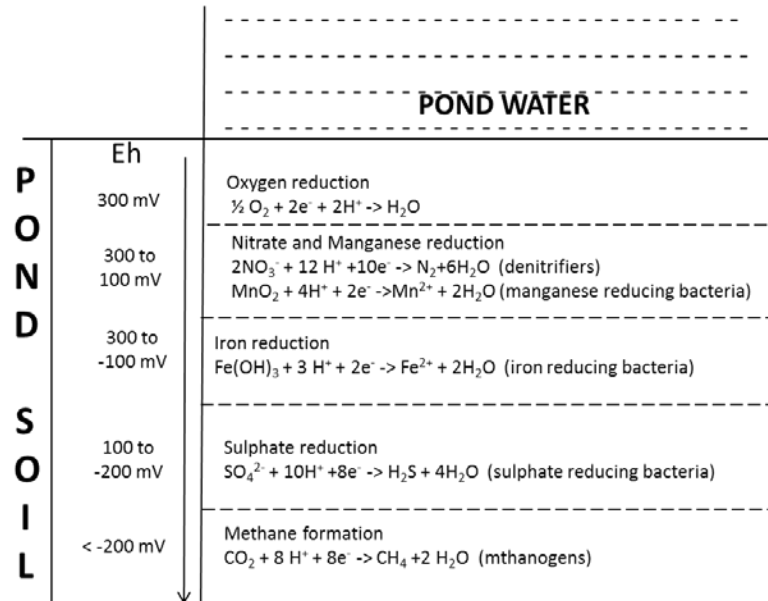




## **Redox potential as an indicator of pond bottom sediment condition**

There is increasing evidence that the condition of pond bottom sediment and the exchange of substances between soil and water strongly influence water quality. Pond bottom condition during culture period deteriorates to a large extent by the accumulation of organic matter residues, such as dead algae, faeces and feed residues leading to high oxygen consumption and the development of reducing (anaerobic) conditions. When reduced species are building up, the pond condition is termed "REDUCED". This condition leads to the diffusion of toxic reduced compounds from the bottom soil upward to the water column, high sediment oxygen demand, deterioration of the pond environment and inhibition of shrimp growth. One of the major and critical parameters that affect processes and condition in the pond bottom soil–water interface (SWI) is the dissolved oxygen (DO) concentration. Pond bottom soils are found to have low dissolved oxygen concentration due to insufficient and slow diffusion of oxygen to the deeper layers. At a depth of only a few millimetres below the soil surface, the demand for DO by microorganisms will exceed the rate that DO can move to that particular depth, and anaerobic conditions will develop. The disposal of accumulated black organic sludge in shrimp pond bottom soil is also a major environmental concern for shrimp growers. This advisory review the important indicators that can be used to understand the deterioration of pond bottom sediment and why redox potential as a better indicator. The advisory is aimed at researchers and technical consultants, who will advise the farmers.



**Anaerobic processes in the pond bottom with decreasing redox potential and metabolites/greenhouse gas formation**

The redox system in the pond bottom is made of both organic components as well as reduced inorganic species such as sulphides, Fe and Mn ions. The sequence of redox reactions in flooded soils and pond sediments is indicated in figure. Microbial transformations of elements in anaerobic soils play a large role in biogeochemical cycling of nutrients and in greenhouse gas emissions. Some microorganisms decompose organic matter in anoxic sediments by fermentation reactions that produce alcohols, ketones, aldehydes, and other organic compounds as metabolites. Some of these metabolites viz., ammonia, hydrogen sulphide, nitrite, manganous ions and certain organic compounds, are potentially toxic to fish and shrimp. Anaerobic microbial processes including denitrification, methanogenesis, and methanotrophy are responsible for releasing greenhouse gases (N<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>) into the atmosphere. Facultative and strict anaerobic bacteria have the ability to use other oxidizing agents/electron acceptors to carry out respiration. Oxygen is the most efficient electron acceptor, while carbon dioxide has the least amount of reduction potential. When available oxygen is depleted and nitrate is available, denitrification, the reduction of NO<sub>3</sub><sup>-</sup> to NO, N<sub>2</sub>O, or N<sub>2</sub>, primarily occurs. Sulphides are present in sediments as a result of the reduction of sulphates or other oxidized sulphur species under very low redox conditions. Sulphide is highly toxic and affects shrimp at a very low concentration.

## **Why redox potential is a better indicator to understand the pond bottom deteriorating condition?**

1. Organic carbon (OC) content of soil is one index of pond sediment condition. High OC values imply more organic matter accumulation on pond bottom.
  - The pond bottom soil organic matter contains a large fraction of stable, slowly degradable OC and hence, it is not a sensitive indicator. Conventional soil organic carbon determination procedure includes exposing the soil to air and drying. A part, often an appreciable part of the reducing components such as sulphides, Fe or Mn ions are oxidized when soil is exposed to air and not included in the subsequently measured redox system. Such components may be a major part of the bottom soil redox, especially in high saline shrimp culture ponds, where sulphides constitute a major component.
  - Estimation of easily oxidisable organic matter (EOM) determine that fraction of the redox system that identifies with or is related to the active redox pool in pond bottom soils, as a better indicator of pond bottom soil properties and changes compared to conventional organic matter (OM). However, this is time consuming as analysis has to be done in the laboratory.
2. Concentration of soluble iron and manganese (reduced species) is more sensitive indicator of the redox conditions. The oxidized species,  $\text{Fe}^{3+}$  ion and the  $\text{Mn}^{4+}$  ions form highly insoluble salts, oxides and hydroxides in the pond bottom soil, whereas the reduced species, the divalent (2+) ferrous or manganous ions form soluble species in the pond bottom soils. However, being tedious procedure this is not being used in general.
3. Redox potential also called as oxidation-reduction potential (ORP) is an important parameter to measure the relative degree of oxidation and reduction in aquaculture ponds. ORP in the pond soils decreases and the capacity of the reducing species in pond bottom soils increases with time during culture period. Though highly variable, ORP values denoted by Eh and quantified in milli volts (mV) are best used as an indicator to understand relative status of the soil.

