

Historical ocean chemistry changes in relation to modern ocean chemistry with the addition of anthropogenic factors

Kristen Waltos

Department of Biology
Lake Forest College
Lake Forest, IL 60045

The Earth's oceans are valued for their beauty and resources. Across the globe people use the oceans for entertainment during summer holidays, as a source of income, and a source of food. Standing on the shore or on the deck of a cruise liner, the waters may seem pristine and never-ending. However, the continuation of life in the ocean is a delicate and ever fluctuating balance between the organic and inorganic. Fundamental ocean chemistry is at the heart of the balancing act and marine life forms can be sensitive to changes in the chemistry of the aqueous environment they live in. In the past, major changes in ocean chemistry have been linked to mass extinction events. These historical events, in some ways, parallel changes that can be seen in the oceans of the modern world. One component of chemical change in the oceans is not comparable to past events given the added man-made chemicals to the system. The additional human modification of ocean composition will have cumulative consequences beyond what might be expected based on historical records.

Oceans cover the majority of the Earth's surface and play a large role in the global carbon cycle and in the climate system as a whole (Royal Society, 2005). The chemistry of the ocean includes the chemical reactions and interactions in the marine waters covering the Earth's surface. Water, and its rather unique qualities, is the basis of ocean chemistry. The most relevant property of water is its use as a solvent. Water is commonly called the "universal solvent" due to its ability to dissolve many other substances. As a result, individual ions of different kinds are present in water; in marine water the most common ions, those making up salt, lead to the characteristic salinity of ocean water (Hill et al., 2008).

Salinity is measured as the grams of dissolved organic matter per kilogram of water. Seawater in the open ocean is more or less uniform in salinity, hovering at about 1000 milliosmoles. Teleost fish and mammals are hyposmotic to the seawater they live in, with the bony fish ranging from 300-500 milliosmoles. Behavioral and physiological adaptations allow these organisms to survive this way; fish drink water and actively pump out salt and mammals are able to produce concentrated urine. In contrast, elasmobranch fish are hyperosmotic and hypotonic to the seawater and thus have their own adaptations to survive their marine environment but with different mechanisms than teleost or mammals. Different still, most marine invertebrates are isosmotic to the sea water, leaving them most affected by subtle changes in this component of ocean chemistry. Salinity changes occur in areas like estuaries where fresh water pours into the ocean from land. Such areas are called brackish waters and animals living here have unique adaptations to the fluctuations in environmental concentrations. Animals that migrate from fresh water to ocean water, called euryhaline, have even more specialized adaptations to deal with extreme salinity changes (Hill et al., 2008).

The wide array of adaptations to the saline environment of the world's oceans demonstrates the collection of biodiversity present there. Maintaining this type of diverse biological population is essential to maintaining the overall ecological health of the ocean. The groups described above are generalized compared to the total ocean diversity. Many species are sensitive to changes in the chemical composition of their environment and so ocean chemistry fluctuations should be closely monitored.

Ions are not the only chemicals that can be dissolved in water. The world's ocean has many kinds of gases dissolved within it. The two that are most important to sea life are oxygen and carbon dioxide. The use of oxygen as a final electron acceptor in the process of producing energy for cells is vital to most life forms on the planet. For the organisms living in the ocean, it can be more difficult to obtain oxygen required to live, especially in comparison to those on land. The partial pressure of oxygen in water is dramatically lower than in air. Oxygen is not very soluble in water. In the ocean the solubility is lowered further because in aqueous solutions the solubility of gases decreases with increasing salinity (Hill et al., 2008). Because the resource of oxygen is so vital to marine ecosystems and yet so relatively scarce, any changes in oxygen composition would have drastic and potentially devastating effects on marine life. The other major gas dissolved in the waters of the ocean, carbon dioxide, can have just as much of an impact.

