



## Effect of Pollutants on Biochemical Profile and Population Dynamics of Zooplankton

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### Abstract:

Ocean is considered as the most stable ecosystem pertaining to its vast body, various currents, its physical and chemical phenomenon and self-sustainability. For centuries ocean owned a great buffering system resisting any change in its profile. However humans have managed to exhaust this ability of oceans by endlessly polluting it and hence the changes in the physical and chemical characteristic of ocean are now very prominent. There is enormous scientific literature which asserts the negative impact of pollutants on marine life. Zooplanktons and phytoplanktons marks the beginning of aquatic food web hence any change at this level will be significantly seen on the higher trophic level due to the phenomenon of bioaccumulation and biomagnification. The following review deals with the effect of various physical and chemical parameters such as temperature, UV radiation, pesticides, fertilizers, petroleum and its derivatives, plastic, metals and heavy metals etc. on numerous characteristics of sea water. These changes consequently affect the biochemical profile of planktons, the mechanism of which has been further discussed in this review.

**Keywords:** Biochemical parameters, population dynamics, zooplanktons

### 1.0 Introduction:

Since the first industrialization and agriculture revolution, we have managed to disrupt what was once the most stable ecosystem, the ocean, where life originated about 3.5 billion years ago. We have destroyed the same place where it all began. According to The International Census of Marine Life, ocean is home to more than 250,000 known species and since many species are yet to be discovered, the total number of species, excluding microbes, could reach or surpass one million mark. With these many number of species, the food web of ocean is bound to be complex. This mega web starts from planktons, which varies in size from few microns to meters. Plankton is not one particular species but a diverse group. They can be phytoplankton, "the plant of sea" and Zooplankton which are of animal origin. Zooplanktons are diverse group of organisms. Most of them are floating with water current but many are equipped with good swimming power. Many of them are marine habitants while others are freshwater. Phytoplanktons are the producers of this vast food web and zooplankton are primary and secondary consumers.

Planktons are morphologically and taxonomically diverse group of organism and are the initiators of aquatic food chain. No plankton equals to no life. The diversity is also seen in distribution of planktons in ocean. Continental influence affects temperature, salinity and productivity of ocean. Depending upon variations in given characteristics, dominance of particular species of zooplankton is observed as different potential habitat for different species of zooplanktons. The zooplankton diversity in vertical zonation of sea is less as only few species of zooplanktons are adapted to survive in temperature drop from surface to base of ocean, food scarcity and less photic environment which decreases primary productivity in deeper waters (Ruthford *et al.*, 1999). Due to such difficult condition to live in, lower species diversity is observed in deeper waters than surface waters of ocean (Smith and Brown, 2002). The above findings indicates that the Zooplankton ecology might be different at different places depending upon the varied physical and chemical properties of water (Bonecker *et al.*, 2014).

Ocean can be considered as the most stable ecosystem pertaining to its vast body, various currents, its physical and chemical parameters and its self-sustainability. For centuries ocean owned a great buffering system resisting any change in its profile. However humans have managed to exhaust this ability of ocean and changes in the profile of ocean are now very prominent. Industrial, domestic sewage disposal and agricultural runoff are major concern for the physical and chemical characteristic of sea water of a region. Various sources introduce pesticides (POP), heavy metals, petroleum products and other various organic and inorganic products. Over 80% of marine pollution is due to land based activity. These pollutants alter the physical and

## 2.0 Effect of Pollutants on Sea Water Quality:

### 2.1. *Effect of physical pollutants on sea water quality:*

Study performed by Sekar *et al.* (2009) in Thoothukudi costal area showed that surface water temperature is governed by the atmospheric temperature. Other than the general fluctuation of pH due to seasonal variation higher pH values are observed due to effluent discharge from the salt pans nearby. Reduced Dissolved Oxygen was reported near the site of release of untreated domestic sewage. Ammonia concentration was mainly affected by runoff and raw sewage and effluent. Similar pattern was observed for phosphate concentration. Higher value of salinity in month of May was justified by shallowness and effluent discharge from salt pan nearby. High level of turbidity in areas such as Mahim, Shivaji Park, Girgaon beaches in Mumbai, India were found to be 84, 38 and 32 NTU respectively in 2014. Researchers also stated that the DO observed was practically zero. All samples under their investigation had alarming increase in BOD. These high level of characters of water was correlated with high influx of domestic and industrial waste (Sawant and Bhave, 2014).

### 2.2. *Effect of chemical pollutants on sea water quality:*

Research paper entitled 'The coral reef crisis: The critical importance of <350 ppm CO<sub>2</sub>' by Veron *et al.* (2009) pointed out that ever increasing pollution is causing a constant rise in the CO<sub>2</sub> concentration of atmosphere, coupled with high temperature, it is causing mass coral bleaching and mortality. They have stated that if the concentration of CO<sub>2</sub> rises by 445ppm coral reefs will undergo massive and terminal decline

chemical properties of water which in turn causes either increase or decrease in organic and inorganic content of water.

