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## Analysis of Long-Term Response of Seawater to Change in CO<sub>2</sub>, Heavy Metals and Nutrients Concentrations

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Abstract: The seawater is subject to multiple external stressors (ES) including rising atmospheric CO2 and ocean acidification, global warming, atmospheric deposition of pollutants and eutrophication, which deeply alter its chemistry, often on a global scale and, in some cases, at the degree significantly exceeding that in the historical and recent geological verification. In ocean systems the micro- and macronutrients, heavy metals, phosphor- and nitrogen-containing components exist in different forms depending on the concentrations of various other species, organic matter, the types of minerals, the pH etc. The major limitation to assessing more strictly the ES to oceans, such as pollutants (atmospheric greenhouse gas, heavy metals, nutrients as nitrates and phosphates) is the lack of theoretical approach which could predict the ocean resistance to multiple external stressors. In order to assess the abovementioned ES, the research has applied and developed the buffer theory approach and theoretical expressions of the formal chemical thermodynamics to ocean systems, as heterogeneous aqueous systems. The thermodynamic expressions of complex chemical equilibria, involving acid-base, complex formation and mineral ones have been deduced. This thermodynamic approach utilizes thermodynamic relationships coupled with original mass balance constraints, where the solid phases are explicitly expressed. The ocean sensitivity to different external stressors and changes in driving factors are considered in terms of derived buffering capacities or buffer factors for heterogeneous systems. Our investigations have proved that the heterogeneous aqueous systems, as ocean and seas are, manifest their buffer properties towards all their components, not only to pH, as it has been known so far, for example in respect to carbon dioxide, carbonates, phosphates, Ca2+, Mg2+, heavy metal ions etc. The derived expressions make possible to attribute changes in chemical ocean composition to different pollutants. These expressions are also useful for improving the current atmosphereocean-marine biogeochemistry models. The major research questions, to which the research responds, are: (i.) What kind of contamination is the most harmful for Future Ocean? (ii.) What are chemical heterogeneous processes of the heavy metal release from sediments and minerals and its impact to the ocean buffer action? (iii.) What will be the long-term response of the coastal ocean to the oceanic uptake of anthropogenic pollutants? (iv.) How will change the ocean resistance in terms of future chemical complex processes and buffer capacities and its response to external (anthropogenic) perturbations? The ocean buffer capacities towards its main components are recommended as parameters that should be included in determining the most important ocean factors which define the response of ocean environment at the technogenic loads increasing. The deduced thermodynamic expressions are valid for any combination of chemical composition, or any of the species contributing to the total concentration, as independent state variable.

Keywords: atmospheric greenhouse gas, chemical thermodynamics, external stressors, pollutants, seawater

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