} (b = -0,138; a = 3,130); water temperature is more to 50 ^{0}F: K_2=3,05 x 10^{-4} (b = -0,138; a = 1,855).

Modification of the constant coefficients was performedin accordance with the SI system (Kulišić, 1989), and oxygen consumption of PO_2 was expressed in g/100g weight of fish per day.

Water temperature is less than or equal to 10^0C: **PO_2=0,05676 x $T^{1,2100199}$ x $M^{-0,1355334}$**
Water temperature is more to10 ^{0}C: **PO_2 = 0,1310712 x $T^{0,8843114}$ x $M^{-0,146128}$**

The amount of available oxygen was calculated by the formula: **R_{O2} = Pv x (O_2 – 5) / 1000**

Defined formulas do not show oxygen consumption depending on the used amount of food. According to various authors coefficients amount of oxygen consumed per kilogram of used food range from 0,20 to 0,40, depending on water flow (Wheaton, 1977; Soderberg, 1994; Timmons, 2001).

In this paper, the ratio of oxygen consumption of 0,40 is used in accordance to a pound of food, because the insufficient number of changes of water for 24 hours is taken into account:

$$PO_2 = \frac{0{,}40 \text{ x kg food}}{Pv} \text{ x } 1000$$

Where: Pv – water flow l/24 hours

Concentracion of dissolved oxygen in water (Ce_{SL}) at normal atmospheric pressure of 760 mm Hg (101,325 kPa) and different temparatures were calculated according to the modified formula by Soderberg (1982, 1994):

Ce_{SL}=14,161 – 0,3943 t + 0,0077147 t^2 - 0,0000646 t^3

Correction factor for altitude is calculated using the formula:

$$Ce_k = \frac{760}{760 + (3{,}28 x Nv) / 32{,}8} \quad \text{or} \quad Ce_{k(a)} = \frac{Nv}{760}$$

Steady state of dissolved oxygen with atmospheric pressure, at different water temparature and altitude, is obtained by Soderberg equation (1982, 1994):

$$Ce_{SL}{}^1 = Ce_{SL} \text{ x } Ce_k \quad \text{or} \quad Ce_{SL}{}^1 = Ce_k - Ce_{k(a)}$$

The concentration of ammonia (Piper et al., 1982) based on the quantity of food and water flow:

$$Fn = \frac{NH_4 - N \text{ x } Pv}{\text{food (kg/day)}} \qquad NH_4\text{-N (g)} = \frac{Fn \text{ x food (kg/day)}}{Pv}$$

Depending on water temperature and pH values, the concentration of nonionic NH3 is calculated, compared to the total ammonia concentration of NH4-N to the tabular values (Emerson, 1975; Piper et al., 1982):

$$\mathbf{NH_3\,(mg/l)} = \frac{NH_4 - N \times \%NH_3}{100}$$

Where: NH4-N-total ammonia; Fn-factor of the ammonia; Pv-flow L/24 hours

Predicting ammonia is also calculated based on concentrations of total protein content in foods and modified conversion factor (Colt, 1986):

$$\mathbf{NH_4\text{-}N\ (mg/l) = (1\text{-}Fp) \times 1000 \times} \frac{\%\ protein}{6{,}25}$$

Where: Fp- conversion factor (0,65-0,80)

RESULTS AND DISCUSSION

The results achieved by weight increase, weight gain and linear increase in linear dimensions (Table 1) indicate the normal dynamics of achieving production parameters during the test. This fact confirms the value of total specific growth rate that was 120% during the test.

Mortality during the experiment had a minimum value, because of total cultivated fish until the end of the experiment died 52 individuals or 1,57%. From the results of fish mortality in this study, it can be concluded that the applied ichthyohygienic measures had a positive effect on reducing mortality of cultivated fish. Flow index (Ip) and the density index (Ig) are among the most important ichthyosanitary parameters because according to their values the optimum of density plantation of fish is estimated. Flow index indicates the amount of fish per unit volume compared to the flow of water, and the index of density is expressed as a ratio of weight of fish per unit area. Practically, this means that in spite of adequate water flow and adequate oxygen concentration too many fish in relation to the area can cause many adverse situations. By most authors,the determined Ip values of 1,021 to 1,917 and Ig values of 0,048 to 0,091 are in accordance with recommended standards of fish planting (Piper et al., 1982; Meade, 1989; Klontz, 1991)