Though reduced species presence and OC content can be used as indicators for pond bottom deterioration, estimation of these takes more time and hence cannot be used as fast

indicators to plan management practices for improvement of pond bottom condition. It is possible to evaluate the intensity of the pond anaerobic conditions by measuring the sediment redox potential.

### **Variability in redox potential**

Changes in ORP values are the result of combined effects between chemical and biological processes. ORP is an electrical measurement that shows the tendency of a soil solution to transfer electrons to or from a reference electrode and measured as voltage between the environment and a standard reference electrode. This measurement can estimate whether the soil is aerobic, anaerobic, and whether chemical compounds such as Fe oxides or nitrate have been chemically reduced or are present in their oxidized forms. But Eh can fluctuate and varies from place to place in a pond and even at different points in polythene bag with pond bottom sediment. Low ORP values are due to rapid consumption of oxygen by soil microbes which are not uniformly distributed in the pond bottom sediments and thus ORPs are not uniform throughout the soil matrix.

It is very difficult to get a uniform ORP value at different sampling places at any time of measurement throughout the culture. In order to understand the temporal and spatial variability in the measurement of ORP, CIBA carried out temporal (at different DOC) and spatial measurement at three places from each area viz., water pumping area (WPA), pond centre (PC) and sluice gate (SG) in eight white leg shrimp, *Litopenaeus vannamei* culture ponds stocked at 15, 20 (2 ponds), 32 (2 ponds), 38, 40, 50 nos./m<sup>2</sup>. The ORP in the pond soil was measured by two protocols a) at a soil water interface (SWI) by a multi parameter probe and b) at 10-cm depth soil collected in in a polythene bag under air tight condition using a portable redox meter. Though lot of variation exist in ORP values within a pond, as a whole the values were low (more -ve) at SG followed by PC and WPA. For example, at r stocking densities above 20 nos./m<sup>2</sup>, ORP values measured at SWI and 10-cm depth during third month of culture period were low (-140 to -290 mV) and this was associated with low pH (6.7 - 7.3) and low dissolved oxygen level, indicating reduced condition.

Along with ORP, analysis of other parameters viz., pH and OC in soil, TAN, NO<sub>2</sub>, SO<sub>4</sub> and S<sup>-</sup> in water and enumeration of microbial parameters, total heterotrophic bacterial count (THBC), ammonia and nitrite oxidising bacteria (AOB & NOB), sulphur oxidising and reducing bacteria (SOB & SRB) were measured. Low redox values were positively

correlated with OC content in soil and SRB and negatively correlated with AOB and NOB. Organic carbon was significantly correlated with THBC and ORP. Soil pH and Eh were also positively correlated. From the study, it can be concluded that measurement of redox potential (ORP) either with a probe at SWI or with redox meter at 10-cm depth soil near sluice would give an idea on pond bottom condition.

In intensive shrimp culture ponds, the accumulated black sludge on the pond bottom leads to reducing conditions and negative redox values. This problem can be avoided by providing proper aeration uniformly throughout the pond by placing aerators at right place, chain dragging along the pond, central drainage system and disposal of sludge through heavy duty pumps.

### **Protocol for the measurement of redox potential**

In order to measure the redox potential of pond bottom sediment at any point of time during culture period, the following steps are recommended.

1. ORP can be measured at soil water interface (SWI) near sluice gate and away from the aerators by a single parameter ORP or multi parameter probe.
2. If probes are not available, the sediment sample at 10-cm depth is to be collected in a polythene bag under air tight condition near sluice gate and away from the aerators. Once the sample was brought out of the pond, immediately ORP has to be measured under air tight condition by using a portable redox meter.
3. Single redox measurements at one place can be insufficient in describing fluctuating redox conditions in pond soil systems. Hence, in order to minimise the errors, minimum of three sampling places have to be fixed near SG and repeated measurements are to be taken at each sampling place (SWI or 10-cm depth soil in polythene bag) and the average value can be taken as final value.

### **What type of instrument to be used for the measurement of redox potential?**

- ORP can be measured with any equipment containing three basic pieces viz., platinum electrode, reference electrode and Voltmeter. Platinum electrodes consist of a small piece of platinum wire that conducts electrons from the soil solution to the wire to which it is attached. Reference electrodes provide a standard redox reaction that will accept or give up electrons to the soil solution. Two types of reference electrodes are in use: Ag/AgCl and Calomel. Voltages produced by oxidation-reduction reactions are

small (range from +1 to –1 volts i.e., +1000 to –1000 mv), hence the voltmeter selected must be capable of measuring these small voltages.

- The redox potential is an intensity parameter, like soil pH and any pH meter can be converted to redox meter by changing the glass electrode in pH meter with platinum electrode. Now only single combined electrodes (platinum and calomel) are being used for the measurement of redox potential.
- The electrodes have to be checked for accuracy by calibrating with commercially available stable standard redox potential solutions.

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**March, 2014**

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