International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2018; 6(1): 2063-2066

Received: 08-11-2017
Accepted: 09-12-2017

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Chemistry of aquaculture pond sediment

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Abstract
Soil and water interaction is a key factor in aquaculture practice. There is a direct impact of the physical chemical, biological process that takes place during the culture period on the pond sediment. The soil water interaction, microbial activity, presence of oxidized layer, sediment oxygen demand, organic content and nutrient availability are some of the crucial phenomenon that decides the fate of pond sediment. Pond sediment management practices have to be adopted accurately for improving the pond productivity and maintaining the pond bottom sediment.

Keywords: Mineralization, equilibrium, oxidized layer, agricultural lime, sediment oxygen demand, diffuse

Introduction
The success of aquaculture can be assured by selecting a site with suitable soil and a high quality water supply. Before the commencement of culture it is essential to understand the pond soil and water characteristics and their optimum requirements to increase the productivity of the ponds. The study of soil chemistry for agriculture purpose has been done to a greater extend. Very little knowledge on the pond sediment chemistry for aquaculture ponds is studied. Soil is the key factor in aquaculture, but much less attention is given to soil parameters as compared to water quality. This is very much required as in aquaculture there is a greater interaction and exchange of substances between the soil and water that strongly affects the water quality and thus influencing the productivity of the system. (Boyd, C.E., 1995) [3].

Soil-water interaction
During the initial stage of construction of pond the original, terrestrial soil profile is greatly altered. The newly finished pond bottom has low concentrations of organic matter and nutrients. Once the pond is filled with water and aquaculture operations initiated, formation of sediment or pond bottom soil profile begins. Dead plankton, feces of culture species, organic fertilizers and uneaten feed will settle to the pond bottom in the form of nutrients and organic residues. (Boyd, C.E and Julio, F., 2014) [7] These tend to accumulate at the bottom and are thus, to some extent, removed from the water phase. (Morshed, A.T., *et al*., 2017) [9] There would be continuous deposition, resuspension, and redeposition of these contents in a pond resulting in grading up of particles (Munsiri, P., *et al*., 1995) [10].

In course of time equilibrium exists between the concentration of a substance in the soil and its concentration in the water. If the concentration in the water increases, the soil will adsorb the substance until equilibrium is reestablished. Conversely, if the concentration in water decreases, the soil will desorb the substance until the aqueous concentration is again at equilibrium (Avnimelech. Y and Gad Ritvo, 2003) [1]. The fine clay and organic matter particles settle in the deeper water and the coarser particles settle in shallower water. This results in gradual depositon and filling up of deeper areas that will finally end up in decreasing the pond volume. Sediment thickness in deep areas of aquaculture ponds usually increases at 0.5 to 1 cm yr-1. (Munsiri, P., *et al*., 1995) [10]. However, an excessive accumulation beyond what could be defined as the carrying capacity of the sediments may result in the deterioration of the pond system (Avnimelech. Y and Gad Ritvo, 2003) [1].

Microbial activity in pond bottom soils
Sediments are enriched with nutrients and organic matter by sedimentation of organic materials from the feed, feces and fertilizer to the pond bottom.

The concentrations of nutrients in the pond bottom soil are typically several fold high in order than those found in the water (Table 1). The amounts of nutrients in a 1-cm layer of the pond bottom are normally about 10 or more times higher than the equivalent amounts in a 1-m deep water column. This makes the pond bottom a favorable site for microbial activity. Easily decomposable organic matter, such as simple carbohydrates, protein, and other cellular constituents, is quickly degraded. More resistant material, such as complex carbohydrates and other cell wall components, accumulates as it is degraded slowly. Microbes consume large amounts of oxygen and sediments become depleted with oxygen causing an anoxic condition below the surface. The density of aerobic and anaerobic bacteria in the pond bottom soil is two to four orders of magnitude higher than the density of these groups in the water column (Ram *et al*., 1981, 1982) [11].

Table 1: Approximate concentrations of chemical components in pond water and bottom soils

Component		Unit	Concentration range
		Water Pond	bottom soil
Dry matter	%	10^{-3}–10^{-1}	20– 80
Organic matter	mg/kg	10–100	10,000–200,000
Total N	mg/kg	1 –10	1000–20,000
Total ammonium N	ppm	0.1–10	1– 1000
Total P	ppm	0.01– 1	1000–20,000

Adapted from Avnimelech (unpublished) and Boyd (1990, 1995) [3].

