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Alkalinity and Hardness Variation in Ground Waters of East Godavari District due to Aquaculture

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Abstract
In aquaculture systems alkalinity leads to stable pH, lower toxicity of ammonia and carbon dioxide and healthy biofilter operations. High concentrations of hardness block the toxic effects of copper and zinc. For waters where alkalinity is high and calcium is low, photosynthesis may increase the pH to levels that are toxic to fish. Excess alkalinity in an ecosystem can reduce that ecosystem's ability to sustain life. Ground water contamination with salt water due to aquaculture and thereby changes in alkalinity, hardness and other parameters are discussed.

Keywords: Bio-filtration, salinity, toxicity, phytoplankton, autotrophic, photosynthesis, respiration, nitrification

1. Introduction

Water alkalinity and hardness are functions of the geology of the area and the percolation of rain and surface water along with the dissolved carbon dioxide of the atmosphere. Rain water is naturally acidic, which tends to dissolve some minerals more easily [3]. Surface and ground water sources in areas with limestone formation are especially likely to have high hardness and alkalinity due to the dissolution of bicarbonates and carbonates [6, 7]. Groundwater is considered as the most desirable source of supply for aquaculture because it has more consistent diurnal and seasonal physico-chemical parameters than surface water, and much less likely to be contaminated by pathogens and mostly saline in nature [1, 2]. In aquaculture systems, compounds that affect pH are generated continuously. The most influential of these are carbon dioxide and ammonia. When carbon dioxide is added, hydrogen ions are released, the pH drops and the water becomes more acidic. Ammonia works in the opposite way. Ammonia (NH_3) can combine with hydrogen ion (H^+) to form ammonium (NH_4^+). Ammonium is less toxic than ammonia, so, if the water is acidic, more of the ammonia will convert into ammonium, which is less dangerous to the fish and prawn. However, more hydrogen in the water inhibits carbon dioxide from converting carbonate ions. In basic water, the ammonia is more toxic but the carbon dioxide is less problematic. The ideal pH of water for aquaculture is 7.0 and 8.0 where the smallest fractions of both carbon dioxide and ammonia can co-exist [11]. Nitrogen is used by organisms in many chemical reactions and is found as a building block of amino acids in proteins. The form of nitrogen excreted by fish and prawn is most commonly ammonia, which is toxic at higher concentrations. This ammonia is breakdown by bacteria into less toxic form of nitrate in nitrogen cycle. Nitrification is a two-step process by which autotrophic bacteria oxidize un-ionized ammonia, first to nitrite and then to nitrate, which use compounds such as ammonia and nitrite for energy when they reproduce. If insufficient alkalinity is available in water within the biofilter, nitrification will be inhibited. Carbonic acid is also formed in the biofilter, requiring a supply of alkalinity for it to be neutralized [5].

There are no direct effects of alkalinity on fish and prawn. However it is an important parameter due to its indirect effects. Most importantly, alkalinity protects the organism from major changes in pH. The metabolism and respiration of aquatic animals and micro-organisms, particularly phytoplankton and bacteria can produce wastes and byproducts, which can change pH. In addition some biological processes can change alkalinity itself by producing or consuming acids or bases.

Pond CO_2 concentration and pH are affected by respiration and photosynthesis. Carbon dioxide is released during respiration and consumed during photosynthesis. Carbon dioxide may build up in water as a result of respiration by aquatic animals and bacteria. In poorly buffered waters, this can cause a drop in pH below 7.0 that can inhibit nitrification. Aeration can drive of CO_2, and in that process the pH is increased. Adequate alkalinity will ensure stable pH and provide carbon for nitrifying bacteria [5]. Sea water has a mean total alkalinity 116 mg/l. Dissolved from practically all solids and rocks but especially from limestone, dolomite and gypsum, calcium and magnesium are found in some brine. Magnesium is present in large quantities in sea water in amounts of about 1300 ppm. After sodium, it is the most commonly found cation in oceans. Magnesium mainly present as Mg^{2+} (aq), $MgOH^{+}$ (aq), $Mg(OH)_2$ (aq) and $MgSO_4$ in sea water. Water solubility of $Mg(OH)_2$ is 12 mg/l, $MgCO_3$ (600 mg/l) and $MgSO_4$ (309 g/l) at 10 ^{0}C. It causes most of the hardness.