These contaminants of sea water do not just remain localized but become global due to events such as precipitation, wind current, rain, ocean currents, upwelling etc. Hence pollution in a particular area is a not a local concern but a global one. The present review article focuses on the change in the physical and chemical parameters of ocean due to pollution and its resultant effect on population dynamics and biochemical profile of zooplanktons.

worldwide due to bleaching, ocean acidification and other impacts. The concentration of CO<sub>2</sub> by 2015 is 400 ppm! Corals are important ecosystem as they serve as breeding and nursery ground for many fishes. Rich zooplanktonic population is seen in this ecosystem. This ocean acidification causes deformities in zooplankton exoskeleton. Similar negative impact is also seen on fish larva which are part of planktonic population. This concludes that ocean acidification affects micro to macro organismic levels and has determinant effect on plankton. Runoff of persistent pesticides such as Organophosphorus and Organochlorine are also menace to the ocean. Sankaramakrishnan *et al.* (2005), clearly noted out in their survey about presence of high amount of organochlorine and organophosphorus pesticides in surface and ground water in Kanpur, India. Malathion, Dieldrin and  $\gamma$ -HCH were also found in water.

Sarkar *et al* (1997), observed that the marine and eusterine sediment of West Coast of India is contaminated with concentration levels of HCHs, DDT, Aldrein and other Organochlorine and Organophosphorus pesticides. In their investigation sediment samples from near and off shore sample site were examined and it was concluded that the concentrations of pesticides decreased gradually as they moved off shore. Pp'-DDE and  $\alpha$ -HCH were dominantly seen in both near and off shore sediment of sample sites. Contamination of water with toxic metal is found to be high in region highly influenced by human activity. Increased Copper was seen at anthropogenically influenced sites, e.g. Copper concentration in Uttan region, Mumbai in India were found to be high and these high values are justified as in this region is in vicinity of biggest garbage dump in Greater Mumbai. High annual average of total Cadmium also corresponds to high

industrial effluents and domestic sewage and waste material (Pahalawattaarachchi *et al.*, 2012)

Pre monsoon and post monsoon water and sediment sample of coast of Mumbai also proves the constant influx of industrial and domestic waste. Many sites are small harbours which add crude oil pollution to the already heavily polluted coast line. Result of these pollutions is presence of toxic heavy metals such as Mn, Fe, Pb, Co, Cu, Zn and even Hg at elevated levels (Aranguiz-Acuna and Serra, 2016). Surface sediment samples collected from Bay of Bengal and Off Chennai too shows high enrichment and contamination factors of various heavy metals such as Cd, Cu, Pb, Zn, Fe, Hg etc. Cd and Cu values are seen high in pre and post monsoon season (Solai *et al.*, 2013). In Patancheru industrial town near Hyderabad, India, various reports of releasing effluent untreated form chemical and pharmaceutical industries were reported. Parameters such as Sr, Ba, Co, Ni, Cr in surface and ground water were estimated to be a result of anthropogenic and geogenic source, whereas Fe, As, Mn, Zn were result of anthropogenic activities (Krishna *et al.*, 2009) Generally speaking, the concentration of metals varies in both the coastal regions of India depending upon the effluents released and various other factors. E.g.: Copper was found to be 0.259ppm and 0.78-4.63ppb in Western and eastern coast respectively. Zinc concentration ranges from 6.78ppb- 119.8ppb in Western coast to 1.19-21.48ppb in Eastern coast (Mehta and Amin, 2009) (Anand and Kala, 2015)

### **3.0 Effect of Changes in Physical and Chemicals Parameters on Plankton with Special Reference to Zooplankton:**

#### **3.1. Effect of change in physical parameter of water on zooplanktons:**

Not all zooplanktons are equally affected by contamination. The observed differences in physical parameters in Eastern Bering Sea shelf during summer between 1999 and 2004 were accompanied by significant differences in the zooplankton community. Scientist found that mean abundance of the small copepods *Oithona* sp. and *Pseudocalanus* sp., was higher by over 3–5 times in 2004 relative to 1999 and that abundance of the zooplankton species, *Calanus marshallae*, *Thysanoessa* sp. and *Sagitta elegans*, had reduced substantially by 2004 (Coyle *et al.*, 2008)

#### **3.1.1. Ultra Violet radiation pollution:**

##### **3.1.1.1. Effect on biochemical profile of planktons:**

Wolinski *et al.* (2016) rightly pointed out how Ultra violet radiation (UVR) along with temperature and food quality acts as stressor for zooplanktons. They focused on the effect of these stressors on Alkaline Phosphatase Activity (APA) and Glutathione S-Transferase (GST) of *Daphnia commutata*. They carried out experiments by exposing them to UVR along with varied temperature and quality of food. This was followed by luminic and dark phase for recovery. The correlation between UVR and enzymatic activity put forward by them that the enzyme activity gets affected by UVR as it increases reactive oxygen species. GST increase with UVR exposure whereas APA was negatively affected by UVR. APA was enhanced under high temperature and low food quality. This indicates how the physical pollution affects the biochemical activity of zooplanktons.

