XIX CONGRESO ECUATORIANO DE ACUICULTURA

Tecnologías para una producción sustentable

Selected Water Quality Topics Related to Larval Shrimp Culture

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Chlorination Chemicals

Chlorine gas	Cl_2
Sodium hypochlorite (bleach)	$NaOCl$
Calcium hypochlorite (HTH)	$Ca(OCl)_2$
Chlorine dioxide	ClO_2

Chlorine dioxide usually generated on site from sodium chlorite and hypochlorous acid:

$NaOCl + HCL \rightarrow HOCl + NaCl$

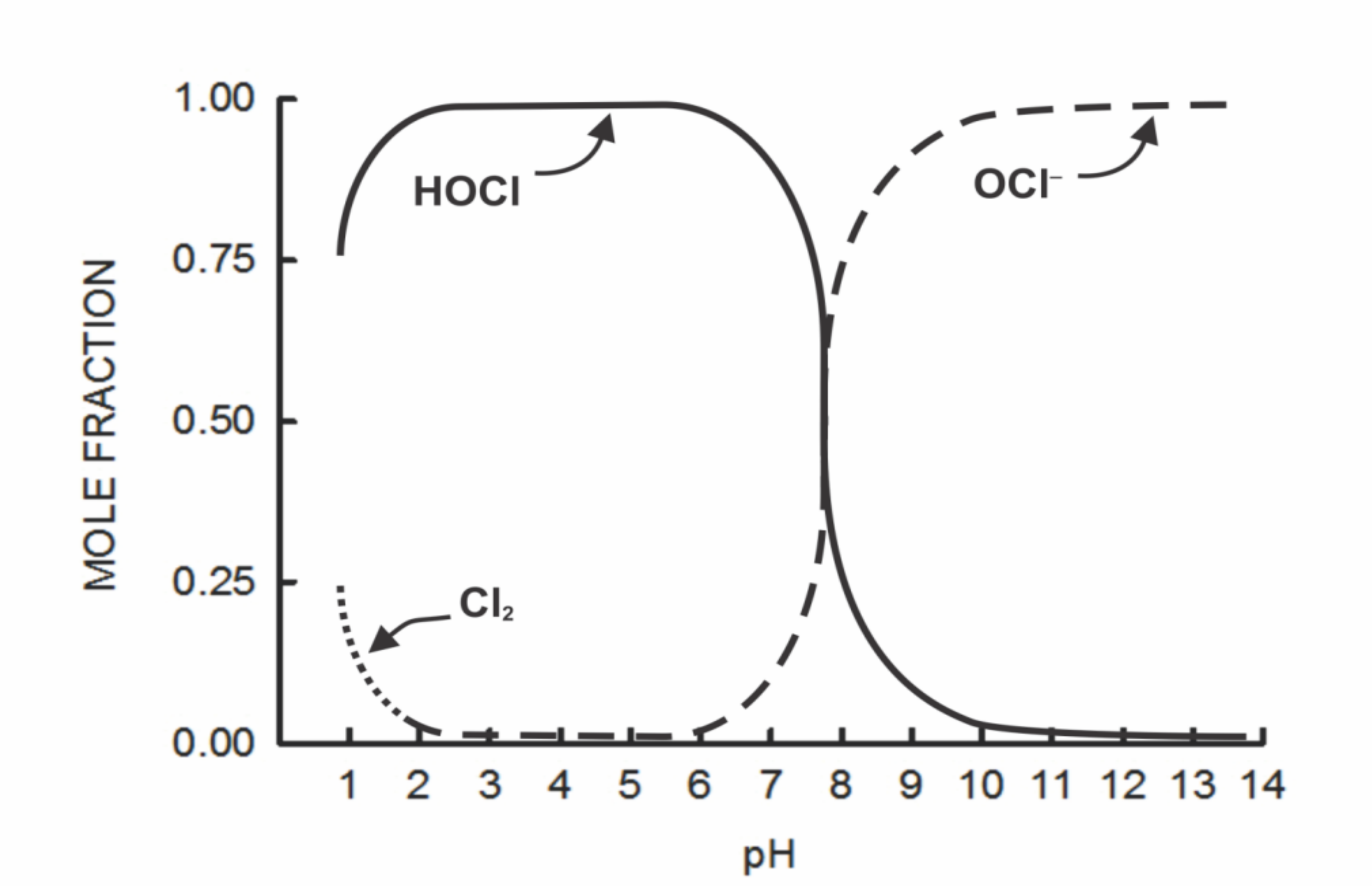
$NaOCl_2 + NaOCl + 2HCl \rightarrow 2ClO_2 + H_2O + 2NaCl$