Water with alkalinity at or above 20 mg/l, trap CO_2 and increases the concentration available for photosynthesis. If alkalinity is too low (less than 20 mg/l) the water may not contain sufficient carbon dioxide (CO_2) or dissolved carbonates for photosynthesis to occur, thus restricting phytoplankton growth. In aquaculture systems alkalinity is most often influenced by the bicarbonate ions of $NaHCO_3$, when kept above 100 mg/l alkalinity will usually be an effective buffer, depending on the level of carbon dioxide in the water. Alkalinity should not fall below 80 mg/l as it is a source of carbon for nitrifying bacteria during nitrification. Fertilizers perform better in waters with high alkalinity. Ground water usually has high alkalinity (>500 mg/l) when compared to surface waters. Excess alkalinity in an aquatic ecosystem can reduce that ecosystem's ability to sustain life. Alkalinity decreases with increasing productivity. The associated carbonates and bicarbonates comprising the major part of alkalinity may also affect the bioavailability and toxicity of several metallic environmental contaminants and pesticides to non-target and target organisms.

Hardness in addition to alkalinity is an important parameter for aqua culture and is commonly reported aspect of water quality [8]. It is a measure of the quantity of divalent ions, such as calcium and magnesium. Calcium has an important role in the biological processes of fish and prawn. Generally fresh water fish do best when hardness is maintained near 100 mg/l. Hardness is important for bone and exoskeleton formation and for osmoregulation [10]. It is necessary for blood clotting and other metabolic reactions. Fish and prawn can absorb calcium for these needs directly from water or food. Hardness has been associated with the mitigation of the toxicity of some metals to gill breathing organisms. Calcium and magnesium are important parameters of drinking water and both have direct and indirect significance on human health [9]. A certain minimum amount of these elements in drinking water is desirable since their deficiency poses at least comparable health risks as exceedance of the limit for strong toxic substances does. Although a certain minimum quantity of these elements is desirable, it definitely does not mean the more the better, while considering high levels of magnesium and calcium in drinking water [4]. Not only the absolute content of these elements but also the fact that higher water Mg and Ca levels are mostly associated with higher levels of the other dissolved solids that may not be beneficial to health.