#### **3.1.2. Thermal pollution:**

##### **3.1.2.1. Effect on biochemical profile of planktons:**

Thermal pollution of aquatic environment is matter of high concern. Even moderate changes in the water temperature do affect the metabolism, hence affecting physiochemical changes as well. Many metals, most of which are mentioned previously, also affect the energetics of metabolism. Rate of metal absorption is positively correlated with high temperature. This conclusion is with reference to fact that increased temperature aids in solubility of metal and hence its availability to organism, however there are many independent studies that suggest that temperature change and concentration of metal have negligible effect but other factors such as selective abortion and membrane permeability. Active and passive transport should also be taken into consideration.

Redalje and Laws (1983), point out that temperature is one of the most important factor regarding the biochemical composition of zooplankton. They studied the effect of this factor on fatty acid composition of zooplankton. They suggested that temperature is principle external environmental parameter which causes variation in fatty acid composition. This suggests that even though many studies say that change in the ocean temperature is not significant, but the near shore site, where thermal pollution does affect the water temperature, can shows these kind of change in biochemical composition of zooplanktons. The

effect of water temperature on metabolism of zooplankton is well documented phenomenon. During diurnal migration of zooplanktons, while descending in water column after feeding helps zooplanktons to metabolize the food as the warm water in water column helps to ease up metabolism.

**3.1.2.2. Effect on planktons by means of bioaccumulation and biomagnification:**

Study by Sokolova and Lannig (2008) has shown that higher temperature and heavy metal concentration are directly proportional to ventilation and feeding rate. Many heavy metals also affect respiratory organs and cellular respiration. This causes animal to increase respiration to suffice the need of oxygen. Many times food required for energy conservation is depleted too, which causes increased feeding rate. This increased feeding and respiration rate exposes the aquatic organism to more pollution. This study also indicated that higher ventilation rate was observed in oysters which were introduced to more Cadmium containing water. Acclimatization to various temperatures is also related to change the membrane composition which increases or decreases membrane fluidity, which can be correlated to the passive and active transport of metals across the membrane.

**3.2. Effect of chemical pollutants on plankton:**

**3.2.1. Metal pollutants:**

Watling (1982) showed that *C. gigas*'s larvae which are planktotrophic, have been affected by reduced growth, high mortality and high abnormality by varied concentration of Zinc, Cadmium, and Copper. Similar effect were also shown by Paul *et al.* (1989), where metals such as Ag, Cd, Cu, Pb, Zn and pesticides such as DDT and Dieldrin, have negative impact on Sea urchin in all its developmental stages. Fertilization and embryo development is more sensitive to metal whereas larval stage and adult organism are more sensitive to pesticides. Reduced larval weight is also associated with such contaminate. *P. japonicus* tolerance to Copper shows positive correlation with that of developmental stages. For e.g. the tolerance to Copper was found to be least in nauplii stages with 48hrs LC<sub>50</sub> 1µg Cu/L, whereas that of post-larvae stage was 96hrs LC<sub>50</sub> 20-1450µg Cu/L (Bambang *et al.*, 1995). Even arsenic hampers the quality of eggs of *B. calyciforus*, in experiments when this species were exposed to arsenic even healthy looking eggs had lower hatching success (Aranguiz-Acuna and Serra, 2016).

Comparative toxicology study on zooplanktons such as copepod species— *Sctuellidium* sp., *Paracalanus parvus* and *Acartia simplex* suggest that copper is the most toxic heavy metal followed by cadmium and zinc (Bambang *et al.*, 1995). There are various papers which explain the toxicity of copper on plankton. Researcher carried out study in which effect of various concentration of copper was observed. They took two types of sample under consideration: one from polluted area of Saronic Gulf, Greece and one from unpolluted region (Moraitou-Apostolopouloa and Verriopoulos, 1979). It was observed that various concentration of copper affects the copepod *Acartia clausi*'s feeding rate, respiratory rate, fecundity and longevity. It was seen in their research that specimen from the polluted area were more sturdy than specimen from unpolluted area to varied concentration of copper. However, all the samples did show reduced feeding activity, longevity, fecundity and respiration rate.

**3.2.1.1. Effect on population dynamics of planktons:**

Some planktons are sensitive to particular contaminant while other are sturdy or have regulation or detoxification mechanism. Many opportunistic species changes entire population dynamics in such water. Four yearlong observations of species richness and community biomass by Youngbluth (1976) conclude that acidic and metal contaminated Clearwater lake underwent reduction in species richness and biomass. Species dominance by *Bosmina longirostris* was seen in lake under the study suggesting that this species is more sturdy species in pollutant stress. Study also indicates that the biomass of zooplanktons was not significantly correlated with pH, Cu, Ni concentration. This seems to be in contrast with the basic stance of phytoplanktons and zooplankton inter relation. However author did observe change in species community dynamic in other acidic lakes which were not contaminated with Cu or Ni which ultimately suggest that heavy metals do affect the zooplankton community enough to change the dynamics of community. Even though considered as sturdy planktons, *Cladocerans* are not resistant to all pollutant stressors. Havens (1994), proved by his study that they are sensitive to copper and carbonyl gr. In response to both the stressors, the population decline was observed. It was seen that their decline also may have affected food web. *Ctenophores* and *medusae* are also found to be sensitive of copper.