Table 1. The average values of productions parameters during the test

Parameters	**days**			
	1	**30**	**60**	**90**
The total number of fish	3370	3347	3330	3318
Average length,cm	17,92	19,10	23,20	24,80
Average weight,g	65,20	81,10	134,50	172,00
Mortality %	-	0,687	0,510	0,361
The average weight gain,g	-	15,90	53,40	37,50
The total gain weight,kg	-	51,72	176,44	122,81
Total gain kg/m3	-	2,05	7,00	4,87
The average increase in length,cm	-	1,18	4,10	1,60

The average increase in length per day,cm	-	0,039	0,136	0,053
The averaga weight gain per day, g	-	0,53	1,78	1,25
Condition factor, FK	0,0113	0,0116	0,0108	0,0112
The total mass of fish, kg	219,72	271,44	447,88	570,69
Number of fish, m^3	133,73	132,81	132,14	131,66
Density index, Ig	0,048	0,056	0,076	0,091
Flow index, Ip	1,021	1,184	1,608	1,917
The average feed intake, kg/day	2,63	3,53	5,82	7,42
Feeding coefficient, HK	-	0,068	0,032	0,060
Daily food consumption per fish, g	0,78	1,05	1,74	2,23
Specific growth rate, G %	-	54,82	178,00	125,00

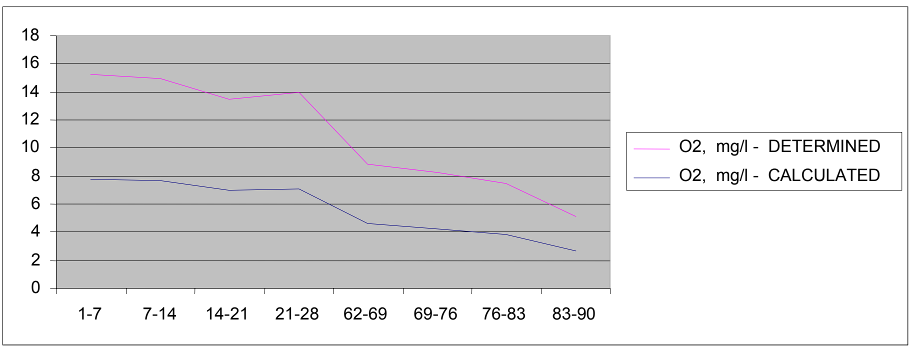
Conduction of basic biological and biochemical processes directly dependent on water temperature, and which is particularly important when converting ammonia into nitrites and in which the intensity of transformation increases with increasing temperature. For trout, the optimum temparature at which they maximum grow, take adventage of food and have the greatest immune potential is from 12-16 ^{0}C, but the tolerant values of the temparature are from 10 to 18 ^{0}C (Sedgwick, 1990). Water temparature values (Table 2) during the study period ranged from 12,30 ^{0}C to 14,00 ^{0}C. The determined pH values had a lot of consistent values and ranged from pH 7,40 to pH 7,90. The concentration of dissolved oxygen inlet water was 10,00 mg/l to 10,90 mg/l. Most authors found (Piper et al., 1982; Boyd et al., 1982; Meade, 1989; Rounds, 2003) values of these parameters of water were in the optimum range for trout water.

Available oxygen for fish is the difference between the amount of dissolved oxygen in the incoming water and physiological minimum concentration, which, for the trout, is 5 mg / l (Wheaton, 1977; Walker, 1994). Exposure of trout to concentrations of dissolved oxygen from 3 to 5 mg/l increases food consumption, interferes with general health and survival, and decreases of oxygen levels below 3 mg/l for trout has a lethal effect.

The amount of oxygen consumed during the experiment was directly proportional to the number or weight of fish, then the water temperature, intensity of metabolic processes and quantity of meals. These data (Table 2, Graph 1) indicate that oxygen consumption increased with increasing water temperature and fish biomass.Some authors, such as Pillay (1992), reported that the cultivation of trout in 1m^2 pond water at the temparature of 10 ^{0}C spends about 70 mg of oxygen, and at the temparature of 20 ^{0}C to 150 mg.

