נושאי הלימוד בשני המפגשים הקרובים

הקדמה לאיכות מים במערכות גידול אינטנסיביות – דרישות

תהליכים במעגלי החנקן והזרחן וביופילטרציה

מערכת הקרבונט-אלקליניות, pH + מעבדה

סקירת מערכות טיפול ביולוגיות ולמוצקים – עקרונות פעולה

WATER QUALITY,

Determined by:

- Source of water (salinity + proportion of ions + other pollutants or components)
- Feed – the only significant constituent that is being introduced
- To limited periods – additives (medicines; disinfectants; herbicides etc)
- Production of Gasses by fish and treatment (namely O2 CO2 and at times H2S)

Implications:

- In the pond – Growth rate; Stress susceptibility to diseases etc.
- In the environment – effluent discharge and potential pollution

Water quality

This talk will discuss :

- General water quality Criteria for aquaculture (only in principal since different species may have different requirements) and its importance - WQ deign target .

- Major nutrient cycles (P, N, S,) in aquaculture systems – importance and the use of the balance approach to study these cycles in aquaculture systems .

- Review of the different systems with the working principals that are commonly used to treat aquaculture effluents in RAS.

- (later on we will discuss some design considerations for these systems)

Table 4.1 Water Quality Parameters for a Cool and Warm Water Species

Parameter	Tilapia	Trout
Temperature, °F (°C)	75 to 85 (24 to 30)	50 to 65 (10 to 18)
Oxygen, mg/L	4 to 6	6 to 8
Oxygen partial pressure, mm Hg	90	90
CO_2, mg/L	40 to 50	20 to 30
Total suspended studies, mg/L	<15	<10
Total ammonia - N, mg/L	<3	<1
NH_3-N	<0.6	<0.02
Nitrite-N	<1	<0.1
Chloride, mg/L	>200	>200

Water quality criteria

Metals:

- In general toxic to fish at very low concentrations.
- Solubility increase as pH decrease.
- Effective Concentrations change with species, temperature alkalinity etc.

Aluminum - <0.01

- some times used to remove turbidity in aquaculture and it consumes alkalinity ➔ reduce pH and increase toxicity.
- Usually applied with $Ca(OH)_2$ to counter acidity.
- $AL_2(SO_4)_3 \cdot 14H_2O$ = $6H^+$ = 3 $Ca(OH)_2$ or in other words for each 1 mg/L of alum 0.37 mg/L of $Ca(OH)_2$ should be added.

As, Ba, Cd, Cu, Pb, Fe, Zn (alkalinity dependent) – heavy metals toxic

- Usually availability of Ca and Mg that are not toxic, reduce metal toxicity since they compete on the uptake sites on the fish gills.

Ni, Se, Ag, Mn, Hg (Less alaklinity dependent)

Ca - 4 – 160 (mg/L)

Mg - <15

Na < 75

Salinity; (conductivity) – Culture specific

Specific Ions - Calcium

- metabolism
- skeletal-strengthening material, cell walls of some alage
- HCO_3-CO_3 equilibrium
  - main buffering system
  - marl formation

Salinity

- Salinity is the sum of anions and cations

cations	anions
Ca^{+2}	CO_3^-
Mg^{+2}	SO_4^{-2}
Na^+	Cl^-
K^+	HCO_3^-

- Conductivity/specific conductance: the measure of electrical flow through water

  - high salinity = high conductivity

Sources of Salinity

1. weathering of rock or soil leaching
2. chemical reactions
   1. redox
   2. acid-base reactions
   3. formation of complexes
3. atmospheric precipitation and fallout
4. evaporation

Effect of Salinity in aquaculture

Treatment	Nominal environment (mg/L)							Percent	
	Sea salt	Na	K	Ca	Mg	TDS	N	Molted	Survival
1	2,000	600	22	23	77	2,000	28	39	96
2	0	625	22	23	77	2,000	25	68	56
3	0	566	100	23	77	2,000	23	52	52
4	0	541	22	100	77	2,000	25	60	60
5	0	482	100	100	77	2,000	25	52	80

Hardness (as $CaCO_3$)- >100

Hardness – divalent soluble cations in the water

Calcium and magnesium are the most abundant alkaline earths in normal freshwaters, and their concentration as equivalent calcium carbonate usually has been taken as a measure of total hardness.

For sanitary engineering purposes water was divided into classification:

0-75 mg/liter	Soft
75-150 mg/liter	Moderately hard
150-300 mg/liter	Hard
300 plus mg/liter	Very hard.

Analyses – ICP; AA; ion chromatograph; some with

Chlorine

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-. \quad (13.8)$$

Hypochlorous acid dissociates to produce hydrogen ion (H^+) and hypochlorite ion (OCl^-) according to the following equation:

$$HOCl = H^+ + OCl^-. \quad (13.9)$$

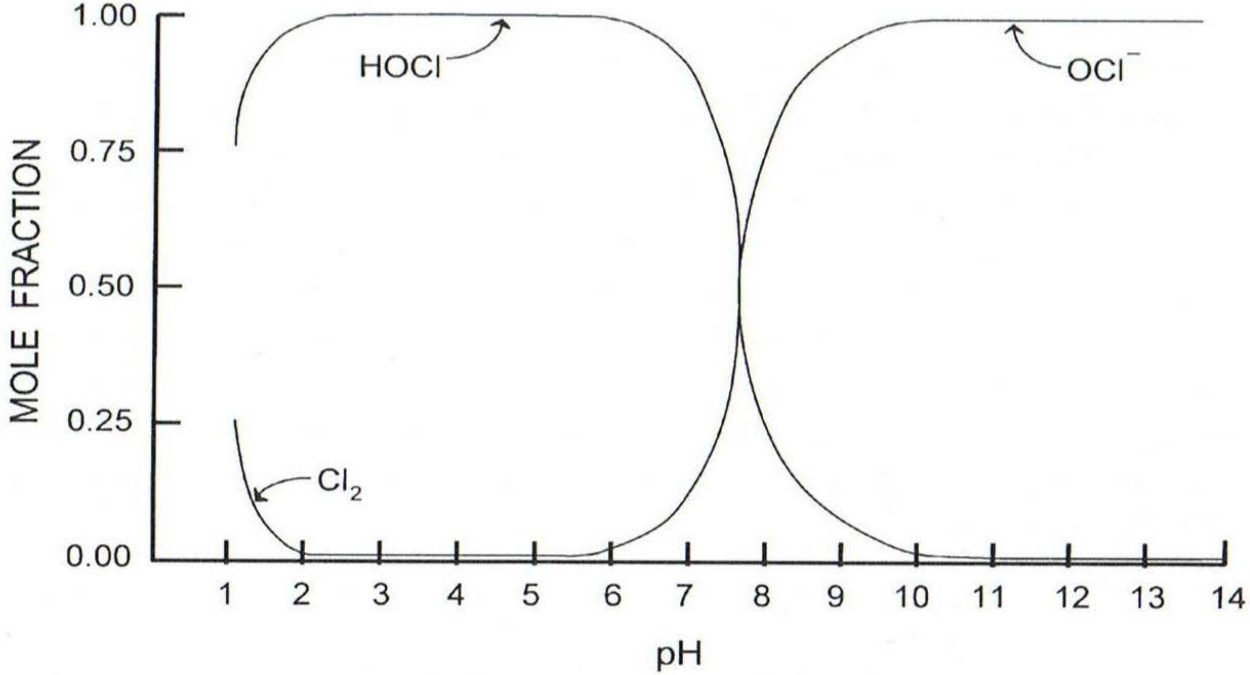

Figure 13.3. Effects of pH on the relative proportions of HOCl and OCl^-.

$$NH_3 + HOCl = NH_2Cl + H_2O, \quad \textbf{(13.11)}$$
$$NH_2Cl + HOCl = NHCl_2 + H_2O, \quad \textbf{(13.12)}$$
$$NHCl_2 + HOCl = NCl_3 + H_2O. \quad \textbf{(13.13)}$$

Free chlorine residuals can oxidize chloramines to produce nitrogen gas or nitrate. Several reactions are possible, but the primary one is as follows:

$$2NH_2Cl + HOCl = N_2 + 3H^+ + 3Cl^- + H_2O. \quad \textbf{(13.14)}$$

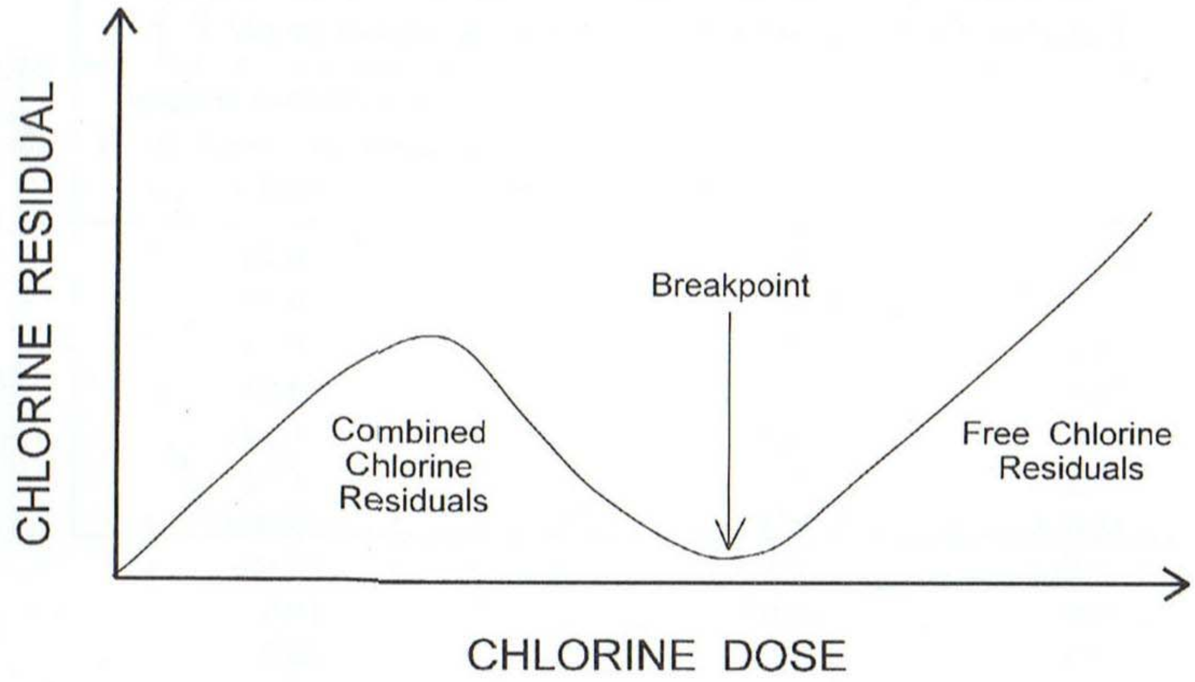

Figure 13.4. Illustration of breakpoint chlorination.

Measurement of Water Quality

Physical Analyses

Solids (Residue)

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Total Solids

Total Solids = Residue After Evaporation at 103°C

Total Solids =

Dissolved Solids

\+ Suspended Solids

Suspended Solids

Solids Retained on a Glass Fiber Filter Mat and Dried at 103^{o}C

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Fixed (Non-Volatile) Suspended Solids

Residue Remaining on a Filter After Burning Off the “Volatile” Fraction at 600°C

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Volatile Suspended Solids

Usually Considered to be The Organic Fraction. e.g. Used to Determine the Amount of Microorganisms (MLVSS) or MLSS in an Activated Sludge Unit.

Solids Analysis

Total Solids (TS) = Dissolved Solids

+ Suspended Solids

Solids Analysis

Total Solids (TS) = Fixed Dissolved Solids (FDS)

+ Volatile Dissolved Solids (VDS)

+ Fixed Suspended Solids (FSS)

+ Volatile Suspended Solids (VSS

Solids Measurement

- Total Solids (TS) Measured Using an Evaporating Dish
- Suspended Solids (SS) Measured Using A Glass Fiber Filter

Solids Measurement - TS

Evaporating Dish

Dry Dish

Tare Dish

Add Sample

Dry at 103^{o}C

TS = Dry Weight – Tare Weight

Fire at 600^{o}C

TFS = Dry Weight – Tare Weight

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Solids Measurement - SS

Glass Fiber Filter

↓

Dry Filter

↓

Tare Filter

↓

Add Sample →

Dry at 103°C

↓

TSS = Dry Weight – Tare Weight

↓

Fire at 600°C

↓

TFSS = Dry Weight – Tare Weight

Solids Relationships

- TVS = TS – TFS
- TVSS = TSS – TFSS
- TDS = TS – TSS
- TFDS = TFS – TFSS
- TVDS = TDS - TFDS

Turbidity

- Definition – The ability of a material to absorb and reflect light in water.
- Measurement
  - Old Method – Jackson Candle Turbidimeter measuring Jackson Turbidity Units (JTU)
  - New Method – Nephelometry measuring Nephelometric Turbidity Units (NTU)

Solids in aquaculture

TSS < 80
TDS < 400 (site and species specific)

Alkalinity – 50 – 300

p. 39 Boyd

- Source of C
- buffer capacity
- most often Ca + Mg source
- reduce metal toxicity

pH

pH = - log [H]

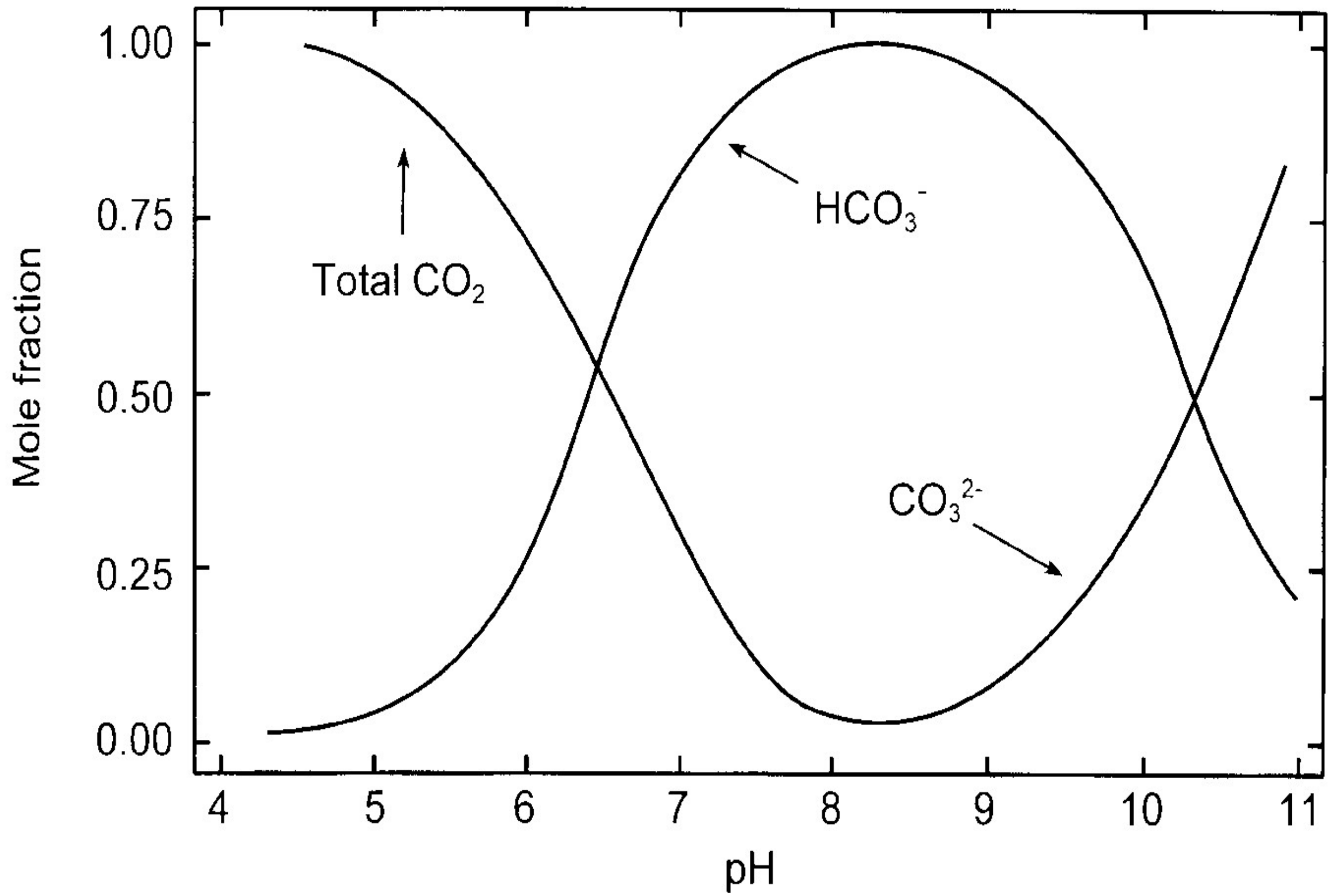
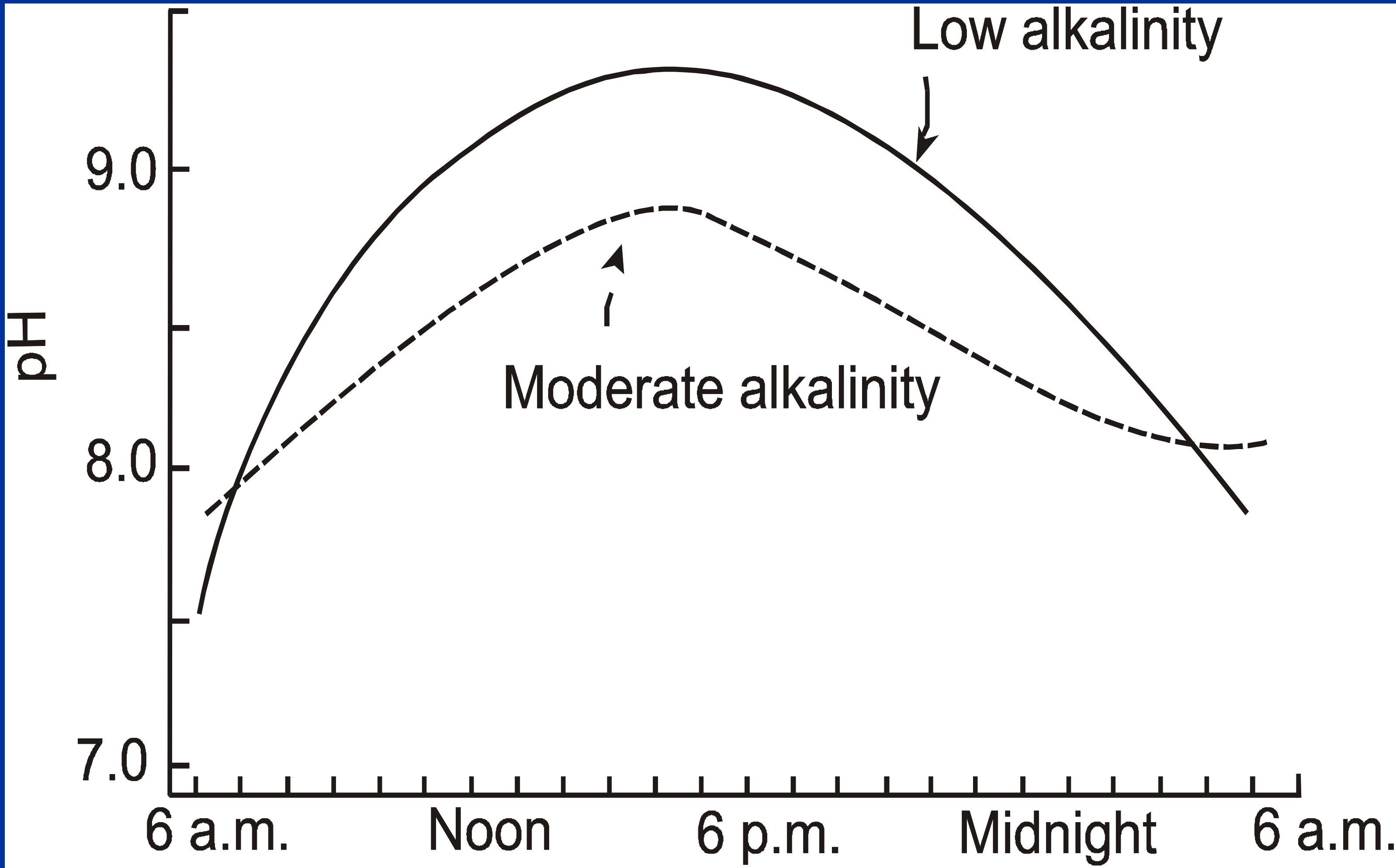