Oceans are an integral part of the global carbon cycle. Exchange of carbon dioxide is constantly taking place between the atmosphere and the oceans. During this exchange the carbon dioxide is transformed into carbonic acid, H₂CO₃. This weak acid dissolves into bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions that act as a natural buffer against pH changes; the ocean remains relatively alkaline around pH 8. However, buffers only have a certain capacity and if pushed beyond that capacity dramatic pH changes can occur rapidly. An increase in atmospheric carbon dioxide can eventually lead to an overwhelming of the natural buffer system resulting in ocean acidification. Escalating carbon dioxide in our atmosphere has been occurring since the industrial revolution as a direct result of humans burning of fossil fuels (Royal Society, 2005). Increased carbon dioxide and the resulting acidification effects have been proposed as extinction mechanisms in historical mass extinction events.

Vernon (2008) defines mass extinctions as high taxonomic level biodiversity changes of plants and animals by extinction over the same geological interval of time. Calcifying organisms are often examined in trying to determine causes and mechanisms of extinction. These organisms, like reef communities and some phytoplankton and zooplankton, are most affected by changes in the carbon system since they rely on carbonate to form hard shells and plates (Royal Society, 2005). Reef structures before the Permian-Triassic barrier were diverse and widespread (Vernon, 2008).

The Permian mass extinction occurred approximately 251 million years ago and was the most devastating of the big five extinctions on the planet, during which time almost all calcifying organisms went extinct (Vernon, 2005). Extreme volcanism at a site called the Siberian Traps, the largest volcanic event known to Earth's history, is thought to have released vast amounts of carbon dioxide and other gases into the atmosphere, creating environmental stress (Isozaki et al., 2007; Kamo et al., 2003). The eruption, by some calculations, increased CO₂ levels to

fifteen times what is present in the current atmosphere and could have also discharged H₂SO₃ and other acids into the atmosphere (Kamo et al., 2003). Gases diffuse from high partial pressure to low partial pressure according to Henry's Law (Hill et al., 2008). With the increased partial pressure of CO₂ in the atmosphere the driving force would be toward the carbon sink of the oceans. The elevated CO₂, if high enough to overwhelm reservoirs, alters the carbonate/bicarbonate balance so that the calcifying organisms are unable to create or maintain hard shells. After an extinction event, calcified reef systems take as long as millions of years to recover, accounting for the 'reef gaps' in the paleontological record following these events (Vernon, 2008).

Acidification is occurring in oceans today, both from natural and anthropogenic sources. Volcanic carbon dioxide vents, that are the same ambient temperature as the surrounding water column and without sulfur compounds, exist at various places on the sea floor. These areas were used to examine the effects of acidification on the communities nearby. By looking at areas of normal pH to lowered pH vents the researchers were able to see ecosystem-wide effects. The communities went from being abundant in calcareous organisms to a reduction in the sea urchin and coralline algal species and completely lacking scleractinian corals. At a pH of about 7.6 the gastropod shells were beginning to dissolve due to sub-saturation of carbonate and sea-grass production was high (Hall-Spencer et al., 2008). This is a natural mechanism of ocean acidification. Anthropogenic CO₂ deposits an excess of carbon dioxide into oceans that will cause more than localized changes in ecological structures of the ocean's communities.

Acidification in the Southern Ocean by anthropogenic CO₂ has been observed. This area has seasonal variability in carbonate and pH levels with lower levels in winter and higher levels during summer. Researchers calculated the affect that this natural variability combined with anthropogenic uptake of carbon dioxide will cause under saturation of carbonate material by the year 2030, as soon as atmospheric CO₂ levels reach a threshold value of approximately 450ppm. The study explains that this would negatively affect species using the aragonite form of carbonate, such as certain types of plankton like *Limacina helicina* (McNeil & Mearns, 2008). A negative impact on plankton species would have far reaching implications, as plankton are the base of many ocean food webs.

Another experiment focused on the effects of ocean acidification on crustose coralline algae which are a cosmopolitan species and that are present in both tropical and polar benthos at all depths. In coral reefs these algae cement carbonate to the reef structure and so act in building the stable framework of the reef. By setting up mesocosms, the researchers were able to show that acidification negatively affected calcifying algae. Colonies on cylinders in acidic environments had less cover than controls. In addition coverage by non-calcifying algae was higher in the acidic environments (Kuffner et al., 2008).