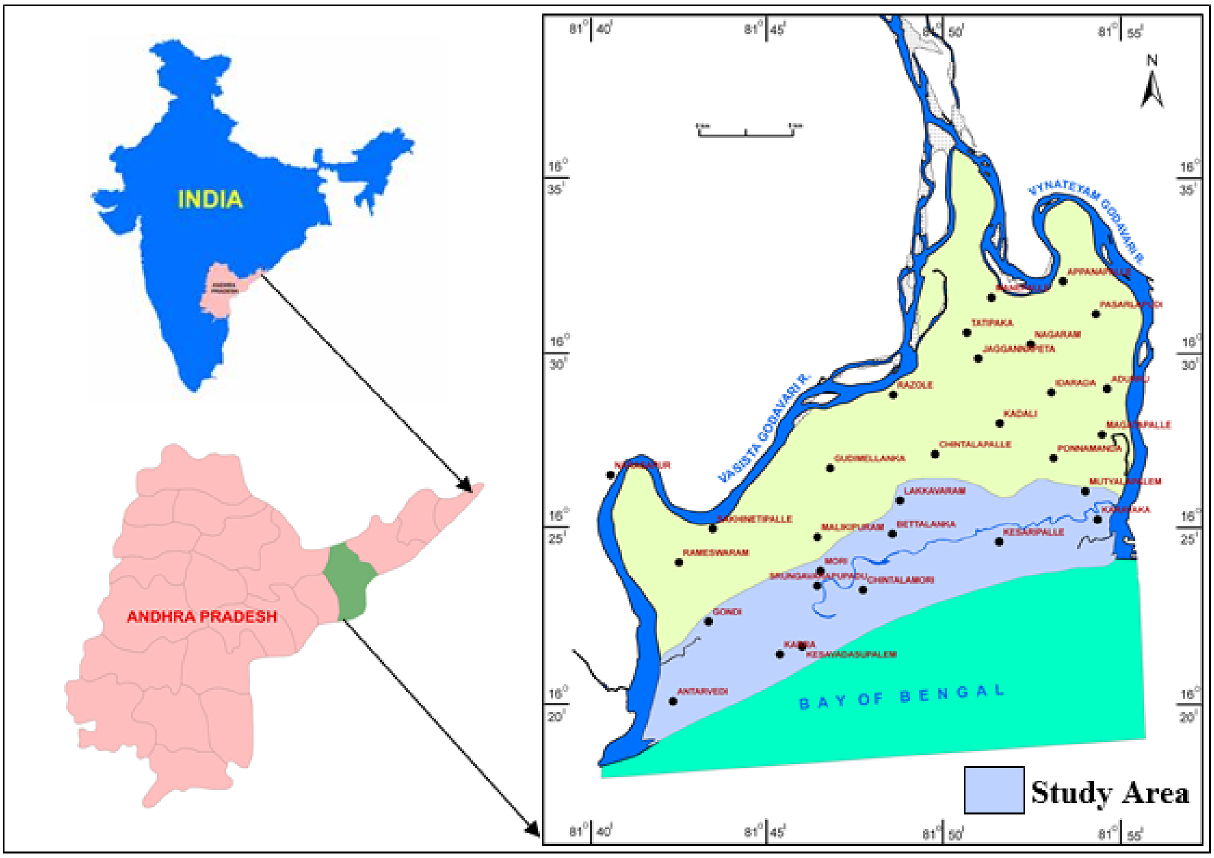

Fig 1: Location map of the study area

2. Study Area
The study area is situated on east coast of India between Vasista Godavari River and Vainateyam Godavari River of East Godavari District, Andhra Pradesh. The study area (Figure-1) admeasures to an extent of 125 sq.km, lies within the geographical coordinates of N16^0 18' to 16^{0}23' latitudes and E81^{0}42' to 81^{0}57' longitudes and falls within the survey of India toposheet numbers 65H/11 and 65H/15. It is extended 5 km from the coast line of the central delta covering Antarvedi, Kara, Chintalamori, Mori, Kesanapalli, Karavaka, Mutyalapalem, Lakkavaram, Battelanka, Visweswarapuram, Adavipalem, Gudapalli, Katrenipadu, Katrenipadu Kodapa, Toorpupalem, Padamatipalem, Sankaraguptam, Kesavadasupalem and Gondi villages of Razole, Sakhinetipalli, Malikipuram and Mamidikuduru, Mandals of East Godavari District, Andhra Pradesh.

3. Scope and Objectives
The principal objective of the present study is to understand the hydrochemistry of ground waters and the impact of aquaculture on ground water quality with special emphasis of alkalinity and hardness; which are the important parameters for pisci and prawn cultures as well as for drinking water sources.

4. Methodology
It includes field work and laboratory analysis. The field work consists of collection of groundwater samples from dug wells, bore wells and hand pumps with the help of Global Positioning System (GPS) a Garmin eTrax vista. The ground water samples were collected in two seasons (pre-monsoon and monsoon) and have been analyzed in the laboratory for various parameters like pH, alkalinity, hardness, chlorides, TDS, salinity, ammonia, nitrites, nitrates, sulphates, sodium and potassium.

5. Results and Discussion
Alkalinity and hardness values are analyzed for all the water samples. It was observed that in some villages alkalinity and hardness values are closely related with one another but not identical (with alkalinity values slightly higher from 1.0 to 2.0 times than hardness) as shown in Table-1. In these samples it may be assumed that it is due to the dissolved calcium carbonate. (In water when the concentration of hardness and alkalinity are the same, but not identical both are probably from dissolved calcium carbonate). However in most of the villages of study area alkalinity values are very high in comparison to hardness shown in Table-2. Alkalinity and hardness are related through common ions formed in aquatic systems. They are the cations (Ca and Mg) associated with the bicarbonates. Carbonate fraction of hardness is chemically equivalent to the bicarbonates of alkalinity present in water, in areas where the water interacts with limestone. Any hardness greater than the alkalinity represents non-carbonate hardness. In very few villages hardness values are higher than alkalinity values in ground water samples of study area as shown inTable-3.