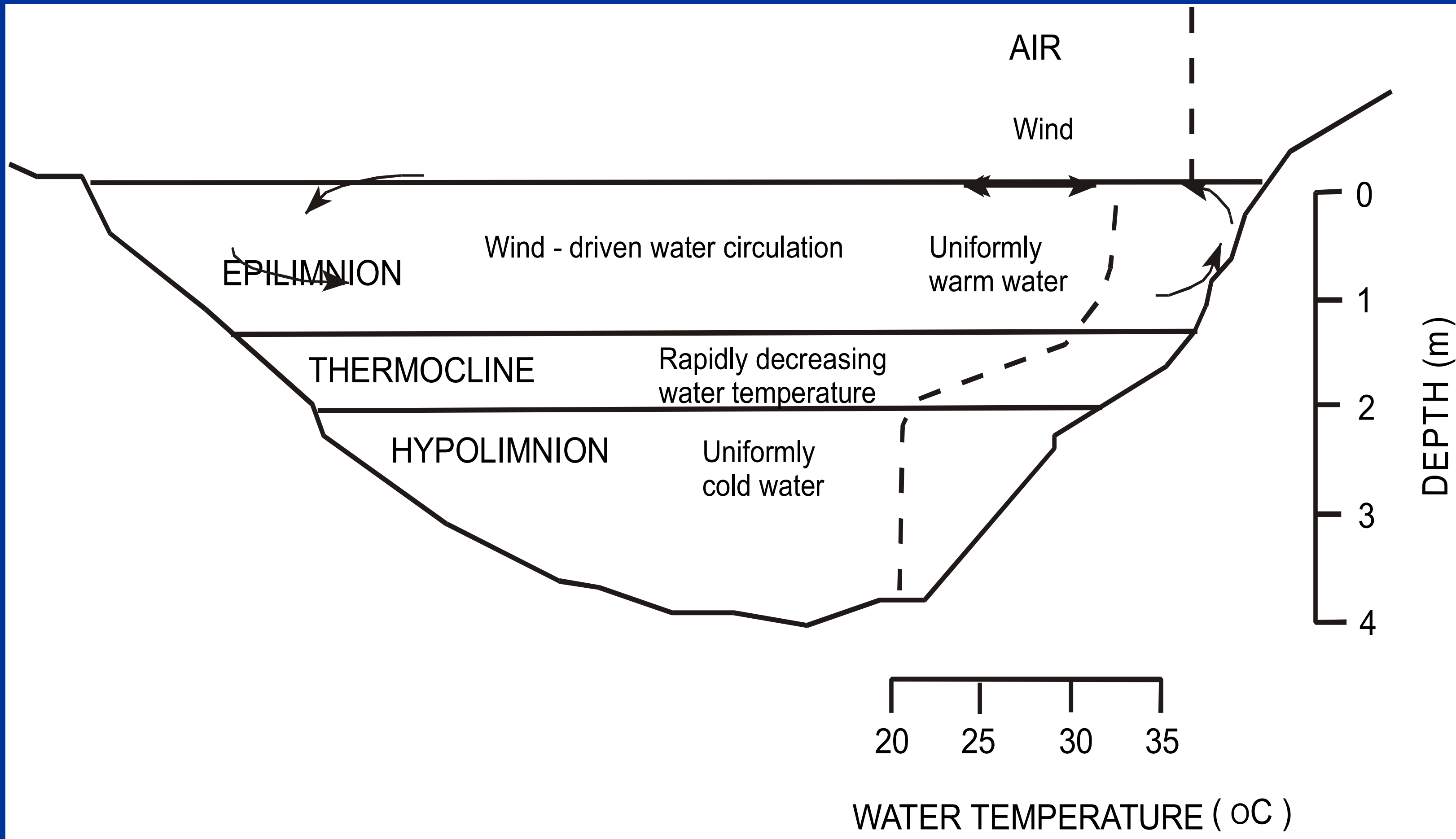
Figure 2.12. Changes in the relative concentrations of carbon dioxide, bicarbonate, and carbonate with pH. The mole fraction of a component is its decimal fraction contribution to the total moles of inorganic carbon ($CO_2 + HCO_3^- + CO_3^{2-}$) present. [From: Boyd (1990).]

pH	Effect
4	Acid death point
4-5	No reproduction
5-6	Slow growth
6-9	Best growth
9-11	Slow growth
11	Alkaline death point

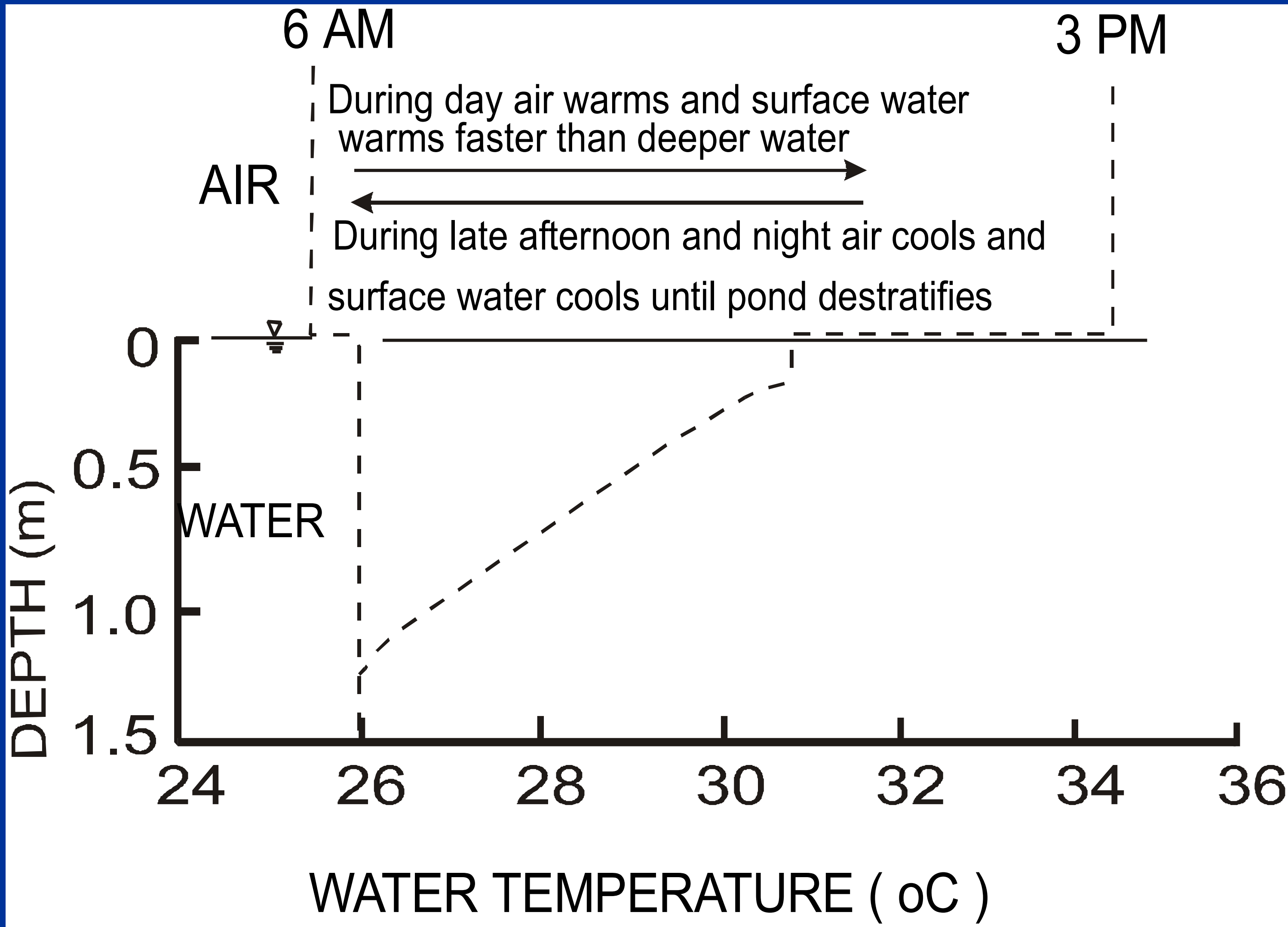

Low alkalinity
Moderate alkalinity
pH
9.0
8.0
7.0
6 a.m.
Noon
6 p.m.
Midnight
6 a.m.