The Kuffner et al. study indicates that even cosmopolitan species will be vulnerable to the acidification of the world's oceans in the future when more anthropogenic carbon dioxide dissolves into the waters, not just in the Southern Ocean. Furthermore, although the initiation of acidification may take time because of the natural buffering system present in ocean water, so too will it take time for CO₂ levels to decline and normal alkalinity to be restored. Restoration of the normal alkaline state depends on, of course, if anthropogenic carbon dioxide is still being pumped into the atmosphere. If carbon dioxide continues to enter the atmosphere and into the ocean sink, then it could be even longer than the millions of years of recovery time after the Permian extinction. This is especially true

considering that organisms in ancient oceans may have actually been less susceptible to acidity changes because they relied on calcitic skeletons rather than the aragonite or high-magnesium calcite that are used by marine calcifying organisms in today's waters (Vernon, 2008).

With no continental ice sheets existing during the Permian period and with the only land mass of Pangaea, ocean circulation would probably have been minimal. There would not be enough oxygen supply to deep waters and ocean anoxia would develop as well as a buildup of CO₂ on the ocean floor. Besides the Siberian traps, another hypothesis of the dramatic increase in carbon dioxide during this time period is the rapid turnover of oceans worldwide introducing toxic levels of CO₂ into the water and atmosphere. In addition to changes in acidity caused by increased CO₂ levels, hypercapnia itself can result in widespread death of both ocean and land based creatures. Just as CO₂ disrupts acid-base chemistry of ocean waters, it can disrupt the balance within the fluids of ocean creatures, leading to narcotizing acidosis (Knoll et al., 1996). Since the partial pressure of carbon dioxide in aquatic animals is not very different from the ambient partial pressure, this is a real threat. The increase in acidity of the internal fluids causes respiratory pigments to change conformations and therefore decrease affinity for oxygen (Hill et al., 2008). Animals with active circulation systems would be able to cope with increase CO₂ levels better than those with passive gas exchange (Knoll et al., 1996). Hence, in the end-Permian event those animals at greatest risk are organisms such as corals.

Anoxic waters are thought by many researchers to have been a major cause of both the Permian and Devonian mass extinction events. Wignall and Hallam (1991) examined the possibility by looking at elemental ratios in rocks from the Permian/Triassic boundary. They found a negative Cerium anomaly, Pyrite formation with decreased light sulphur isotopes, and low organic carbon to pyrite sulfur ratios. These ratios would develop under euxinic, anoxic conditions and indicated a stagnant and anaerobic environment in the world's oceans during the Permian period. Another study by Kijiwara et al. (1994) also found a change in ratios of carbon, oxygen, sulfur, and strontium. These shifts occurring in synchronization imply a common mechanism of change during the period. The researchers hypothesize that an aerobic-free anoxic basin full of sulfate reducing bacteria would have existed. Transgression of the oceans and change from a stratified ocean to a thoroughly mixed one could have lead to the spread of anoxic conditions and demise of organisms unable to cope with these conditions.

Kump et al. (2005) studied another consequence of an anoxic basin full of sulfur reducing bacteria. The bacteria that use sulfur as their final electron acceptor in the electron transport chain of the mitochondria produce H₂S as a byproduct. This weak acid would remain below the chemocline; the boundary between oxygenated waters and lower anoxic waters. However, with a significant buildup of H₂S, the chemocline could become unstable. Kump et al. did many calculations to establish the exact tipping point and determined that if the partial pressure of oxygen in the atmosphere was lower than today, which it probably was, then a dramatic upward excursion of the chemocline would take place. This would release toxic levels of H₂S into the above waters and into the atmosphere. Not only is sulfuric acid at high concentrations directly toxic to organisms on land and sea, but through subsequent chemical reactions would lead to a decrease in surface OH, an increase in methane, and a drastic decrease in ozone column depth. These combined effects would have drastic impacts for life on the planet and led to massive extinction.

*This author wrote the paper as a part of BIOL484 under the direction of Dr. Menke

Anoxic events such as this are also theorized to have contributed to the end-Devonian mass extinction event. Evidence for widespread anoxic environments at the end of the Devonian comes from the Hangenberg Shale, a part of a global layer of black mudrock indicating anoxia. Increased phytoplankton production and subsequent sedimentation could have led to anoxic bottom waters and transgression, just as theorized for the Permian/Triassic boundary, would have spread this toxic environment. The spread of anoxic waters would have reduced ecological niches as organisms and communities were pushed closer to shore (Caplan & Bustin, 1999). Overcrowding and competition along with the increasingly toxic environment would have led to widespread death of benthic organisms.