Experiments performed by Foster (1976), showed that 10g/lit of copper reduces the filtering capacity of copepod. In presence of chelating agents the effect of copper was not harmful even at high concentration. They also reported that 3gm/lit of mercury concentration affects feeding rate of copepod, however it had positive effect on growth of phytoplankton. Definitely this means that presence of mercury can change the dynamics of plankton population. If mercury content is found to be high the phytoplankton will positively increase which will aid in dominance of herbivorous plankton and other aquatic organism. As the sensitivity to the pollutant varies in species, pollution will also affect ratio of various species which will change the community dynamics.

**3.2.1.2. Effect on biochemical profile of planktons:**

Study by Yan and Strus (1980), estimated toxicity of various toxic metal such as Cu, Fe, Ba, Ni, Cr etc. on *Daphnia magna*. Various lethal concentrations showed reproductive impairment. Loss in weight was observed in surviving specimen in contrast to the control specimen weight. The toxicity was correlated with variation in total protein and glutamic oxalo-acetic transaminase activity and various toxic metals. Logarithm of equilibrium constant of metal ATP complexes were positively correlated with toxicity. This shows that the toxicity of pollutant can be estimated by effect on biochemical parameter of specimen which can give more insight into the mode or effect of toxicity on specimens at physiochemical level. 14C-benzopyrene, 3H-methylcholanthrene from seawater solution is easily absorbed by many species of zooplankton such as *copepod*, *euphausiids*, *amiphipods* etc. of various coasts such as California, British Columbia and even Arctic. The metals are metabolised differently in different species of plankton. These pollutants are metabolized to various polar metabolites and hydroxylated derivatives (Lee, 1975). Hg in zooplankton causes saturation of metallothionein. High Hg is also related with decreased amount of Cu and Zn in tissue. The Hg in zooplankton causes changes in structure of metallothionein which causes displacement of Cu and Zn (Brown and Parsons, 1978). Effect of metals such as Hg, Cd, Ag, Mn, Zn etc. is also associated with degree of binding to sulphur (Hook and Fisher, 2002). Scientist have pointed out that toxic metal concentration in *copepod* species under investigation is directly proportional to affinity of sulphur with that metal, these forms various metal sulphides which interferes by binding to enzyme

required in egg production. Many other heavy metals acts as chelating agent which also affects various enzymes, co factors etc. which hinders the biochemical process, ultimately impairing important life process or causing mortality.

Metallothionein is cysteine rich metal binding protein whose synthesis is induced by metal, many of such metals are usually accumulated in body by complexing with various ligand hence to study the actual contaminant present in body it is suggested that we should investigate the ligand pool of organism rather than just non transformed contaminant. Concentration of Cu-thione in crab larvae was corresponding to sea water concentration of copper this was also negatively correlated to larval growth by Sanders and Jenkins (1984).

**3.2.1.3. Effect on planktons by means of bioaccumulation and biomagnification:**

Oil combustion and industries are also responsible for higher concentration of trace metals in water bodies. According to studies done by Albert Calbet *et al.* (2016), despite presence of high concentration of trace metals in water bioaccumulation in zooplankton for trace metal was moderate, this study differs from other experiments which indicates how zooplankton has good ability to bio-accumulate metal pollutants. Bioaccumulation and biomagnification is major issue that needs to be addressed. Since zooplanktons and phytoplanktons form the base of food chain, there are major possibilities that the effect of pollutant on them will ultimately show up in higher trophic level. This becomes a higher concern if the animal is of higher trophic level e.g.: Arctic cod fish, whose diet contains majorly planktonic copepods. Study showed that in Arctic cod from Northern Baffin Island showed high level of Cd in its liver along with other metals, either equally distributed to whole body or concentrated to particular organ. Upon the inspection of gut content of the fish, planktons, especially copepod, were found to be in major concentration. The unsorted copepod of the regions where found to be bio-accumulating Cd at levels 5 to 8 times higher than Arctic cod (Macdonald and Sprague, 1988) This shows that the presence of pollutant in water is not the only factor by which bioaccumulation and magnification can take place, but the transfer of pollutant by diet is also an important factor to be considered. This especially is major concern in higher trophic level which is selective in diet and the prey is accumulating more pollutant. Cd concentration causes reduction in



percentage of adult producing young, number of brood per individual, generation time etc.