Table 2. Parameter values of oxygen consumption by periods

PARAMETERS	DAYS							
	1-7	**7-14**	**14-21**	**21-28**	**62-69**	**69-76**	**76-83**	**83-90**
temperature ^{0}C	12,50	12,30	13,20	13,50	12,80	13,10	13,90	14,00
pH	7,70	7,60	7,40	7,55	7,80	7,75	7,80	7,90
Input-determin. O_2, mg/l	**10,90**	**10,70**	**10,20**	**10,40**	**10,60**	**10,30**	**10,10**	**10,00**
satiety $O_{2,}$ %	106,24	103,82	100,99	103,66	104,02	101,75	101,57	100,78
O_2 Ce_{SL}, mg/l	10,31	10,36	10,15	10,08	10,24	10,17	9,98	9,97
O_2 $Ce_{SL}{}^1$, mg/l	9,89	9,94	9,74	9,68	9,83	9,76	9,59	9,57
available O_2, g/day	6117	5961	5391	5598	5806	5495	5287	5184
consumption O_2, g/day	1804	1769	1927	1980	2860	2941	3160	3929
consumption O_2, mg/l	1,74	1,71	1,86	1,91	2,76	2,84	3,05	3,79
consumption O_2 fish,g/day	0,54	0,52	0,57	0,59	0,86	0,88	0,95	1,18
% utilization O_2	29,49	29,67	35,74	35,37	49,26	53,53	59,77	75,79
consumptionO_2+food,mg/l	3,10	3,06	3,22	3,27	5,99	6,04	6,23	7,38
Out-calculated O_2, mg/l	**7,80**	**7,64**	**6,98**	**7,13**	**4,61**	**4,26**	**3,87**	**2,62**
Out- determin. O_2, mg/l	**7,45**	**7,30**	**6,50**	**6,85**	**4,20**	**4,00**	**3,65**	**2,50**



Graph 1. Determined and calculated values of O_2 mg/l at the exit of water from the pool

The calculated concentration of dissolved oxygen at the exit from the pool have showed higher values in control sections compared with the measured values. The average difference between the expected and theoretically determined oxygen concentration was 5,72%, on this basis we can conclude that the empirical oxygen consumption was greater than the theoretical and the numerical differences ranged from 4,09% (21-28 days) to 9,76% (62-69 days).Most authors found (Boyd, 1979; Meade, 1989; Summerfelt, 1990; Klontz, 1993) oxygen consumption and ammonia excretion in fish subject to a variety of daily variations and change of values over an hour depending on the mode of nutrition and overall physical and chemical properties of water. For comparison, 1 kg of fish food to feed the fish bass affects the creation in water: 0,28 kg CO_2; total 0,03 kg of ammonia; 0,3 kg of suspended solids, and also 0,2 kg of dissolved oxygen is spent (Colt, 1986).

Based on these results, which are presented in Table 3 and Graph 2, it can be concluded that the established concentration of NH_3 at the exit of the pool had a higher value of the used theoretical models. The average total difference between the established and the obtained values ranged from 7,66% for the method of Piper and associates, (1982) to 11,16% for the Colt's method (1986). According to the shown results it is noticed the highest concordance of the results between theoretical methods of Piper et al.,(1982) and determined concentration of NH_3.

The creation of nitrogen in fish pond water is directly dependent on water temperature, pH fluctuation, water flow, number of changes of water for 24 hours, the protein content in food, number and weight of fish and quantity of meals. In aqueous solution there is a constant balance between nonionic form NH_3 and ammonium ions NH_4^+ depending on other parameters of water, where special significance is given to pH and temperature, because with increasing pH value of water increases the concentration of ammonia, and reduces the amount of ammonium ions (Thurston, 1988).