Table 1: Alkalinity and Hardness values nearer to each other (1.0 to 2.0 times)

S. No	Village	Alkalinity (ppm)	Hardness(ppm)
1	Gondi	1212	836
2	Visweswarapuram	452	272
3	Battelanka	412	204
4	Adavipalem	252	172
5	Mori	228	136
6	Lakkavaram	208	120

Table 2: Alkalinity Very Much Higher than Hardness (>2.0 times)

S. No	Village	Alkalinity (ppm)	Hardness(ppm)
1	Mutyalapalem	1060	132
2	Gubbalapalem	716	116
3	Antarvedi	696	296
4	Gudapalli	312	100
5	Toorpupalem	304	68

Table 3: Hardness Higher than Alkalinity

S. No	Village	Alkalinity (ppm)	Hardness (ppm)
1	Kesavadasupalem	360	396
2	Padamatipalem	220	320
3	Katrenipadu	100	264
4	Karavaka	70	82

However, where sodium bicarbonate is responsible for high alkalinity, it is possible to have low hardness and low calcium. High alkalinity in water comes from a high concentration of carbon based molecules suspended in the water. A low $CaCO_3$ hardness value is a reliable indication that the calcium concentration is low. However high hardness does not necessarily reflect a high calcium concentration. A high hardness could result from high magnesium concentration with little or no calcium present as shown in Table-5 and Figure-3a & 3b.

The presence of free calcium (ionic) at relatively high concentration in culture water helps to reduce the loss of other salts (e.g. sodium and potassium) from fish body fluids (i.e. blood). Calcium reduces toxicity of metals, ammonia and the hydrogen ion. Calcium hardness protects fish from copper toxicity but magnesium hardness provides no protection [12].So it is important to measure calcium hardness of water before using copper sulphate in water with low alkalinity. In addition, due to higher ion (Ca and Mg) concentration in hard water, suspended soil particles settle faster in hard water than soft water [13].

High alkalinity due to excess minerals suspended in water causes turbidity, a fogging up of clear water due to suspended particles. Alkalinity is increased in the study area from summer to rainy season due to presence of more carbonates and bicarbonates in the water as shown in Table-4 and Figure-2.

Table 4: Seasonal variations of alkalinity

S. No	Village	Alkalinity (ppm)	
		Pre-Monsoon	Monsoon
1	Gondi	1265	1212
2	Mori	1040	696
3	Antarvedikara	838	816
4	Antarvedi	720	696
5	Visweswarapuram	613	457
6	Toorpupalem	444	304
7	Lakkavaram	393	208
8	Gudapalli	365	196
9	Chintala Mori	343	312
10	Adavipalem	258	252
11	Kesanapalli	140	136
12	Katrenipadu	140	200
13	Padamatipalem	185	220
14	Karavaka	241	300
15	Kesavadasupalem	337	360
16	Battelanka	180	412
17	Gubbalapalem	258	716
18	Mutyalapalem	855	1060

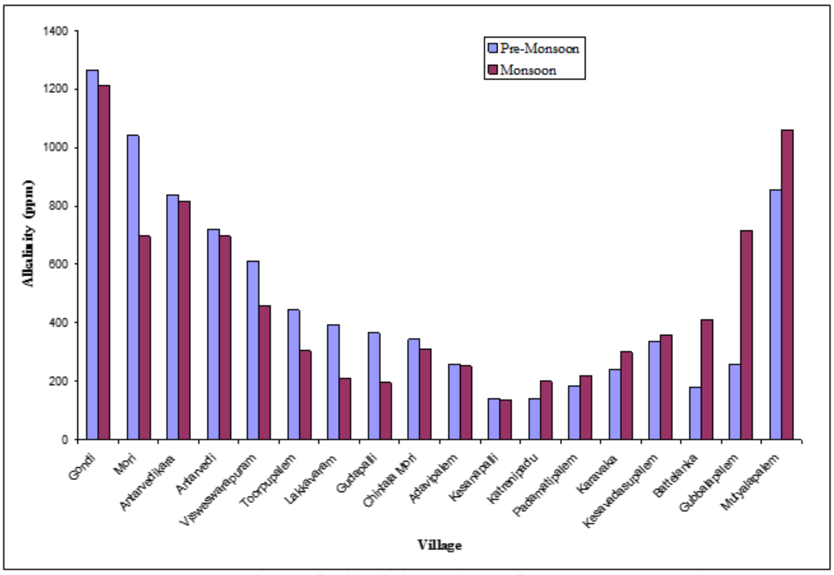

Fig 2: Comparison of Alkalinity values of pre-Monsoon and Monsoon of ground water samples in the study area