A proposed mechanism for the production of anoxic waters in the Devonian period is eutrophication. This eutrophication was thought to be caused by the evolution of rooted vascular land plants during this time period (Algeo & Scheckler, 1998). Researchers Algeo and Scheckler theorize that trees and seeding plants would have accelerated the development and weathering of soils by stabilizing surfaces allowing for more weathering time; time for the decay of complex carbons. Surface water run-off would have deposited these broken down nutrients into oceans, triggering algal blooms that deplete oxygen levels in the water. Evidence for such eutrophication of ocean water can be found in the fossil record. During the time just before and immediately following the end-Devonian event, fossils show an over-representation of suspension feeders compared to framework builders, an indication of eutrophic conditions (Caplan & Bustin, 1999). Eutrophication is common in our oceans today as well.

Hypoxia occurs naturally in modern oceans, often seasonally. Seasonal hypoxia occurs when there is an increase in ocean stratification due to thermal or saline gradients, seasonal warming of ocean waters, and an increase in freshwater deposition such as monsoons. Hypoxic waters also occur in frequent upwelling regions such as East Pacific, West African, and North Indian Oceans where nutrient rich water replaces depleted surface water. This nutrient flux induces primary production and oxygen depletion. Natural hypoxia in our oceans today even leads to extensive mortality. Some examples are rock lobster aggregating inshore during water column anoxic events, fish mortality on large scales following hydrogen sulfide release (mentioned previously) caused by anoxic conditions, and Humboldt squid swimming to their deaths onto the California shoreline in 2004 and 2008 in an attempt to avoid anoxic oceans (Levin et al., 2009). Even with such occasional mortalities, the natural cycles of hypoxia are stabilized in the environment. Human caused hypoxia by eutrophication, however, disrupts communities not adapted to seasonal hypoxic conditions.

Human induced hypoxia via eutrophication occurs near watersheds and areas of high agricultural activity. Eutrophication occurs with increased nitrogen and phosphorous availability (Levin et al., 2009), such as in our fertilizers. Run off from areas that humans have used nitrogen and phosphorous rich fertilizer moves these limiting nutrients into oceans. This creates algal blooms of longer duration and greater frequency, leading to hypoxia and overall degradation of the area. Although phosphorous inputs have decreased due to better waste-water management, a majority of the estuaries in the United States have been degraded due to pollution induced hypoxia (Howarth et al., 2011). These pollutants are flowing into ocean waters not naturally accustomed to eutrophication events. Humans add chemicals to our oceans that marine organisms are not evolutionarily adapted to deal with and these chemicals go beyond just nitrogen and phosphorous.

The development of modern agriculture came not only with fertilizers containing high levels of select nutrients like nitrogen and phosphorous, but with pesticides to protect our plants as well. Many of the organochlorine pesticides such as DDT, used in the past, had extremely detrimental and long lasting effects on marine life. These pesticides are accompanied by other chemicals like polychlorinated biphenyls (PCBs) that have made it into modern oceans from machinery and plastic production. Organochlorine pesticides were first introduced in the 1940s but have been banned and regulated in the United States since the 1970s (Iwata et al., 1994). During the time it was used, it is estimated that about 25% of the production of DDT reached the ocean (Portmann, 1975). This is probably an underestimate since the research was done many years ago and the chemicals are continuing to be found in ocean food webs in high concentrations today.