Rainbow *et al.* (2003), showed that in an experiment with barnacle *Elminius modestus*. Accumulation of metals such as Cd, Cr, Se and Zn was mainly due to assimilation of phytoplankton and zooplankton which themselves accumulated these heavy metal from solution and diet. Assimilation efficiency was found to be higher from the zooplankton diet than phytoplankton. Cadmium easily associates with *Daphiamanga* and *Ceriodaphnia dubia's* carcass. The amount of cadmium absorbed depends upon the concentration of cadmium and duration of exposure. Study also indicated that the amount of cadmium absorbance is positively correlated with the surface area of organism. Studies also indicated that similar adsorption effect are seen in acute high concentration and chronic low concentration (Solai *et al.*, 2013). This suggests that not only concentration but the duration or exposure period too are important consideration when effect of pollutant are studied.

Hook and Fisher (2001), used approach in which they studied effect of Hg, Cd, Ag by concentration resembling that of found in urbanized estuaries. Adult of planktons were fed the food which was exposed to metal stressor. The same stressors were also dissolved in water. Two conclusions were made by them: The amount of stressors found in the internal tissue were result of exposed food whereas the contaminant found on surface of organism was due the dissolved stressor in water. This shows that even minute accumulation in planktonic community can affect the organism dependent on it in two ways, one from the prey and other from water. The effect of sublethal doses of such pollutants cause decreased egg production, less protein in egg, fault in ovarian development, increase in lipid etc. (Hook and Fisher, 2001 and 2002). Sundarbans, India is affected by pollution too. This mangrove ecosystem shows high range of Cd, Zn, Pb, Fe etc. These heavy metals are not only found high in the mangrove system sediments but organism of this system such as Tiger shrimp (*Penaeus monodon*) and Mullet (*Liza parsia*) show high level of bioaccumulation of these heavy metals too. Except Pb, other metals concentration in shrimp showed variation depending upon the localities. Whereas in Mullet Zn concentration showed variation depending upon localities. This study by Guhathskurta and Kaviraj (1988), indicates the persistency of various heavy metals for bioaccumulation and biomagnification varies and

also that the buffering system of such pristine ecosystem are now deteriorating.

Studies show that even small addition of sub lethal dose of stressor can cause long term accumulation even in resistant species. Mercury at the concentration of 0.5 $\mu$ g/lit causes changes in species community dynamics whereas 5 $\mu$ g/lit causes developmental defects in phytoplanktons as well as zooplanktons. 50 $\mu$ g/lit cause inactivation or death of planktons (Kuiper, 1981). This shows that the effect of mercury depends upon the concentration. Study shows that the mercury level varies along the coast of Maharashtra where concentration of mercury is lower than other metals ranging between below detectable value at Mahul region to highest concentration of 4.34mg/lit at Uttan region (Pahalawattaarachchi, 2012). We can make general conclusion that the planktonic community might be already altered if the concentration of Hg is found to be more than 0.5 $\mu$ g/lit. Organisms are affected by pollutants when the pollutants, either from surrounding or from its food, enters the body or gets accumulated and leached in body surface. Studies performed by Gulati *et al.* (1988), showed that pollution exposure to predatory species is not only through water but also through prey, as the pollutants are absorbed on prey surfaces, this means that predator species faces triple threat of exposure of pollutant through water, bioaccumulation by prey, and surface absorbed pollutant by prey. For e.g. scientist have suggested that effect of mercury on plankton also depends upon the surface area available of plankton to exposure of mercury.

As explained previously heavy metals usually form complexes. Even the heavy metal present in water suspension forms complex colloidal macromolecular organic matter. These complexes alter the properties of metal so often increasing hydrophobicity which aids in transport of it across lipid bilayer. Decapod crustaceans show ability of accumulating colloidal complexed heavy metals at environmentally representative concentrations levels similar to those seen in solutions where the ionic metals were high in concentration (Carvalho *et al.*, 1999). One of the published papers by Rainbow and White (1989) gave detailed account on various strategies of accumulation and processing of Zinc, Copper and Cadmium in three species of crustacean of different taxon. Species belonging to class decapoda have ability to regulate the concentration of Zinc and Copper till threshold value. The species *P. elegans* of decapoda can regulate (rate of uptake of metal or contaminant = rate of excretion of metal or

contaminate) and maintain constant level 79µg Zn/gm and 129 µg Cu/gm over varied range of dissolved zinc and copper concentration however after threshold value net gain of contaminant starts, species belonging to class *Amphipoda* and *barnacles* species showed net gain of these metal at varied concentration. No crustacean appears to regulate concentration of Cadmium. Many such crustaceans and other planktons also show detoxification ability of metal which are essential for body but are toxic at high concentration by various mechanism such as binding of Copper to metallothionin which may be treated with lysosome to breakdown this complex to insoluble deposit rich in copper and sulphur (Pullen and Rainbow, 1991).