Water temperature

- Temperature affect all water quality parameters
- Directly - i.e. chemical reaction rate; biological process and (Q10)
- Indirectly – i.e. Water temperature and infectious diseases



דוגמא ממתקן במשאבי שדה (גם בצפון)



6 AM
3 PM
During day air warms and surface water warms faster than deeper water
AIR
During late afternoon and night air cools and surface water cools until pond destratifies
WATER
DEPTH (m)
0
0.5
1.0
1.5
24
26
28
30
32
34
36
WATER TEMPERATURE (oC)

Oxygen – the most critical parameter in intensive aquaculture

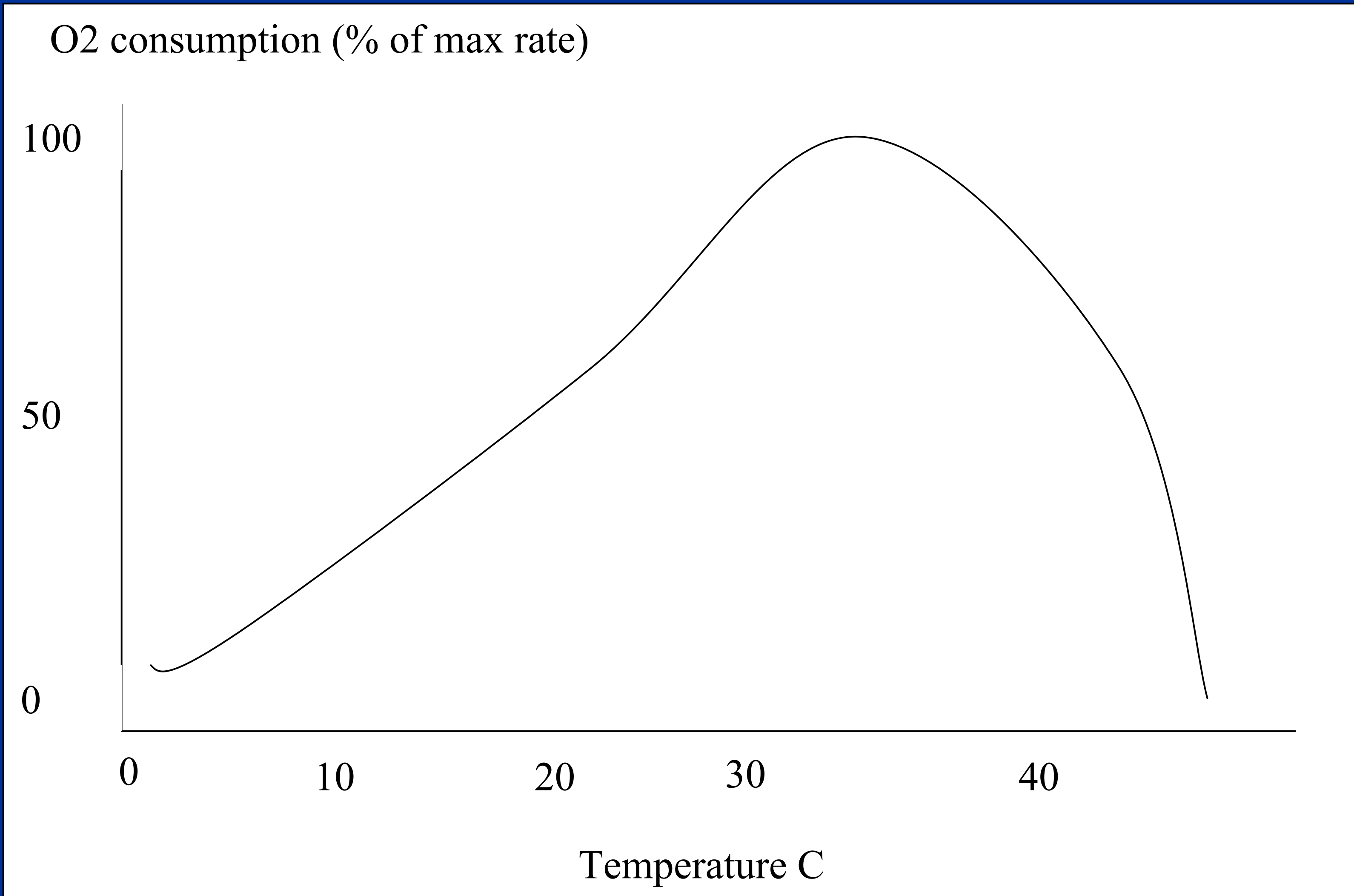
D.O concentration	Effect
Less than 1-2 mg/L	Lethal if exposure last more than few hours
2-5 mg/L	Slow growth if exposure continuous
5 mg/L	Best conditions
Above saturation	Can be harmful if consistent in all pond value (rarely a problem)

In intensive aquaculture ponds must be aerated.

In the past and in less intensive aquaculture only night or emergency aeration was needed
In RAS 24h a day

Oxygen and respiration –

(Bohr effect and the Hb affinity for O_2 pH decrease affinity decrease ➔ release O_2 in cells (where CO_2 is high) and vise versa in the lungs).


O2 consumption (% of max rate)
100
50
0
0
10
20
30
40
Temperature C

Oxygen in water and saturation point

21% O_2 in atmosphere @ standard conditions O_2 pressure 760 mmHg x 0.21 = 159.2 mmHg

When air O_2 = Water O_2 = Saturation

@ Different atmospheric pressure O_2 solubility changes ==> saturation concentration changes

$DOc = DOt\ [\ BP/760]$

DOc = Corrected DO at saturation (mg/L)

Dot = DO at saturation from table (mg/L)

Where barometric pressure is unknown, the approximate change in pressure with increasing elevation is as follows: 0 to 600 meters — 4% decrease in barometric pressure per 300 meters; 600 to 1,500 meters — 3% decrease in barometric pressure per 300 meters; 1,500 to 3,000 meters — 2.5% decrease in barometric pressure per 300 meters. For example, suppose the elevation at a pond surface is 250 meters and the water temperature is 30°C. The approximate barometric pressure will be:

$$760\text{mm} - 760\left[\frac{250\text{m} \times 0.03}{300}\right] = 741\text{mm}.$$

At 30°C and 760 millimeters barometric pressure, the dissolved oxygen concentration at saturation is 7.54 milligrams per liter (table 6). The actual concentration of dissolved oxygen at saturation for the pond surface is:

$$DO_c = 7.54 \left[\frac{741}{760}\right] = 7.35 \text{ mg/l.}$$

sure. Thus, the solubility of dissolved oxygen at saturation increases with increasing water depth. The approximate increase in pressure with increasing depth is 73.42 milliliters of mercury per meter. Thus, if the barometric pressure is 760 millimeters and depth is one meter, the total pressure is 760 + 73.42 = 833.42 millimeters. Aquaculture ponds are shallow and the effect of depth on the solubility of dissolved oxygen at saturation normally is ignored.

CO_2 20 – 60 mg/L (Species dependent)

- Has narcotic effect ; death; interfere with respiration; Ca deposits in kidney; respiratory acidosis;

- Bohr effect – high affinity to CO_2 and low affinity to O_2 in Hb

Gas super saturation (gas bobble disease) –
TGP (TOTAL DISSOLVED GAS PRESSURE) > 105%

- **Form when dissolved gas becomes a bubble – this can clog gills, vessels etc.**

- **Occur when dP > 50 – 200 mmHg.**

- **Eggs may float to surface, similar with larvae;**
- **can cause 50 – 100% mortalities. vascular emboli – restrict blood flow → anoxia.**

- **Between 25-75 mmHg chronic symptoms (reduced performance)**

- **Tolerance varies among species.**

- In ponds less common but happened because of algae;
- RAS – liquid oxygen; use of diffusers (normally if depth > 1m)
- Less common but - after a mix of cold + warm water because of the different gas saturation points

dP = (dPO2 + dPN2 + dPCO2 + dPH2O) - BP

dP can be measured by saturometer. → can evaluate

dP= TGP- Local BP

% TGP = (BP+dP/BP) X 100

@ saturation TGP = 100%;
SUPER SATURATION TGP >100%

HYDROGEN SULFIDE

Phosphorous – from environmental point of view 0.01 – 3 mg/L

- Not considered toxic to fish but when released to the environment
  can cause:
- Eutrophication.

- Pollute water bodies.
- In pond aquaculture can cause algal blooms.

- Analysis – spectrophotometric; ICP.