Hexachlorocyclohexane (HCH) is another pesticide being deposited in the world's oceans through atmospheric transport from lower latitudes. HCH levels have been found in arctic regions at double the concentrations of tropical regions, which indicates that the arctic oceans are acting as sinks for these chemicals as they are deposited through rain and snow in these regions. The organochlorines are hydrophobic and so aggregate on particulates before sinking to the ocean floor where they accumulate in measurable quantities (Iwata et al., 1994). The chemicals enter the food web as zooplankton accumulate them from the water column and benthic amphipods obtain the chemicals from the ocean floor (Hargrave et al., 1992). Uptake of organochlorines and other chemicals from the ocean floor by the benthic invertebrates and fish at high concentrations is the pathway by which these harmful chemicals move up trophic levels, eventually getting to top predators (Bright et al., 1995). In this way, all trophic levels and all types of marine organisms are affected. The top predators, however, are possibly more susceptible to these chemicals.

Organochlorine and other chemicals humans have introduced into marine food webs are dangerous to all trophic levels. Portmann gives examples from different animal taxa; crustaceans are possibly susceptible to pesticides being related to insects, trout have failed to reproduce in areas of high concentrations of DDT, and DDE and DDT can interfere with calcium metabolism in birds and also cause reproductive failure especially in species that feed on marine fish. However, bioaccumulation means that the higher the trophic level, the higher concentration of contaminants. Since these chemicals are hydrophobic, there is a strong affinity to the lipid tissues (Tanabe et al., 1994) in marine mammals such as seals and cetaceans. Therefore, these top predators are greatly affected by these chemicals in many ways.

Studies show that organochlorines accumulate with the age of the mammal and accumulate more in males than females. The first fact lies in bioaccumulation at higher trophic levels, since the more the animal eats throughout its life the more contaminants it would have. Males have higher levels than females can be explained with the transfer of organochlorines from mother to offspring. A study on Harbor Seals found increased levels of contaminants in non-pregnant females as compared to pregnant or recently pregnant females. Furthermore, still-born pups had increased levels of PCB in their blubber (Reijnders, 1980). Another study on cetaceans found that approximately 60% of the contaminants in the mother are transferred to the offspring through lactation (Tanabe et al., 1994). This is important because it demonstrates that these chemicals stay within body systems of the mammals. Instead of depleting or being broken down, they are simply passed from one animal to the next. The consequences of this can be severe on populations.

Increased abortion rates have been found in Harbor Seals with high concentrations of contaminants such as DDT and PCB. The possible mechanism for this lies in steroid balance. DDT and PCB have been shown to accelerate the breakdown of steroid hormones such as androgens and estrogens (Reijnders, 1980). This is because these chemicals activate cytochrome P-450 monooxygenases. These enzymes modify the contaminants to more toxic compounds, which then disrupt the production and maintenance of steroids (Tanabe et al., 1994). It is possible that the steroid imbalances contribute to lack of implantation or abortion of fetuses if they interrupt normal pregnancy hormone fluctuations. However, even a calf or pup that is born could be at risk from the high levels of contaminants in their system.

A study of Beluga whales found that many females had lesions to mammary glands that could affect the proper feeding of calves (Beland et al., 1993). Similarly, Harbor seal pups were seen with inflamed umbilical regions after birth, an indication of infection (Reijnders, 1980). It has been hypothesized that certain contaminants like PCBs are immunosuppressive. This can be demonstrated with a study on Beluga whales.

Beland et al. looked at the health of beluga whales in the St. Lawrence estuary in Canada. Numerous health problems plague the population. Tumors were found in many of the individuals, in many tissue types, including some that were cancerous. The digestive systems of the whales also had many lesions from the mouth to the intestines. Spinal deformations similar to scoliosis were also found in an abnormally high percentage of the individuals studied. Immune suppression was indicated by ciliate protozoan pneumonia, a herpes-like viral particle, and opportunistic bacterial infections. Overall the presence of high PCBs and organochlorine contaminants in the population was correlated with these health issues (Beland et al., 1993). The sheer amount of health problems puts not only individuals at risk of death from any of these diseases but puts the entire population in jeopardy.