Chlorine Species in Chlorination

$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^-$

$HOCl \leftrightarrow OCl^- + H^+$

Cl_2 = gaseous chlorine	(highly toxic)
HOCl = hypochlorous acid	(highly toxic)
OCl^- = hypochlorite ion	(less toxic)
Cl^- = chloride	(not toxic)



Effect of pH on the concentration of free chloride residuals in water.

Chlorine Demand and Free Chlorine Residual

- Oxidizes reduced inorganic ions (Fe^{2+}, Mn^{2+}, NO^{2-}, H_2S, etc.) and organic matter. In these reactions Cl_2, HOCl, and OCl^- are reduced to Cl^-.
- Forms chloramines, e.g., $NH_3 + HOCl = NH_2Cl + H_2O$.
- Forms organochlorine compounds with phenol, humic acid, and organic nitrogen compounds.
- Cl_2, HOCl, and OCl^- remaining after reactions is the free chlorine residual.

Effective Chlorine Dose

- Chlorine residual = chlorine dose – chlorine demand.
- Chlorine dose = desired chlorine residual + chlorine demand.
- For drinking water treatment, the goal usually is to obtain a free chlorine residual of 0.2 to 0.5 mg/L.
- But, in shrimp hatcheries, a concentration of 1-2 mg/L would likely be better.

Kill Time

Disinfection (kill) is proportional to disinfectant concentration × exposure time

$$\text{Kill time (min)} = \frac{\text{K}}{\text{Free chlorine residual (mg/L)}}.$$

K for free chlorine residuals (>10°C):

pH	K	pH	K
6.5	4	8.0	16
7.0	8	8.5	20
7.5	12	9.0	24

Example: Kill time for 1.1 mg/L residual chlorine at pH 8.0 at which K = 16:

$$\text{Kill time} = \frac{16}{1.1} = 14 \text{ min.}$$

Deactivation of Chlorine Residuals

- **Sunlight**

  $2HOCl \rightarrow 2H^+ + 2Cl^- + O_2$

- **Sodium thiosulfate:**

  $2Na_2S_2O_3 \cdot 5H_2O + Cl_2 = Na_2S_4O_6 + 2NaCl + 10H_2O$.

  7 mg/L sodium thiosulfate will remove 1 mg/L Cl_2.

Alternative Methods of Water Disinfection

- **Ozonation – ozone (O_3), no residues.**
- **Chloramination – Chloramine (NH_2Cl); longer residual time than chlorination**
- **Bromination and Iodinization – less toxic to pathogens than chlorination.**
- **Filtration – requires very fine filter.**
- **UV Radiation – UV is toxic and it also generates ozone.**

Ionic Imbalance

- Salinity results almost totally from major ions, but even with acceptable salinity, ionic imbalances may occur.
- Ionic imbalance can result in molting problems, stress, poor growth, and mortality of shrimp.
- The most important concern is the molar ratio of Na^{+}/K^{+}, but the molar ratio Mg^{2+}/Ca^{2+} also is important.

Contrations of major ions in normal seawater.			
Anions	mg/L	Cations	mg/L
Cl^- (chloride)	19,000	Na^+ (sodium)	10,500
SO_4^{2-} (sulfate)	2,700	Mg^{2+} (magnesium)	1,350
HCO_3^- (bicarbonate)	142	Ca^{2+} (calcium)	400
Br^- (bromide)	65	K^+ (potassium)	380

Molar ratios:

$$Na^+/K^+ = \frac{10{,}500\ \mathrm{mg/L} \div 23{,}000\ \mathrm{mg\ Na^+/mole}}{380\ \mathrm{mg/L} \div 39{,}100\ \mathrm{mg\ K^+/mole}} = \frac{0.457}{0.00971} = 47.1.$$

$$Mg^{2+}/Ca^{2+} = \frac{1{,}350\ \mathrm{mg/L} \div 24{,}310\ \mathrm{mg\ Mg^+/mole}}{400\ \mathrm{mg/L} \div 40{,}080\ \mathrm{mg\ Ca^{2+}/mole}} = \frac{0.0555}{0.00998} = 5.56.$$