Figure – next slide

- Toxicity – de-coupler which leads to suppression of metabolic energy
  formation (ATP) usually via the tricarbocylic acid cycle.

- Hyper activity – lethargy, comma, mortality.

- Effect on central nervous system. Occur with in hours to exposure of
  les than 1mg/L (NH_3).

- Long term exposure of low concentration cause osmoregulatory
  disturbances; blood acidosis; and reduced respiratory efficiency. →
  reduced growth and higher susceptibility to diseases.

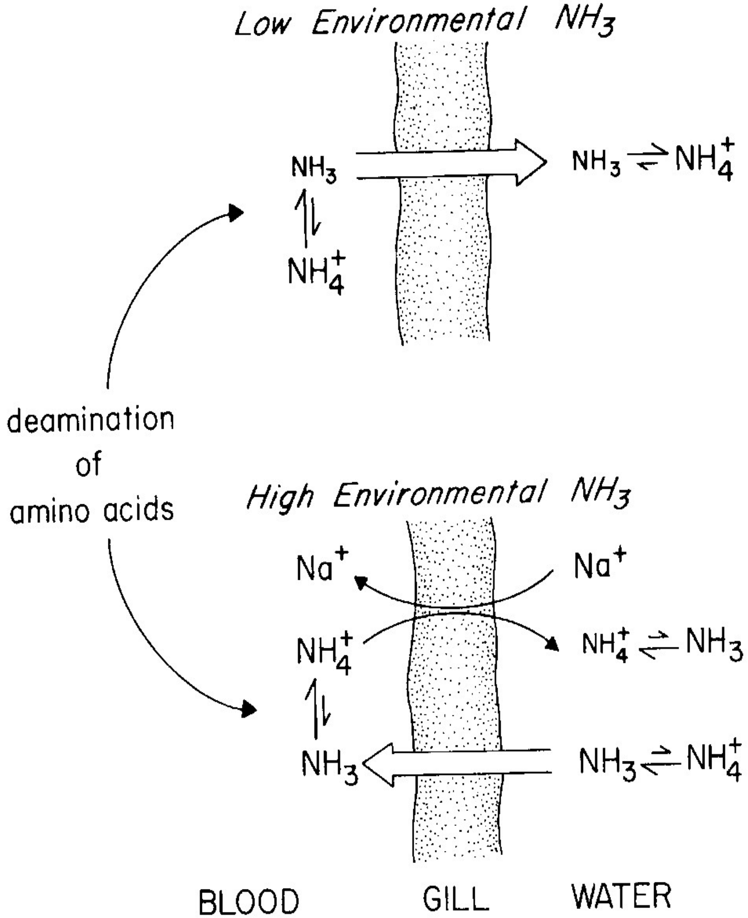


Figure 3.7. Movement of ammonia across the gill membrane of a typical ammonotelic aquatic animal. Un-ionized ammonia can freely diffuse across the gills in response to concentrations gradients. In the upper diagram, un-ionized ammonia is removed from the blood because the external concentrations are low. In the lower diagram, un-ionized cannot diffuse from the blood because external concentrations are high. Ammonium ion cannot diffuse across the gills but may be actively transported across the gill in exchange for sodium. This process becomes increasingly important as the external concentration of un-ionized ammonia increases.

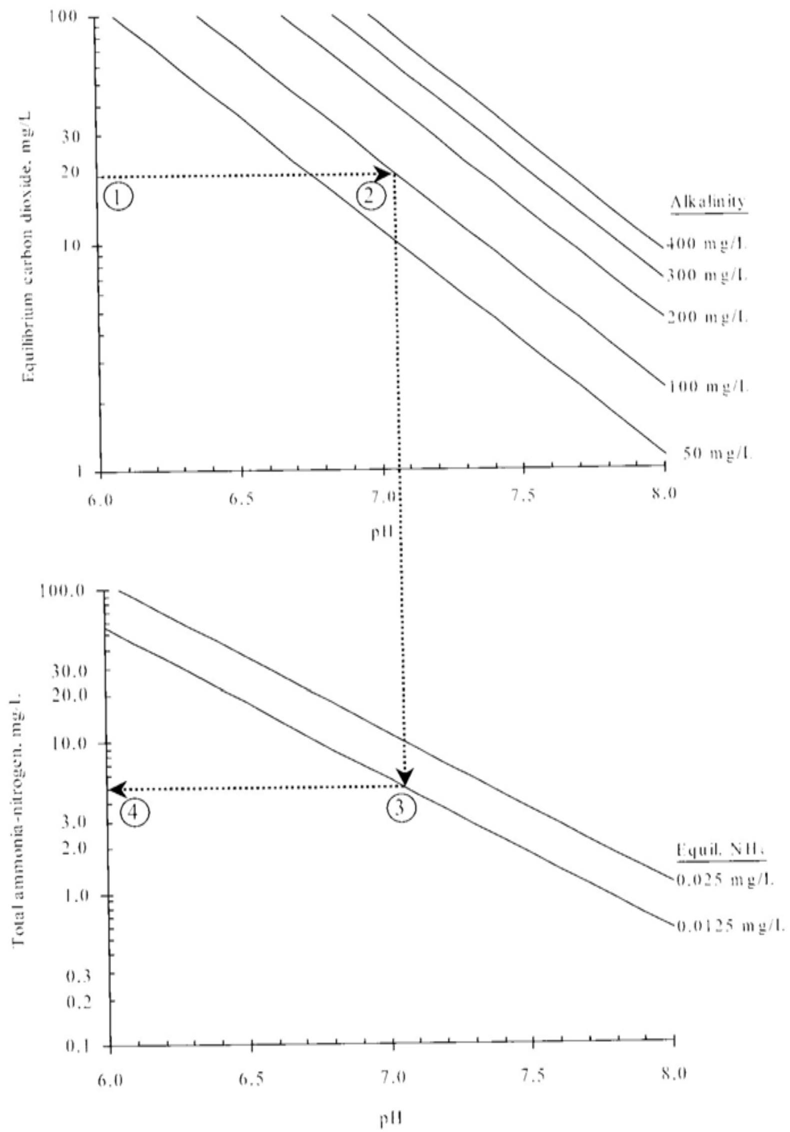
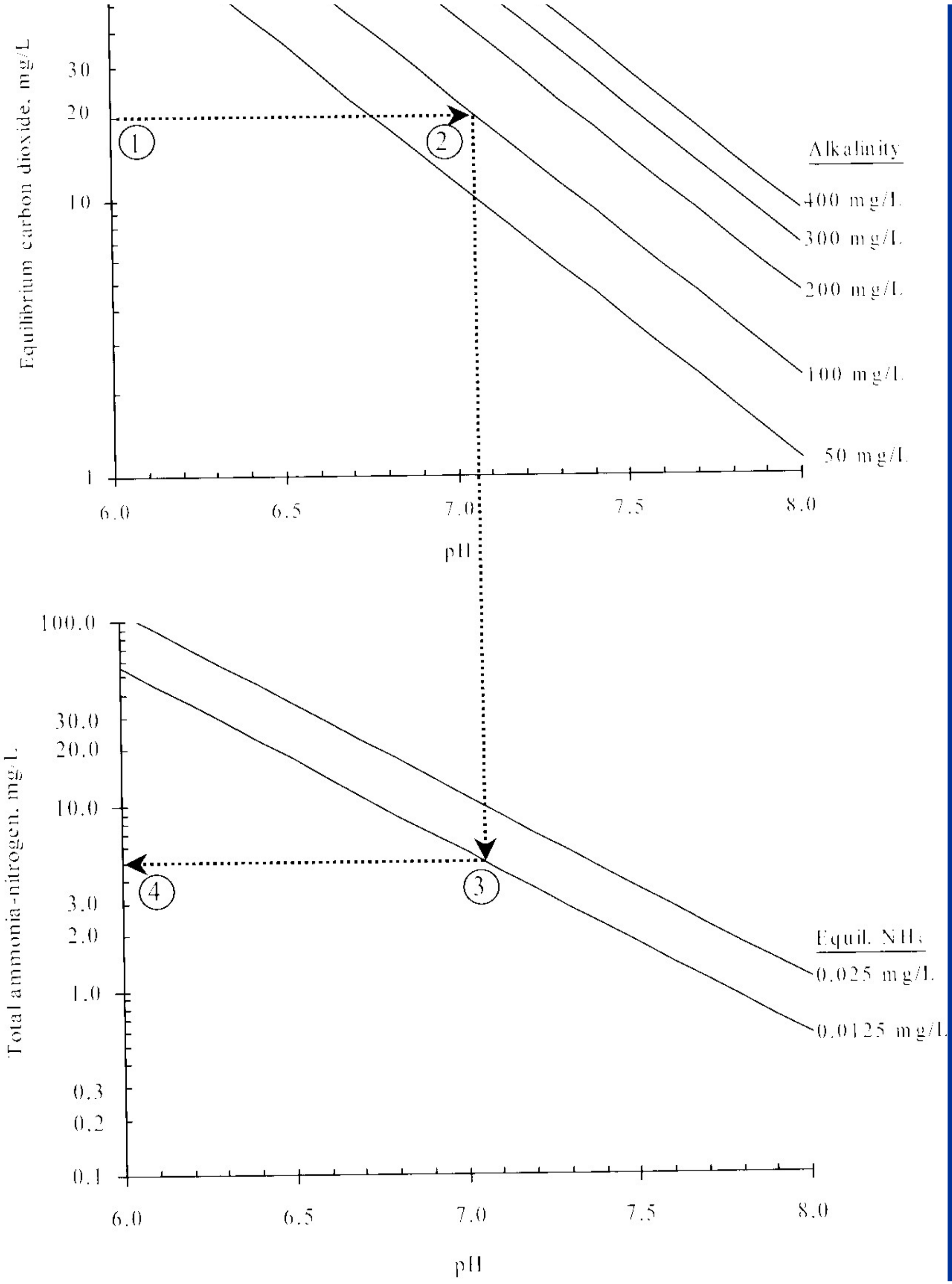


Figure 2.1 Dependence of Dissolved Carbon Dioxide Concentrations on pH and Alkalinity (top graph), and Un-ionized Ammonia Concentrations and Total Ammonia-nitrogen (bottom graph), According to Acid-base Equilibrium at 15°C. Dashed lines indicate how setting a maximum limit of 20 mg/L on the concentrations of dissolved carbon dioxide (1) and of 0.0125 mg/L on un-ionized ammonia (3), at an alkalinity of 100 mg/L (2), will set the minimum operating pH (about 7.06) and the maximum allowable TAN (4) (about 5.0 mg/L), from Summerfelt et al. 2000A.