Factors that increase the risk of extinction do not work alone. Instead the factors build upon each other and amplify one another in a multiplicative fashion (Brook et al., 2008). The cascading effects of these synergies make predicting future extinction timelines exceedingly difficult. Looking back at the largest extinction events in Earth's history, we can see synergies among the proposed and theorized modes of extinction. In the Devonian anoxia hypothesis, the anoxic waters spread only as a result of the cooling climate, replacing stratified oceans with un-stratified in a massive mixing event (Caplan & Bustin, 1999). The cooling climate and brief glaciations during the time period could have been a driver for the extinction of some species in itself. This climactic cooling, in turn, could have been caused by the evolution of vascular land plants with their increased uptake of CO₂ from the atmosphere, lowering global levels and temperature. The climatic cooling effect would have been in addition to the eutrophication that vascular plants could have caused in coastal areas (Algeo & Scheckler, 1998) creating a web of synergistic factors working together to create one of the big five extinction events known to have taken place.

The factors affecting ocean chemistry in the modern world are also working synergistically, similar to the past extinctions. For example, eutrophication of our oceans could be exacerbating acidification since the increased consumption of O₂ includes an increase in CO₂ production and this gas, as demonstrated previously, is acidic. A warmer ocean, perhaps the opposite of the Devonian situation, is more stratified and holds less oxygen, leading to increased hypoxia (Levin et al., 2009). The problem in comparing our current situation to the previous

mass extinction synergies, however, comes when considering the added human synergistic factors.

Although ocean hypoxia, acidification, and overall chemistry changes can be naturally occurring, humans are exacerbating all natural processes past what could ever be predicted based on historical events. It is estimated that half of all anthropogenic CO₂ is still in the atmosphere (or more since we create more every second) and yet we have used up an estimated third of the capacity of the ocean reservoir (Vernon, 2008). This high level of anthropogenic CO₂ has the potential to accelerate ocean acidification by exacerbating the natural variability already present in ocean acidification cycles (McNeil & Mearns, 2008). Additionally, human induced hypoxia will work synergistically with natural hypoxia episodes to both generate new hypoxic events and intensify existing ones (Levin et al., 2009), possibly even to the point of widespread anoxia. The addition of man-made fertilizer chemicals will act multiplicatively with natural eutrophication cycles making algal blooms more abundant, frequent, and widespread.

All of the natural extinction factors mentioned have the potential to be exacerbated by the current human impact. We can attempt to predict the effects this will have by extrapolating from previous extinction events, although any attempt has the potential to grossly underestimate the global influence. However, we have no reference point for the completely novel chemicals that humans have added to the delicate system in the past several decades. These chemicals have been demonstrated to cause not only negative reproduction consequences, but a wider range of health problems, making these man-made contaminants detrimental to both the young and old in populations of top predators. We cannot base predictions in this case on the historical record; there is no precedent for the contaminants we have added and no species have evolved to deal with such a threat. The current crisis involves layers of multiplicative synergistic factors spanning all taxa and trophic levels. With nothing to base this event on, we might not be able to reverse or prevent the next mass extinction.

Note: Eukaryon is published by students at Lake Forest College, who are solely responsible for its content. The views expressed in Eukaryon do not necessarily reflect those of the College. Articles published within Eukaryon should not be cited in bibliographies. Material contained herein should be treated as personal communication and should be cited as such only with the consent of the author.

References

- Algeo, T. J., Scheckler, S. E. (1998). Terrestrial-marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes, and marine anoxic events. *Philosophical Transactions of the Royal Society of London*, 353, 113-130.
- Beland, P., DeGuisse, S., Girard, C., Lagace, A., Martineau, D., Michaud, R., Muir, D. C. G., Norstrom, R. J., Pelletier, E., Ray, S., Shugart, L.R. (1993). Toxic compounds and health and reproductive effects in St. Lawrence beluga whales. *Journal of Great Lakes Research*, 19, 766-775.
- Bright, D. A., Dushenko, W. T., Grundy, S. L., Reimer, K. J., (1995). Effects of local and distant contaminant sources: polychlorinated biphenyls and other organochlorines in bottom-dwelling animals from an Arctic estuary. *The Science of the Total Environment*, 160/161, 265-283.