Table 5: Seasonal Variations of Calcium and Magnesium

S. No	Village	Pre-Monsoon		Monsoon Season	
		Ca^{++}(ppm)	Mg^{++}(ppm)	Ca^{++}(ppm)	Mg^{++}(ppm)
1	Toorpupalem	25.6	17.2	2.4	12.4
2	Antarvedi Kara	17.6	65.2	3.2	93.6
3	Karavaka	17.6	21.2	4.8	30.4
4	Antarvedi	16.0	18.0	6.4	56.0
5	Kesavadasupalem	25.6	75.2	6.4	76.6
6	Sankaraguptam	24.0	14.0	6.4	25.6
7	Gondi	25.0	138.4	6.4	163.2
8	Chintala Mori	16.0	18.0	8.0	30.4
9	Padamatipalem	17.6	23.2	9.6	25.6
10	Kesanapalli	16.0	2.0	11.2	7.2
11	Mutyalapalem	11.2	4.4	12.8	20.0
12	Battelanka	14.4	12.8	13.6	34.0
13	Gudapalli	14.4	30.8	14.4	12.8
14	Katrenipadu	14.4	2.6	14.4	12.0
15	Adavipalem	14.4	6.8	16.0	26.4
16	Lakkavaram	12.8	13.6	16.8	15.6
17	Gubbalapalem	17.6	9.2	19.2	13.6
18	Visweswarapuram	12.8	15.2	20.8	44.0

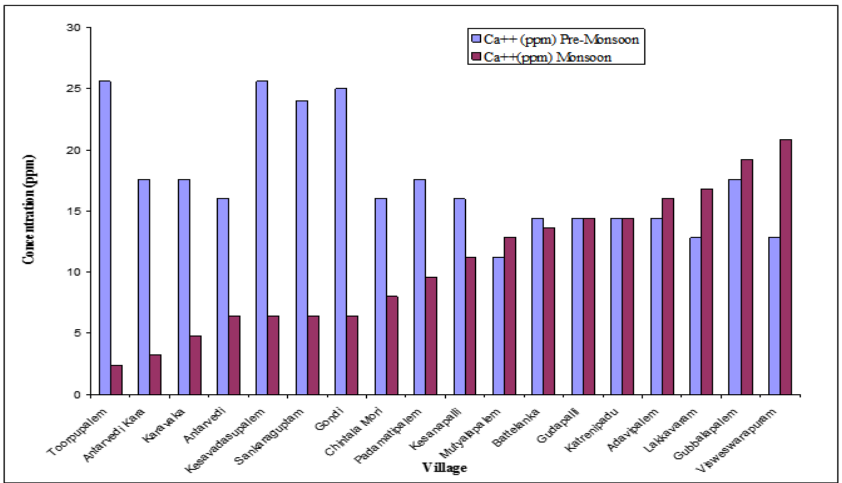

Fig 3a: Comparison of Calcium values of pre-Monsoon and Monsoon of ground water samples in the study area