### **3.2.2. Oil and its derivatives as pollutants:**

High level of polycyclic aromatic hydrocarbon (PAH) is another great concern for seawater. These are released in environment due burning of coal, crude oil etc. PAH level is found low or undetectable in oceanic range whereas higher concentration is recorded in many coastal and estuarine region. Dissolved PAH was found higher near the site of steel manufacturing plant by Law *et al.* (1997), who also stated that along with the above finding the levels of PAH at many sites were too high to produce immediate mortality in exposed organism whereas others had potential to affect chronically the aquatic organisms. Effect of naphthalene on planktons too is documented. The concentration of 1mg/lit for 24 hours affects the fecundity of female planktonic species negatively (Berdugo *et al.*, 1977). Effect on vital process of plankton is also seen due to PAH. Higher hatching success is seen in resting egg, with water having less PAH concentration.

#### **3.2.2.1. Effect on population dynamics of planktons:**

Staniszewska *et al.* (2016) attempted to establish relationship between concentrations of bisphenol A (BPA), 4-tert-octylphenol (OP) and 4-nonylphenol (NP) in zooplankton and seasonal change in composition and biomass of zooplankton. To estimate the pollutant concentration HPLC or FL system were put to use. Their study concluded that juvenile form of certain taxa of zooplanktons are more prone to such pollutant which are endocrine disruptors. With biomass growth the bioconcentration factor also increased. They also pointed out that highest BPA concentration could be connected with anthropogenic sources located in the coastal zone.

#### **3.2.2.2. Effect on planktons by means of bioaccumulation and biomagnification:**

Polybrominated diphenyl ether are hydrophobic, this nature helps in transfer of these contaminant in body of planktons and other animals. PCB too are bioaccumulated and transferred by planktons to higher trophic level such as plankton eating fish and other aquatic organism including aquatic mammals, which are either directly or indirectly dependent on such plankton for nutrition in food web. These contaminants produce numerous obvious biological effects including diseases and disorders in aquatic plants and animals. Nine out of Ten species with highest polychlorinated biphenyl (PCB) levels are marine mammals. Corsolini *et al's* (2006) work shows how Polybrominated diphenyl ethers (PBDEs) are found in lipids in krill, rockcod muscle, rockcod homogenate and penguin eggs. These samples itself show a small food chain. This shows that presence of this contaminant even at minute level can be picked by plankton and concentrated further transferred to next trophic level. Jan P Boon and colleague's work also supports this theory as similar observation were made by them in their research of estimation of PBDEs concentration in different trophic level organism in North sea food web (Boon *et al*,2002).

The zooplanktons show high tendency of accumulating PAHs, pesticides and other agricultural runoffs. The Beluga whales' (*Delphinapterus leucas*) carcass of St. Lawrence Seaway too showed saturated levels of pesticides, herbicides and other agricultural runoff. They have also shown high rate of cancer due to presence of high level of PAHs (Bonecker *et al.*, 2014). It should be noted that their diet mainly consists of fish which are usually highly dependent on planktons for their nutrition. The recent trend has been seen in ocean mammals which are affected by pollution, that bioaccumulation is so high that their carcass has to be handled as toxic waste. Another study has related high BAF (Bio accumulation factor) to the phenanthrene accumulation in zooplankton of Chabahar bay, Iran where major source of PAH compound was pyrolytic source.

Oil pollution is one of the main cause for change in the planktonic community, population and physiochemical parameter. It has been observed that the mortality of mesozooplankton increases with increase in the oil concentration in water. Unfortunately the dispersant used for oil spill treatment seems to do more harm to plankton community, as the combination of oil and dispersant is 2.3 to 3.4 times more toxic. Many

species shows bioaccumulation of PAHs, fluoroethane. However study also suggested that presence of protozoan *Oxyrrhis marina* helped to reduce the lethal effect of oil on *A. tonsa* which hence showed low accumulation of PAHs (Almeda *et al.*, 2013). This shows that there are many species interaction which might help to reduce the stress of pollutant however since the stressor concentration is usually high the reducing effect becomes almost negligible. Coastal zooplankton seems to be less affected by water soluble fraction of oil spill.

*Temora turbinata*, *Acartia onsa* and *Parvocalanus* were the three species of marine copepod studied by researcher. To estimate how much amount of crude oil zooplankton can ingest they investigated and quantified defecation rate of crude oil by above mentioned species. Their experiment showed how the large oil droplet are either rejected or broke down by zooplankton before or during ingestion as the oil droplets found in fecal matter were smaller than the droplet of oil created by physical or chemical dispersion of oil. Approximately 88-100% fecal pellet analysed by them contained oil droplets. The ingestion of oil by plankton causes the surface oil reach the base of ocean and contaminate the sediment quality of ocean floor along with introduction of low solubility, toxic petroleum hydrocarbon in food web. These lower solubility compound prove to be more toxic as they remain in organism's body for longer period of time and can act as carcinogen, teratogen and mutagen (Almeda *et al.*, 2016). Researchers of above experiments shed light on how not only crude oil becomes part of food web but also the dispersant used to treat oil spill are harmful and toxic as these dispersant aids in ingestion of oil droplet as one of the function of dispersant if break down oil spill into smaller droplet which are easily ingested by zooplankton (Almeda *et al.*, 2016). Almeda *et al.* (2013) proved that oil spill and dispersant used for treating it along with the UV radiation is related to high mortality of mesozooplankton. During and after the BP/Deep water horizon oil spill Sammarco *et al.* (2013) found out that total petroleum hydrocarbon accumulation in seafood was high near the spill site.