- Brook, B. W., Sodhi, N. S., Bradshaw, C. J. A., (2008). Synergies among extinction drivers under global change. *Trends in Ecology and Evolution*, 23, 453-460.
- Caplan, M. L., Bustin, R. M. (1999). Devonian-carboniferous Hangeberg mass extinction event, widespread organic-rich mudrock and anoxia: causes and consequences. *Paleogeography, Paleoclimatology, Paleoecology*, 148, 187-207.
- Hall-Spencer, J., Rodolfo-Metalpa R., Martin S., Ransome E., Fine, M. Turner, S. M., Rowley, S. J., Todesco, D., Buia, M. C.. (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature*, 454, 96-99.
- Hargrave, B.T., Harding, G. C., Vass, W. P., Erickson, P.E., Fowler, B. R., Scott, V. (1992). Organochlorine pesticides and polychlorinated biphenyls in the Arctic Ocean food web. *Archives of Environmental Contamination and Toxicology*, 22, 41-54.
- Hill, R.W., Wyse, G. A., Anderson, M. (2008). Animal physiology. Second edition. Sunderland, MA: Sinauer Associates, Inc.
- Howarth, R., Chan, F., Conley, D. J., Garnier, J., Doney, S. C., Marino, R., Billen, G. (2011). Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. *Frontiers in Ecology and the Environment*, 9, 18-26.
- Isozaki, Y., Shimizu, N., Yao, J., Ji, Z., Matsuda, T. (2007). End-Permian extinction and volcanism-induced environmental stress: the Permian-Triassic boundary interval of lower-slope facies at Chaotian, south China. *Paleogeography, palaeoclimatology, Palaeoecology*, 252, 218-238.
- Iwata, H., Tanabe, S., Aramoto, M., Sakai, N., Tutsukawa, R. (1994). Persistent organochlorine residues in sediments from the Chukchi sea, Bering sea, and Gulf of Alaska. *Marine Pollution Bulletin*, 28, 746-753.
- Kajiwara, Y., Yamakita, S., Ishida, K., Ishinga, H., Imai, A. (1994). Development of a largely anoxic stratified ocean and its temporary massive mixing at the Permian/Triassic Boundary supported by the sulfur isotopic record. *Paleoclimatology, Paleoecology*, 111, 367-379.
- Kamo, S. L., Czamanske, G. K., Amelin, Y., Fedorenko, V.A., Davis, D.W., Trofimov, V. R. (2003). Rapid eruption of Siberian flood-volcanic rocks and evidence for coincidence with the Permian Triassic boundary and mass extinction at 251 Ma. *Earth and Planetary Science Letters*, 214, 75-91.
- Knoll, A.H., Bambach, R.K., D. E. Canfield, D. E., Grotzinger, J. P. (1996). Comparative earth history and late Permian mass extinction. *Science*, 273, 452-457.
- Kuffner, I. B., Andersson, A. J., Jokiel, P. L., Rodgers, K. S., Mackenzie, F. T. Decreased abundance of crustose coralline algae due to ocean acidification. (2007). *Nature Geoscience*, 1, 114-117.
- Kump, L. R., Pavlov, A., Arthur, M. A. (2005). Massive release of hydrogen sulfide to the surface ocean and atmosphere during intervals of oceanic anoxia. *Geology*, 33, 397-400.
- Levin, L.A., Ekau, W., Gooday, A. J., Jorissen, F., Middelburg, J. J., Naqvi, S. W. A., Neira, C., Rabalais, N. N. Effects of natural and human-induced hypoxia on coastal benthos. (2009). *Biosciences*, 6, 2063-2098.
- McNeil, B. I., Matear, R. J. (2008). Southern ocean acidification: a tipping point at 450-ppm atmospheric CO₂. *Proceedings of the National Academy of Sciences of the United States of America*, 105, 18860-18864.
- Portmann, J.E. (1975). The bioaccumulation and effects of organochlorine pesticides in marine animals. *Proceedings of the Royal Society of London*, 189, 291-304.
- Reijnders, P.J.H. (1980). Organochlorine and heavy metal residues in harbor seals from the Wadden sea and their possible effects on reproduction. *Netherlands Journal of Sea Research*, 14, 30-65.
- Royal Society. Ocean acidification due to increasing atmospheric carbon dioxide. (2005). Cardiff, UK. The Clyvedon Press Ltd.
- Tunabe, S., Iwata, H., Tutsukawa, R. (1994). Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. *The Science of the Total Environment*, 154, 163-177.