Equilibrium carbon dioxide, mg/L
30
20
10
1
6.0
6.5
7.0
7.5
8.0
pH
Alkalinity
400 mg/L
300 mg/L
200 mg/L
100 mg/L
50 mg/L
1
2
3
4
Total ammonia-nitrogen, mg/L
100.0
30.0
20.0
10.0
3.0
2.0
1.0
0.3
0.2
0.1
Equil. NH_3
0.025 mg/L
0.0125 mg/L

Nitrite

Nitrite transfer through the gills as ion with the same mechanism as chloride (due to similar charge and ion radius).

After getting in the blood it oxidizes the iron in the hemoglobin from Fe^{2+} to Fe^{3+} the resulting product is called **Methemoglobin** .

it has brown color and noticeable when concentration is above 20%

Brown blood disease → low affinity to oxygen → respiratory stress.

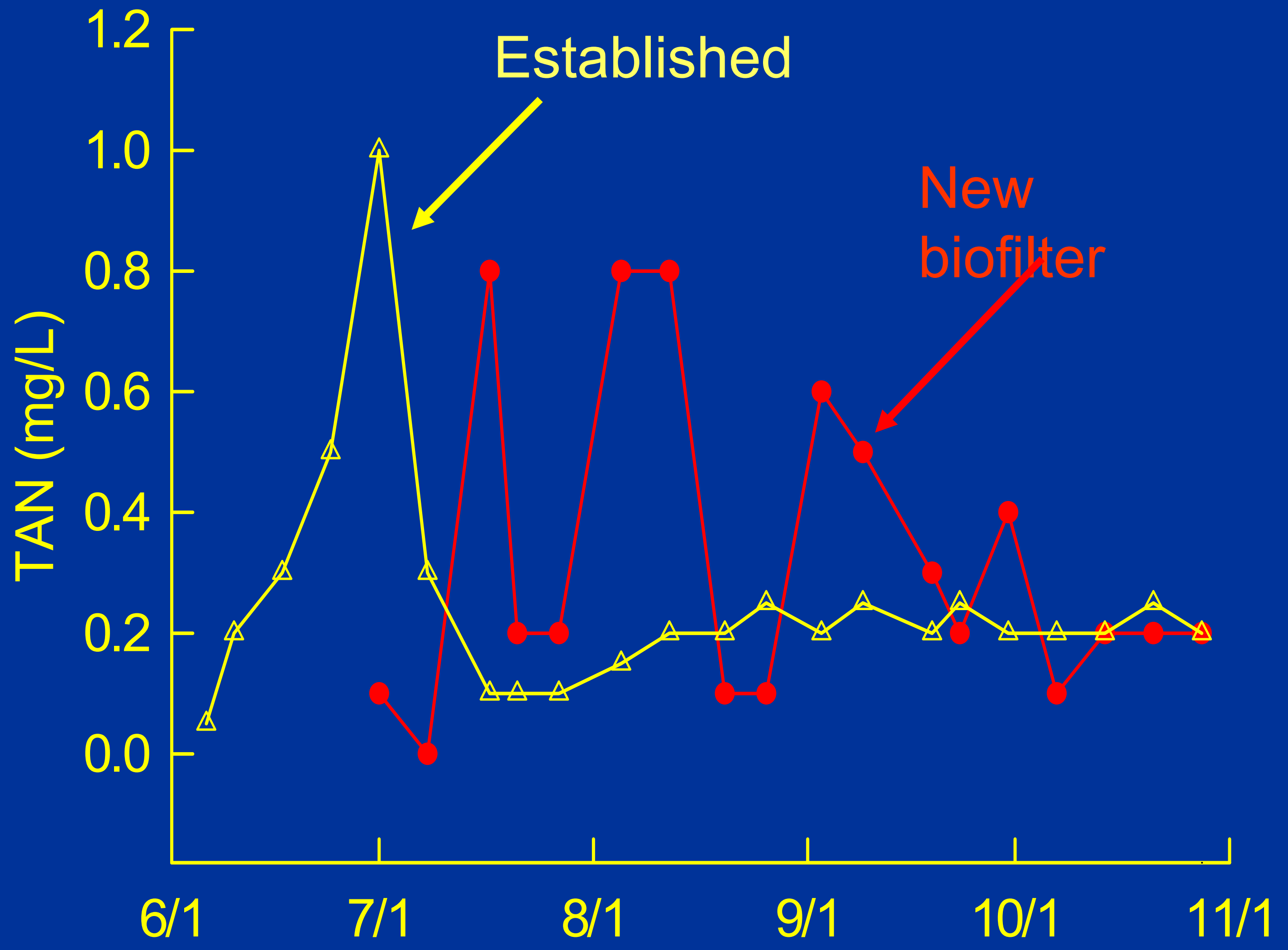
Treatment with Cl^- as it compete with the NO_2 on the sites in the gills. The treatment ratio is usually 1:10.

NO_2-N = <0.3 (sometimes 2 mg/L – N)

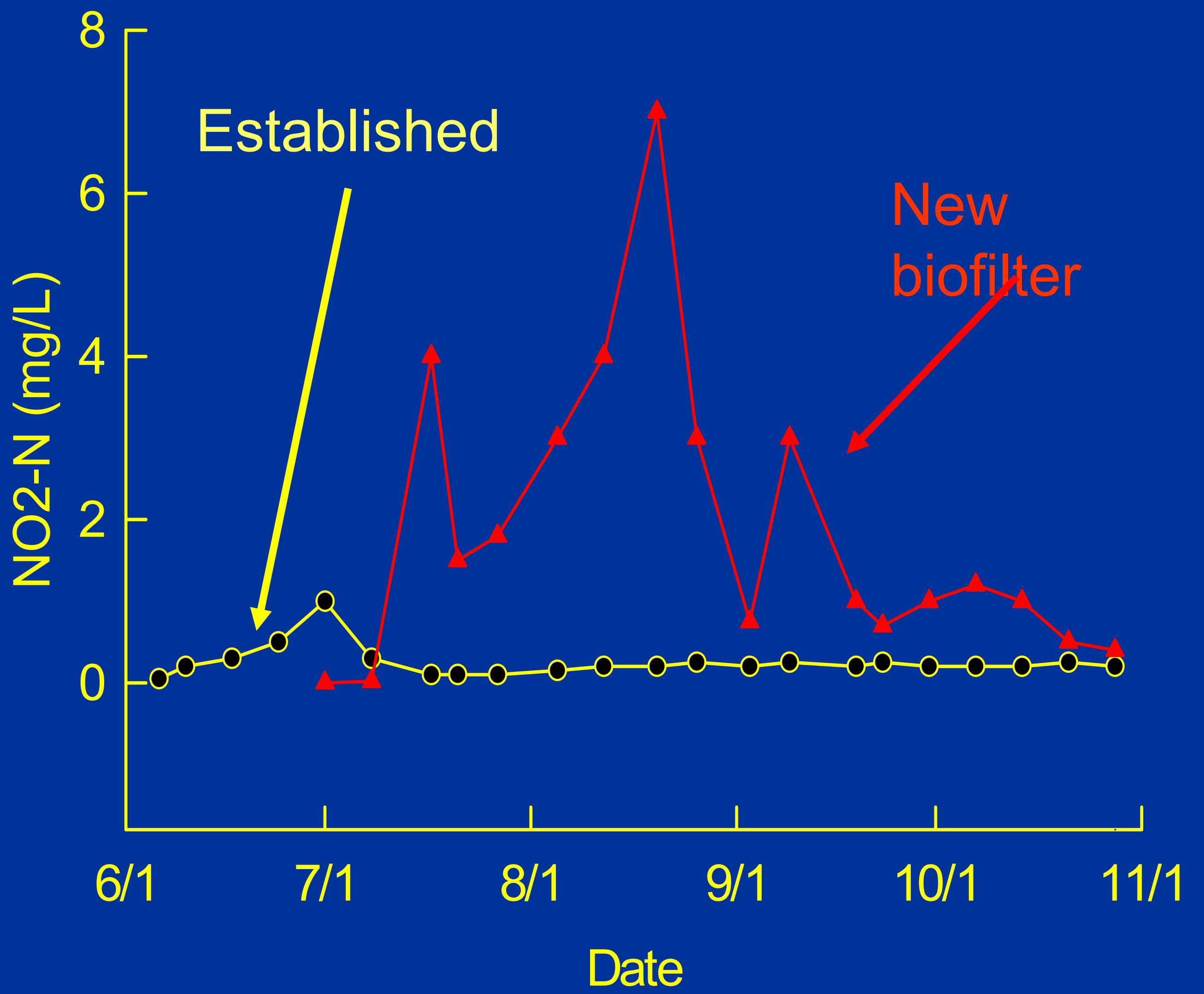
method for analysis – diazo color – spectrophotometric.