### **3.2.3. Agricultural pollutants:**

Studies from last few decades have also concentrated on effect of pollution on phytoplanktons. Since these are the primary producers of the ocean, the pollution effect on them causes a cascade of event in the entire food web of ocean. The growth of phytoplanktons is

directly correlated to concentration of nutrient, effect of light on photosynthesis etc. This might change the biochemical profile of phytoplanktons. Many compounds and pesticides are absorbed by plankton cells, but are not transformed. So when these phytoplankton are grazed by aquatic herbivores, pollutants are passed down to higher trophic level in more concentrated form. Studies also show that zooplankton fed on DDE water containing water grown phytoplanktons affects the growth rate and reproduction in zooplanktons. Wendt *et al's* (2016), study focused on how antifouling biocides affects the zooplankton copepod. They studied various antifouling biocides and showed how various such chemicals causes' mortality, inhibition of egg production and the egg hatching process. This is alarming findings as these chemicals hampers directly the next standing stock of copepod population which are one of the most important food source in aquatic food web.

### **3.2.3.1. Effect on population dynamics of planktons:**

It has been proved by numerous studies done by scientist that agricultural runoff acts as fertilizers on the phytoplanktons resulting in algal bloom. Even though the algal bloom can be result of natural phenomenon, but the bloom occurrence has increased as result of higher phosphorus and nitrogen content from pollution. These algal blooms can threaten the environment, human health or surrounding and is called as Harmful Algal Bloom (HAB). Many species of such phytoplanktons also release toxins which can cause harm to many oceanic species. These blooms also result in eutrophication of water bodies. Initially the population of zooplankton and of herbivorous fishes shows positive growth with the bloom but as the bloom increases, the dead and decaying phytoplanktons starts to disperse down in water column. Many times the growth rate of phytoplankton cannot be matched by zooplanktons which causes change in zooplankton community dynamics. Usually copepod dominates in these regions. The bacteria starts to degrade the dead phytoplankton the process in which they use up maximum dissolved oxygen of water resulting in anoxic condition in which aquatic organisms die due to asphyxiation. Industrial and Urban waste in Vishakhapatnam, India in over last 20 years showed notable change in hydrographic and biotic dynamics. Over the years increase in concentration of nitrites and phosphates was observed. Due to this increase the phytoplankton population, outburst is seen with specific phytoplankton species such as *Skeletonema costatum*. The benthic species such as *Capitella*



*capitata*, which is pollution tolerant, inhabited more in these region (Raman, 1995) This shows that changes in water and sediment characteristics due to pollution affects the dynamics of species composition, richness and diversity ultimately altering the food web of that region as well.

In Kulai and Padubidri coast of Karnataka, India concentration of petroleum hydrocarbon were found to be higher as there is huge influx of fertilizers, petroleum, sewage and industrial discharge. Due to this, dominance of fast growing diatoms was observed. This resulted in lower species richness and diversity. Proliferation of sturdy benthic bivalve species was high. High PHC with Cd and Pb as contaminant and NO<sub>3</sub> and PO<sub>4</sub> as oxidant assisted the growth of phytoplankton and benthic bivalve (Verlecar *et al*, 2016). Vishakhapatnam, India, is one of the busiest harbour. Along with crude oil contamination, there is high influx of industrial and domestic effluent. An overview of 23 years on this site confirms change in biotic community dimensions and that of various water parameters for e.g. Nitrate and Phosphate content haven't rise over the years. Since nitrate and phosphate acts as fertilizer phytoplankton blooms too were reported. The study also noted that effected water area is now dominated by more tolerant species such as *Capitella capitata* (Raman, 1995).

Gordina *et al*, (2001) too have mentioned that in over 25 years nitrate, nitrite, ammonia and total suspended matter content in ocean has increased. All this is leading to species diversity, richness, species dominance and increase in the planktonic mortality. Hurlbet *et al*. (1972), studied the effect of Dursban an insecticide in experimental ponds with different concentration. *Cyclops vernalis* and *Monia micrur* faced high mortality along with insect larvae and nymph, in their cases adult's ability of dispersal helped to resist the reduction in number. In these ponds however the herbivore and carnivore rotifers increased in number proving them to be resistant to the effect of these insecticides. Their population increase was also supported by reduction in number of other species and algal bloom of bluegreen algae. Insecticides have been reported to affect the size of organism, species richness and diversity along with alteration in food web and energy transfer.