Potassium and Magnesium Sources

- Muriate of potash fertilizer (KCl); 50% K^+: 1 mg KCl/L gives 0.5 mg K^+/L.
- K-Mag® (potassium magnesium sulfate); 17.8% K^+ and 10.5% Mg^{2+}:1 mg/L K·Mag gives 0.178 mg K^+/L and 0.105 mg Mg^{2+}/L.
- Epsom salt ($MgSO_4 \cdot 7H_2O$); 9.86% Mg^+: 1 mg/L Epsom salt gives 0.099 mg Mg^{2+}/L.
- Magnesium chloride ($MgCl_2 \cdot 6H_2O$); 12.0% Mg^{2+}: 1 mg/L magnesium chloride gives 0.12 mg Mg^{2+}/L.

Potassium Rate to Balance Na^+/K^+ Ratio

- Suppose water has 19,000 mg Na^+/L
  9 g Na^+/L ÷ 23 g/mole = 0.391 M) and
  0.2 g K^+/L (0.2 g /L÷ 39.1 = 0.0051 M)

- Na^+/K^+ = 0.391/0.0051 = 76.7.
- Na^+/K^+ seawater = 47.1.
- 0.391/K^+ = 47.1; K^+ = 0.0083 M.
- Increase K^+ by 0.0083 – 0.0051 M or by 0.0032 M.
- 0.0032 mole/L × 39.1 g K^+/mole = 0.125 g/L = 125 mg K/L.

Ion concentrations in evaporating seawater at different salinities.

Ion	Salinity (mg/L)					
(mg/L)	28,550	56,390	99,410	206,330	302,050	360,150
Cl	15,820	31,240	55,030	116,700	172,600	188,400
SO_4	2,206	4,367	7,732	13,210	17,290	50,890
Na	8,750	17,310	30,550	64,920	96,070	71,480
Mg	1,056	2,080	3,649	7,744	11,500	36,450
Ca	342	667	1,159	1,017	547	175
K	317	625	1,102	2,337	3,455	10,890
Ratios						
Na/K	46.9	47	47.1	47.2	47.3	11.2
Mg/Ca	5.1	5.1	5.2	12.5	34.5	343.0

Composition (mg/L) for major ions in two commercial ocean water salt mixes as compared to seawater composition.

Ion	Crystal Reef	Instant Ocean	seawater
Cl^-	19,778	19,290	19,000
Na	10,114	10,780	10,500
SO_4	3,324	2,660	2,700
Mg	1,209	1,320	1,350
Ca	380	400	400
K	359	420	380
Br	9	56	65

Quantities of salts diluted to exactly 1.000 L for preparation three selected artificial seawater formulae.

	Salt quantity (g/L)		
Salt	McClendon et al. (1917)	Subow (1931)	Lyman and Fleming (1940)
NaCl	26.726	26.518	23.476
$MgCl_2$	2.260	2.447	4.981
$MgSO_4$	3.248	3.305	3.917
$CaCl_2$	1.153	1.141	1.102
KCl	0.721	0.725	0.664
$NaHCO_3$	0.198	0.202	0.192
NaBr	0.058	0.083	0.096
H_3BO_3	0.058	---	0.026
Total	34.441	34.421	34.481

Calcium Carbonate Saturation Index

- $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$.
- $CO_3^{2-}:HCO_3^-$ ratio increases with greater pH.
- When CO_3^{2-} and Ca^{2+} concentrations exceed the solubility of $CaCO_3$, $CaCO_3$ precipitates.
- Online $CaCO_3$ saturation calculators (best one is Langelier Saturation Index) calculate $CaCO_3$ saturation pH. Need: total alkalinity; calcium; total dissolved solids (salinity); water temperature; pH.

Calcium Carbonate Encrustation

- Calcium carbonate ($CaCO_3$) can precipitate from water in hatcheries.
- A deposit of $CaCO_3$ can develop on shrimp and cause mortality.
- Production in pH by adding acid can avoid this problem.