EXAMPLE FOR TOXICITY ISSUES

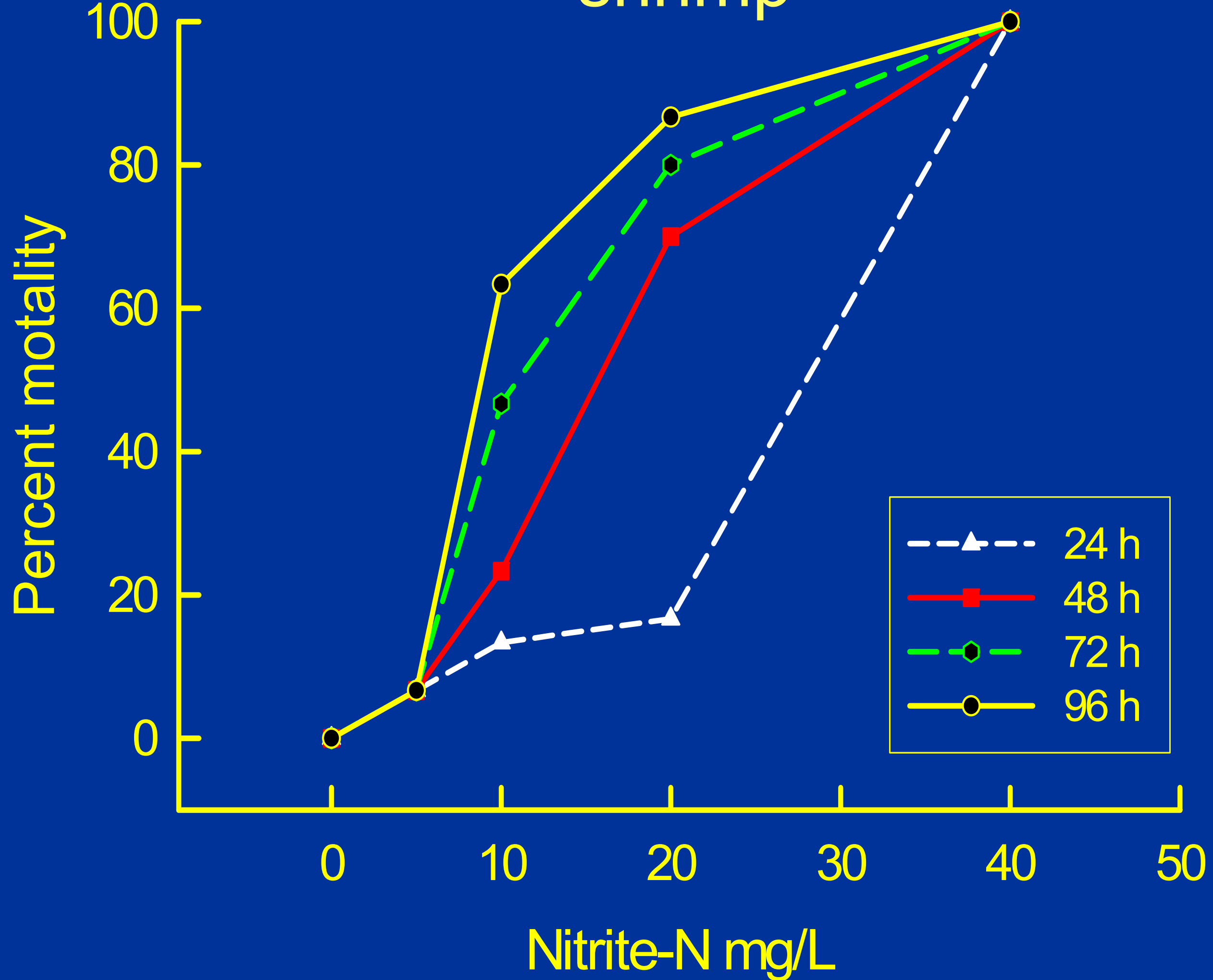
TAN in shrimp ponds with established / new - biofilters



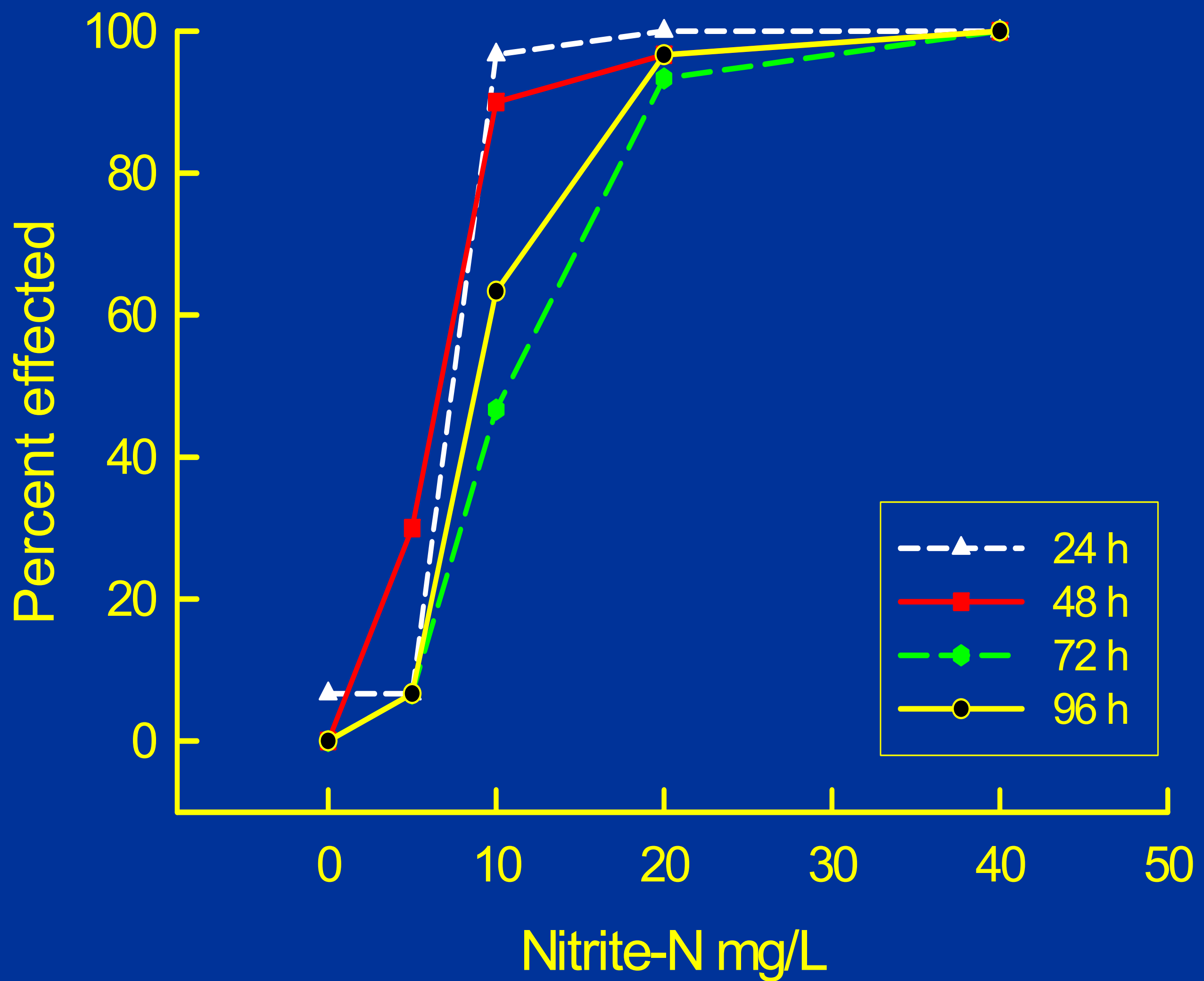
Nitrite-N in ponds with established / new - biofilters