### 3.2.3.2. Effect on biochemical profile of planktons:

Studies conducted by Hasenbein (2016) on potential effect of pesticides mixture on aquatic ecosystem concluded that pyrethroids dissipated

from water column rapidly whereas chlorpyrifos could be detected from water column even after 6 weeks of application. The mixture of pesticides studied were neurotoxins with different neurological target or mode of action. Pyrethroids acts on sodium channel of nerve cell and chlorpyrifos inhibits acetylcholine esterase activity which leads to impairment of body functions due to accumulation of acetylcholine. 10 out of 16 zooplankton taxa under investigation showed response to these contamination. The most sensitive zooplanktons were found to be *H. azteca* and *D. manga* and copepods. They also stated that "these mixture of pesticides continue to impact natural system over multiple weeks, even when no longer detectable in water and bound to particles. Combination of indirect and direct effects caused consequences across multiple trophic level". The effect of POP was more in depth was done in experiment by Fisk *et al*. (2001). They observed that *Calanus hyperboreus* had increased level of lipid content (dry weight) and  $\delta^{15}C$ , whereas water content and  $\delta^{15}N$  decreased significantly. However, when the factors were removed on time the variable lipid and other substances' concentration did not match the description like that of POP, which shows that changes are observed only when they are exposed to POP and that POP does not biomagnify, since the factor changes only followed by POP exposure and removal of POP didn't further gave same variable value.

Insecticides effects various process of zooplanktons. Zooplanktons are found to be more sensitive to dissolved and suspended pollutant rather than the ones transferred via by food. The decline in population of copepod is directly correlated to the concentration of copepod in many studies. It has been proved that on an average zooplanktons are not good degrader of pesticides, the absorbed pesticides are usually found in lipid deposition. However Sameoto *et al* showed that DDT is in fact converted to DDE in three species of euphausiids (Sameoto, 1975). Few species of copepod are able to incompletely depurate hydrocarbon. As mentioned previously larvae and eggs are more sensitive than adult as adult have ability to disperse more. *Mytilus edulis*'s developmental stages are found to be more sensitive to insecticide 'Seyin', as the development proceeds the sensitivity also decreases (Armstrong and Millemann, 1947). Crabs' development also is lengthened due to presence of certain insecticides. Many insecticides are found to be affecting the swimming capability of larvae, increased respiration rate change,

increased ventilation rate etc. If due to pollution larval stages are affected ultimately it will be reflected on the future standing stock.

#### **3.2.4. Plastic pollutants:**

Many aquatic organisms die annually due to plastic pollution in water. Recent studies suggest that nearly 85% of aquatic birds have ingested plastic. Fish and sea turtles are major victims of plastic pollution as most of them mistake plastic as food material. This plastic not only causes cytotoxicity but it also blocks intestine, causes ulcers, deteriorates reproduction etc. Marine animals also get entangled and lose life or damage their body parts in illegal or drifted nets. Zooplankton too are not spared from the cytotoxicity of plastic. Many macrozooplankton too will show similar effect of plastic like other marine organism.

##### **3.2.4.1. Effect on planktons by means of bioaccumulation and biomagnification:**

Matthew Cole *et al.* (2016) showed that fecal matter of *C. typicus* containing microplastic could be transferred to *C. Helgolandicus* through coprophagy that supports the view that sinking faecal matter provides a way by which microplastic can be vertically transported away from surface water. In recent years extensive research has been done on plastic as leading cause of marine pollution. Eriksen *et al.* (2014) presented in their study that plastic particles weighing 268,940 tons are floating in sea. They also revealed that Indian Ocean have greater plastic particles (weigh and count) than South Atlantic and South Pacific combined. From the plastic particles 75.4% were macroplastic, 11.4 % were mesoplastic and rest were microplastic. Rehse *et al.* (2016) proved by their experiments that ingestion of 1  $\mu\text{m}$  sized particles of micro plastic caused immobilization in *Daphnia magna* after 96 hours of exposure. Their experiment underlined how various size of micro plastic affects the Daphnia and its various activities. Recent studies also shows transfer of plastic microparticle to higher trophic level by plankton.

#### **4. Conclusion:**

This shows that pollutants such as heavy metals affect the organism's vital activity in which the sensitive species are most affected, however the same species can be acclimatized to polluted environment to some extent. The underlining principle of sensitivity or tolerance of any stressor must be result of reactions occurring at

biochemical level, as any change or response or mechanism of any organism is result of various biochemical pathway and their products. This definitely shows that pollution does change the biochemical profile of zooplankton which might include change in amino acid, phospholipids, and proteins. Since all these changes should also affect the histology and endocrine system of zooplankton further investigations are required with this regard. This reviews suggest that pollution does not just affect zooplanktons spatially but there is more complex phenomenon of interaction of plankton and pollutant stressors. Many studies have shown that heavy metal, crude oil, PAH, pesticides etc. do effect one or more physiological parameter. Even though there are various study demonstrating effect of some stressors on few biomolecule component or element, a comprehensive comparative study of effect of various pollutant stressors on entire biochemical profile of plankton is wanting. The study of plankton parameters from actual site and unpolluted site along with plankton treated with pollutant parameter showing similar characteristics with respect to effect of biochemical analysis are needed.

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