Carbohydrate Addition in Biofloc Systems

- Ammonia-N is removed from water by bacteria and converted to protein.
- O-C + Ammonia-N → Bacterial-C + CO_2.
- Bacteria have a carbon assimilation efficiency of 5-10%.
- This means that 1 g O-C yields 0.05-0.1 g C in bacteria and 0.90-0.95 g C in CO_2.

Amount of Ammonia-Nitrogen Required in Bacteria Growth

- Bacteria are about 50% O-C and 10% N (dry matter basis).
- Microbial oxidation of 1 g O-C results in 0.1-0.2 g bacterial biomass (e.g., 0.05 g bacterial-C $\div$ 0.5 g C/g bacteria = 0.1 g bacteria).
- It follows that 0.1-0.2 g bacteria contain 0.01 to 0.02 g N (e.g., 0.1 g bacteria $\times$ 0.1 g N/g bacteria = 0.01 N/g).

Removal of Ammonia-N by Bacteria

- When a pure carbohydrate (CH_2O) is the source of O-C, ammonia-N is removed from the water for utilization by bacteria oxidizing the CH_2O. From 0.01 to 0.02 g N will be removed for the oxidation of 1 g O-C.
- Utilization of 1 mg/L CH_2O-C by bacteria will result in the release of 0.90-0.95 mg/L CO_2-C, production of 0.1-0.2 mg/L bacteria, and removal of 0.01-0.02 mg/L ammonia-N.

Ammonia-N Removal by Microbial Utilization of Sugar

- Table sugar or sucrose ($C_{12}H_{22}O_{11}$) contains 42% C.

- To remove 1 mg/L ammonia-N (at 10% carbon assimilation efficiency):

  - 1 mg/L ammonia-N ÷ 0.02 mg N removed/g O-C utilized = 50 mg O-C/L.

  - 50 mg O-C/L ÷ (42% C in sugar/100) = 119 mg sugar/L.

Ammonia-N Removal by Black Strap Molasses (BSM)

- **BSM is 21% C.**
- **50 mg O-C/L ÷ 0.21% C in BSM = 238 mg BSM/L**

Potential O-C Equivalent of Feed

- Feed = 35% crude protein (5.60% N); shrimp = 2.75% N; FCR = 1.5.

- 1.5 kg feed = 1.0 kg shrimp

  0.084 kg N in feed = 0.0275 kg N in shrimp

  Ammonia N = (0.084 kg N – 0.0275 kg N) = 0.0565 kg

- 1 kg ammonia-N = 119 kg sugar

  119 kg O-C/kg N × 0.0565 kg N = 6.7 kg sugar/kg feed.

- For BSM = 238 kg O-C/kg N × 0.0565 kg N = 13.4 kg BSM/kg feed.

Recommendation on Carbohydrate Addition in Biofloc Systems

- **Feed has C/N ratio of 7-8.**
- **Increasing C/N ratio to 12 to 15 will favor bacterial activity.**
- **Apply 0.5-1 kg CH_2O (sugar) per kilogram of feed added.**

Reason that Lower Carbohydrate Rate is Used

- Nitrification – 25 to 50% of ammonia-N is oxidized to nitrate-N by nitrifying bacteria.
- The are some phytoplankton in most floc systems that remove ammonia-N for growth.
- Some ammonia diffuses into the air.
- Some of the organic N in feces and uneaten feed is not oxidized to ammonia-N.

Nitrification

- $NH_4\text{-}N + 2O_2 \rightarrow NO_3^- + 2H^+ + 2H_2O$.
- The reaction requires oxygen and produces acidity (decreases alkalinity and pH).
- For each milligram per liter of ammonia-N oxidized, 4.57 mg/L dissolved oxygen is removed and 7.14 mg/L of alkalinity is neutralized.
- The potential acidity is equivalent to about 0.4 kg $CaCO_3$/kg feed or about 0.67 kg sodium bicarbonate/kg feed.

Aeration Requirements

- In culture tanks, the oxygen requirement is about 1.1-1.2 kg O_2/kg feed.
- In biofloc systems, O_2 is used to oxidize feed waste as well as added organic matter.
- 1 kg CH_2O (40% C), requires about 1.07 kg O_2/kg CH_2O – roughly the same as feed.