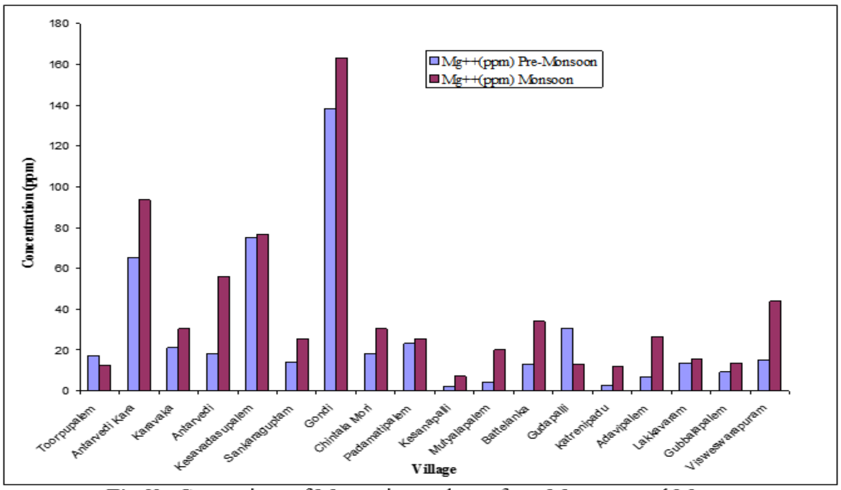

Fig 3b: Comparison of Magnesium values of pre-Monsoon and Monsoon of ground water samples in the study area

Increased magnesium values are an indication of sea water intrusion into ground water. Total hardness is increased due to increase in magnesium from first season to next season. Sulphates are also increased. Sulphate ions were appeared in more sampling points and thereby a slight increase in average value. But chlorides, nitrates, TDS, salinity, potassium values are decreased. Alkalinity is increased which is an indication of increase in concentration of carbonates and bicarbonates of sodium and magnesium. (It may be through sea water). When compared to first Season Sea water spread to more areas. Alkalinity average value is increased from 435.31 ppm of summer season to 450.22 ppm in rainy season. Alkalinity crossed more than 500 ppm in 5 villages out of 18 villages and even crossed 1000 ppm in two villages. The average value of hardness increased from 177.11 ppm to 218.19 ppm. At least in three villages hardness crossed 300 ppm in the study area. Calcium average value decreased from 16.6 ppm in the first season to 10.71 ppm in the next season. Calcium values are decreased even less than 10 ppm in nine villages out of 18 villages i.e. 50% of the villages. Whereas Magnesium average value increased from 27.10 ppm to 38.41 ppm in the same period. Its value even crossed 50 ppm mark in 4 villages. Sulpahate average value increased from135.83 ppm to 138.8 ppm in the same period. Sodium average value is also increased from 185.61 ppm to 232.94 ppm in second season. Sulphates are found only in 6 villages (1/3) in the first period whereas it is found in 12 villages (2/3) in the next season. TDS mean values are decreased 2160 ppm of first season to 1561 ppm of next season thereby salinity from 1.56 ppt to 1.28ppt. Similarly chloride values decreased from 631ppm to 378ppm and nitrate values decreased from 33.47ppm to 16.91ppm .This clearly indicates that there is an increase in magnesium salts particularly magnesium sulpahtes and may be carbonates and bicarbonates of sodium (and magnesium). The decrease in chlorides, nitrates, TDS and salinity is due to dilution of ground water by rain water percolation there by decreased concentrations of calcium and potassium salts (particularly chlorides and nitrates). Increase in hardness is due to increased concentration of magnesium salts may be magnesium sulphate. increase in alkalinity is due to carbonates and bicarbonates of sodium and magnesium. In general it was observed that salt water intrusion (magnesium and sodium salts) and rain water percolation thereby dilution of (Calcium and potassium) salts played a major role thereby increase in hardness, alkalinity, sodium, sulphates and decrease in chlorides, nitrates, TDS, salinity and potassium.

6. Conclusion

Maintenance of proper alkalinity and hardness are important for healthy growth of fish and prawn. It was observed that there is an increase in the concentration of sodium and magnesium salts and decrease is calcium and potassium salts from summer to rainy season in the study area. Similarly optimum values of calcium and magnesium presence in drinking water is also important for human health. Large amounts of magnesium in underground water of study area may be due to sea water intrusion due to aquaculture which may have negative impact on environment. Magnesium in drinking water helps to prevent death from myocardial infarction. Magnesium deficiency effects Neurocardiovascular apparatus and reduces the activation of the neuroendocrine regulatory metabolism [14]. Drinking water containing very high values of magnesium can cause vomiting, diarrhea, thirst, tiredness, slurred speech, confusion, muscular weakness and breathlessness.

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