Table 3. Production of ammonia by periods

PARAMETERS	DAYS							
	1-7	7-14	14-21	21-28	62-69	69-76	76-83	83-90
input-set NH_3, mg/l	for all days <0,0001							
min. conc. NH_4, mg/l	0,050	0,050	0,050	0,050	0,080	0,080	0,080	0,080
max. conc. NH_4, mg/l	0,075	0,075	0,080	0,080	0,185	0,185	0,190	0,190
NH_4-N g/day - **Piper**	54,88	55,15	64,81	76,26	116,69	130,33	144,84	151,36
NH_4-N mg/l/day**Piper**	0,0529	0,0532	0,0625	0,0735	0,1125	0,1257	0,1397	0,1459
NH_3, mg/l - **Piper**	**0,00059**	**0,00047**	**0,00037**	**0,00057**	**0,00164**	**0,00145**	**0,00220**	**0,00289**
NH_4-N g/day - **Colt**	52,07	53,46	59,40	69,89	115,23	128,70	140,58	146,92
NH_4-N mg/l/day- **Colt**	0,0502	0,0515	0,0572	0,0674	0,1111	0,1241	0,1356	0,1417
NH_3, mg/l - **Colt**	**0,00055**	**0,00045**	**0,00034**	**0,00053**	**0,00162**	**0,00143**	**0,00214**	**0,00280**
out-set NH_3, mg/l	**0,0006**	**0,00049**	**0,00042**	**0,00061**	**0,00176**	**0,00158**	**0,0024**	**0,0031**

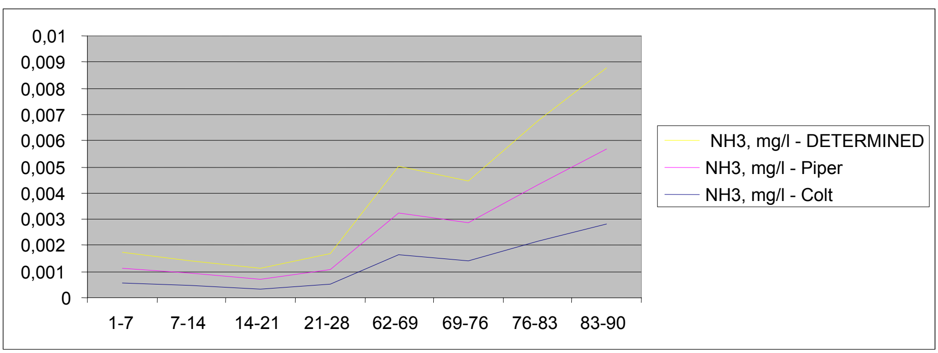


Figure 2. Determined and calculated (method of Piper and Colt) values of NH_3, mg/l at the exit of water from the pool

Excessive concentrations of ammonia cause damage to gills, reducing growth and increasing mortality, but thanks to the developed adaptive organ systems, trout relatively well tolerate more higher concentrations of ammonia than a critical value. The information on limit values of ammonia are different and range from 0,0125 mg/l to 0,025 mg/l (Boyd et al., 1992; Klontz, 1991). Production of toxicants in the aquatic environment is directly correlated with the amount of the daily meal. Coefficients that create important nutritiens in water at fed trouts per kilogram of pellet food at a water temperature from 10 to 15 ^{0}C are: for total amount of ammonia 0,289, for phosphates 0,0162 for suspended solids 0,52 for biochemical oxygen consumption 0,60 for chemical oxygen consumption 1,89 (Haskell, 1959; Liao et al., 1974; Soderberg, 1994).

Bearing in mind the presented results, there is the further task of determining the precise calculation procedures for obtaining more closer values compared with the results of laboratory analysis, which would allow their wider application in the intensive breeding of fish.

CONCLUSION

On the basis of the test the following conclusions can be done:

a) oxygen consumption and ammonia excretion directly depend on the temperature and water flow, pH, the amount of food and protein content in it and the weight of fish.

b) average difference between the expected and theoretically determined oxygen concentration ranged from 4,09% (21-28 days) to 9,76% (62-69 days), or an average of 5,72%.

c) The value of production of ammonia applied by mathematical models differed from the established laboratory values. Closest match was found between the calculated value method of Piper et al.,and determined the concentration of NH3, where the average difference was 7,66%.

d) The theoretical values obtained by the method of production of ammonia by Colt's method most varied from laboratory values, where the average difference was 11.6%.

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