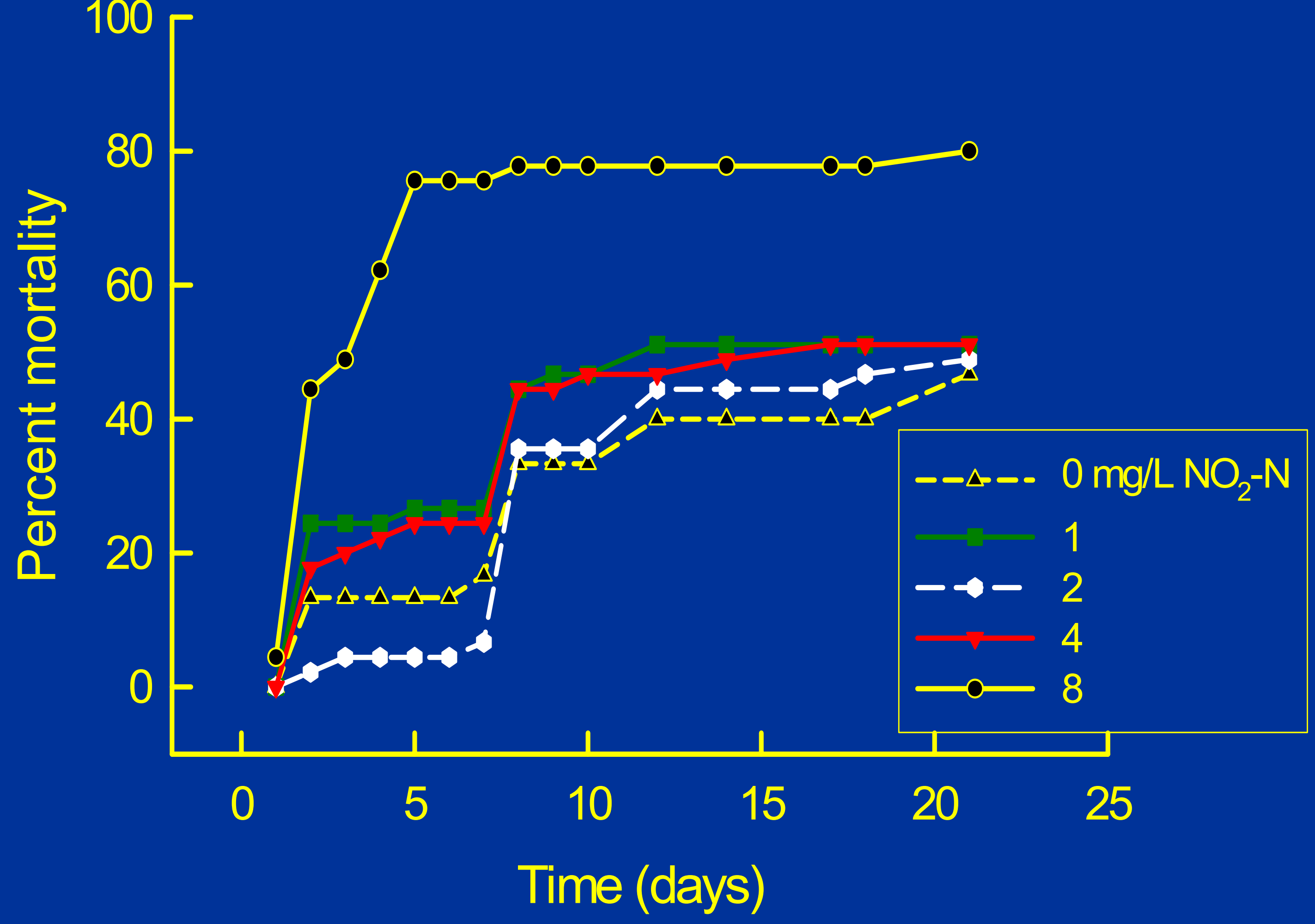
LC50 – White leg shrimp

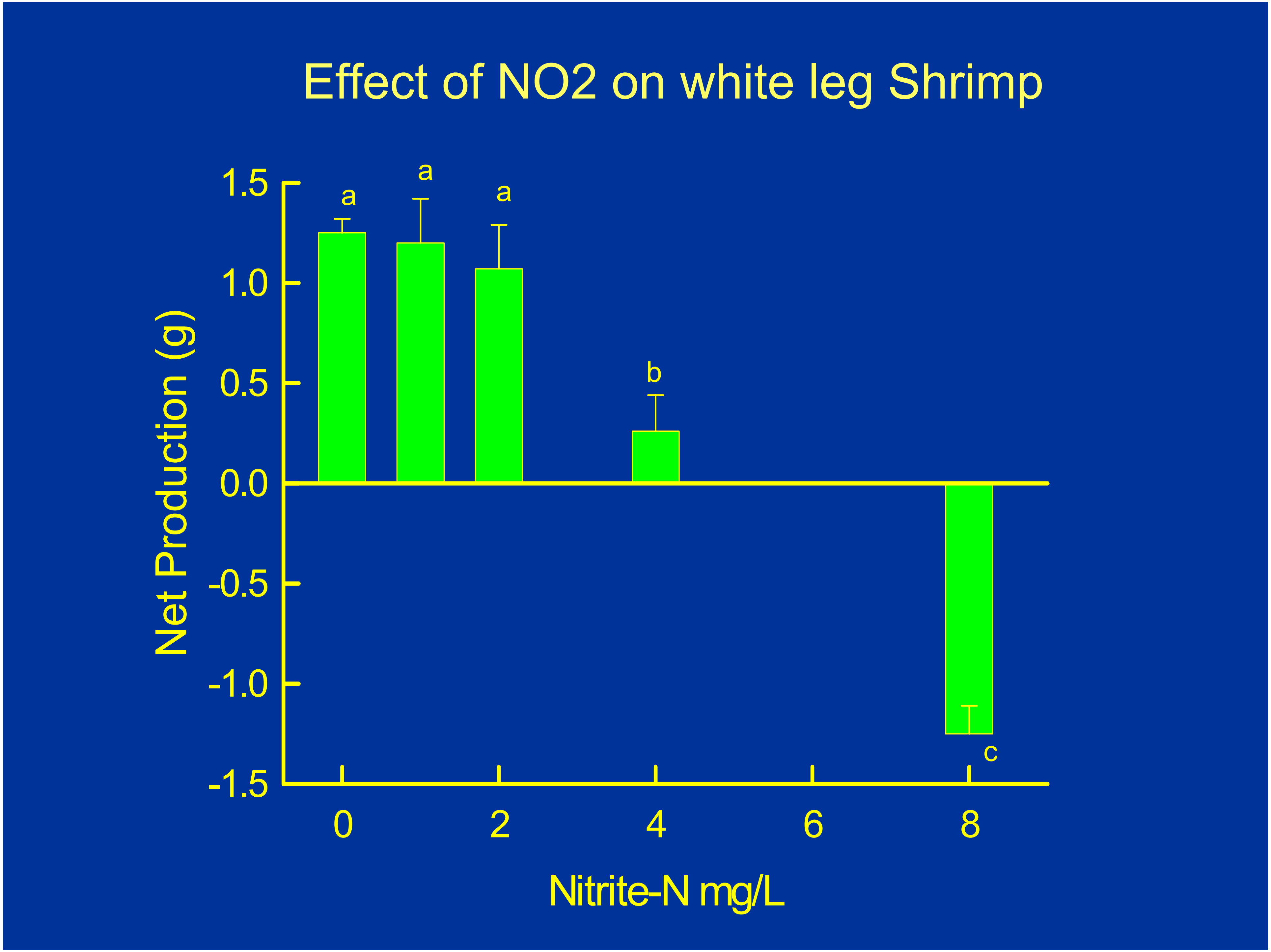


EC50 – White leg shrimp



Effect of NO2 on white leg Shrimp




Effect of NO2 on white leg Shrimp
Net Production (g)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
a
a
a
b
c
0
2
4
6
8
Nitrite-N mg/L

Nitrate

Least toxic. LC50 values for many fish exceed1000 mg/L . In recirculation system trying to keep concentration in less than 100 mg/L

Analysis – several (UV; NAS; REDUCTION; ION CHROMATOGRAPH)

Parameter	Concentration (mg/L)
Alkalinity (as $CaCO_3$)	50–300
Aluminum (Al)	<0.01
Ammonia (NH_3-N unionized)	<0.0125 (Salmonids)
Ammonia (TAN) Cool-water fish	<1.0
Ammonia (TAN) Warm-water fish	<3.0
Arsenic (As)	<0.05
Barium (Ba)	<5
Cadmium (Cd)	
Alkalinity < 100 mg/L	<0.0005
Alkalinity > 100 mg/L	<0.005
Calcium (Ca)	4–160
Carbon Dioxide (CO_2)	
Tolerant Species (tilapia)	<60
Sensitive Species (salmonids)	<20

Chlorine (Cl)	<0.003
Copper (Cu)	
Alkalinity < 100 mg/L	0.006
Alkalinity > 100 mg/L	0.03
Hardness, Total (as $CaCO_3$)	>100
Hydrogen cyanide (HCN)	<0.005
Hydrogen sulfide (H_2S)	<0.002
Iron (Fe)	<0.15
Lead (Pb)	<0.02
Magnesium (Mg)	<15
Manganese (Mn)	<0.01
Mercury (Hg)	<0.02

Nitrogen (N_2)	<110% total gas pressure
	<103 % as nitrogen gas
Nitrite (NO_2)	<1, 0.1 in soft water
Nitrate (NO_3)	0–400 or higher
Nickel (Ni)	<0.1
Oxygen Dissolved (DO)	>5
(see Chapter 4 for more detail)	> 90 mm Hg partial pressure)
Ozone (O_3)	<0.005
PCB's	<0.002
pH	6.5–8.5
Phosphorous (P)	0.01–3.0

Potassium (K)	<5
Salinity	depends on salt or fresh species
Selenium (Se)	<0.01
Silver (Ag)	<0.003
Sodium (Na)	<75
Sulfate (SO_4)	<50
TGP (total gas pressure)	<105% (species dependent)
Sulfur (S)	<1
Total dissolved solids (TDS)	<400 (site specific and species specific; use as rough guideline)
Total suspended solids (TSS)	<80
Uranium (U)	<0.1
Vanadium (V)	<0.1
Zinc (Zn)	<0.005

Source: Meade, 1991; Piper et al. 1982; Lawson, 1995