Sediment oxygen demand in aquaculture ponds

Dissolved oxygen concentration in the sediment is an important critical factor affecting processes and conditions at the sediment–water interface. It cannot enter rapidly in bottom soil because it must diffuse through the tiny, water-filled pore spaces among soil particles leading to sediment oxygen demand. Sediment oxygen demand is an indicator of the intensity of the mineralization process and benthic community metabolism. The diffusion of oxygen from the sediment water interface to the deeper sediment layers is a slow proces. This results in anoxic condition below the upper few millimeters of the sediment surface (Revsbech *et al*., 1980) [12]. The oxidized (aerobic) layer of surface sediment will have a lighter color than the deeper, reduced (anaerobic) sediment. The anaerobic sediment usually will be gray or black, and this color results from the presence of ferrous iron (Boyd, C.E., 1995.) [3].

Significance of oxidized Layer

The oxidized layer at the sediment surface is highly beneficial and should be maintained throughout the aquaculture crop. Metabolic products of aerobic decomposition are carbon dioxide, water, ammonia, and other nutrients. In anaerobic sediment, some microorganisms decompose organic matter by fermentation reactions that produce alcohols, ketones, aldehydes, and other organic compounds as metabolites. Other anaerobic microorganisms are able to use oxygen from nitrate, nitrite, iron and manganese oxides, sulfate, and carbon dioxide to decompose organic matter, but they release nitrogen gas, ammonia, ferrous iron, manganous manganese, hydrogen sulfide, and methane as metabolites (Blackburn, 1987) [2]. Some of these metabolites, and especially hydrogen sulfide, nitrite, and certain organic compounds, can enter the water and be potentially toxic to fish or shrimp. The oxidized layer at the sediment surface prevents diffusion of most toxic metabolites into pond water because they are oxidized to non-toxic forms by chemical and biological activity while passing through the aerobic surface layer. Nitrite will be oxidized to nitrate, ferrous iron converted to ferric iron, and hydrogen sulfide will be transformed to sulfate. Thus, it is extremely important to maintain the oxidized layer at the sediment surface in aquaculture ponds. Methane and nitrogen gas pass through the layer and diffuse from the pond water to the atmosphere. These two gases do not cause toxicity to aquatic organisms under normal circumstances. Loss of the oxidized layer can result when soils accumulate large amounts of organic matter and dissolved oxygen is used up within the flocculent layer before it can penetrate the soil surface. (Boyd, C.E., 1995) [3] Oxidized layers are maintained in the pond sediments due to various process such as aerobic respiration, fermentation, nitrate reduction, reduction of iron and manganese.

Nutrient interaction in pond sediment

Nitrogen and phosphorus form two important nutrients as they can limit phytoplankton growth and are thus called limiting nutrients. Nitrogen is present in the form of fertilizers as urea, ammonium or ammonium phosphate, manures, and feeds. Ammonium may be oxidized to nitrate by nitrifying bacteria, and nitrate may be used by phytoplankton or denitrified by anaerobic microorganisms in the sediment. Nitrogen gas formed by denitrification diffuses from sediment to pond water to the atmosphere. Ammonium is in equilibrium with ammonia, and ammonia also can diffuse from pond waters to the atmosphere. A small amount of ammonium may be adsorbed on cation exchange sites in pond bottom soils. Organic nitrogen in plankton and in aquatic animal feces may settle to the bottom to become soil organic nitrogen (Boyd, C.E. *et al*., 1999) [6].

Phosphorus usually is present in fertilizer as calcium or ammonium phosphate. Phytoplankton can rapidly remove phosphate from water, and phosphorus in phytoplankton may enter the food web culminating in fish or shrimp. Pond soil strongly adsorbs phosphorus, and the capacity of pond soil to adsorb phosphorus increases as a function of increasing clay content (Boyd and Munsiri, 1996) [4]. Most of soil phosphorus is tightly bound, and only a small amount is water soluble. Phosphorus released by decomposition of organic matter in pond bottoms is rapidly adsorbed by soil and little of it enters the water. Soils that are near neutral in pH have less capacity to adsorb phosphorus and a greater tendency to release phosphorus than do acidic or alkaline soils.

Most of the feed is eaten directly by fish or shrimp, but usually only 10 to 30% of phosphorus and 20 to 40% of nitrogen applied in feed is retained by culture animals (Boyd and Tucker, 1998) [5]. The remainder of the nitrogen and phosphorus enters pond ecosystems in feces or other metabolic products-much of the nitrogenous wastes of fish and other aquatic animals is excreted as ammonia. Organic metabolites and uneaten feed are decomposed by microorganisms, and nitrogen and phosphorus are mineralized.

Nutrient budgets reveal that most phosphorus not contained in aquatic animals at harvest is adsorbed by bottom soil or contained in organic matter that settles to the bottom. Nitrogen not removed in the harvest of animals is lost primarily through denitrification, ammonia volatilization, or outflow. A significant portion of the nitrogen also may accumulate in bottom soil. (Boyd, C.E. *et al*., 1999) [6].

pH factor in pond sediment

Pond bottom soil pH can range from less than 4 to more than 9, but the best pH for pond soils is considered to be about neutral (Boyd, 1995) [3]. Maximum availability of soil phosphorus usually occurs at about pH 7. Most soil microorganisms, and especially soil bacteria, function best at pH 7 to 8. The source of acidity in most pond soils is aluminum ion. Clay and organic matter particles in soil are negatively charged and attract cations to their surfaces. Aluminum ions on cation exchange sites in soil are at equilibrium with aluminum ions in the pore water surrounding soil particles. Aluminum ion hydrolyzes to aluminum hydroxide, releasing hydrogen ions. The greater the proportion of aluminum ions on cation exchange sites in soil, the greater the acidity. Other exchangeable ions that occur on cation exchange sites, mainly calcium, magnesium, sodium, and potassium, are basic.

Soils in some coastal areas contain iron pyrite. When such soil is exposed to air, pyrite oxidizes releasing sulfuric acid. These soils are known as acid-sulfate soils. They may have pH values of 5 to 7 when wet, but when dried, pH may fall to 2 or 3. Acid-sulfate soils should not be used for aquaculture ponds if other alternatives are available. (Fleming and Alexander., 1961) [8]. Thus good management practices have to be adopted for maintaining the shelf life of pond bottom sediment and thereby improving the productivity of the system.

Good practices for use in maintaining acceptable pond bottom soil quality.

Problem	Preventative Measures
Low soil pH	• Neutralize acidity of new pond bottom soil before initiating aquaculture. • In old ponds that have never been limed, apply agricultural limestone according to the soil pH or total alkalinity of water. • Use urea and ammonium fertilizers conservatively because they are acid forming. • Monitor total alkalinity of pond waters and soil pH to assure that total alkalinity is above 40 mg/ l in fish ponds (75 mg/l in marine shrimp ponds) and soil pH is above 7.
High soil organic matter	• Select sites without organic soil. • Where soils are organic, apply agricultural limestone and urea (200 to 400 kg ha-1) to encourage degradation of organic matter during fallow periods. Repeat after each crop. • Use moderate stocking rates to avoid high inputs of nutrients and organic matter in fertilizers, manures, and feeds. • Dry ponds between crops, apply agricultural limestone according to soil pH (see text), and till heavy-textured soils to encourage oxidation of organic matter by bacteria. • Monitor soil organic matter concentrations annually (about 6% organic matter suggests excessive organic matter.
Loss of oxidized layer	• Practice preventive measures for avoiding accumulation of organic matter in soil. • Where a surface layer high in organic matter has developed in bottom soils, use a mould-board plow (turning plow) to bury this layer and expose higher quality soil. • Monitor the appearance of the soil. The upper few milliliters should be natural soil color or brownish. A gray or black color at surface indicates reduced (anaerobic conditions).
Excessive accumulation of soft sediment	• If water supply has high concentrations of suspended solids, pass water through a settling basin before putting it in ponds. • Establish grass cover to minimize erosion on watersheds and embankments of ponds. • Use proper side slopes and compaction when constructing new ponds or renovating old ones. • In ponds with mechanical aeration, install aerators to prevent water currents from eroding insides of embankments. • When ponds are empty between crops, remove sediment from deep areas and place it on the areas from which it eroded. Proper sloping and compaction, establishment of grass above water level, or installation of rip-rap will lessen erosion potential. • Do not leave ponds empty longer than necessary during rainy weather to prevent erosion of soil from shallow area with deposition of soil in deeper areas. • Monitor pond bottoms for soft sediment and remove such sediment periodically instead of waiting until a severe problem has developed.

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