

Editorial

Special Issue on Complexation of Metals in Natural Fluids: Simulations, Experiments and Applications

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The complexation of metals in natural fluids, such as natural waters and biological fluids, is a key process in the context of environmental and biological phenomena. The study of the formation of complexes is crucial in processes such as the removal of contaminants from natural waters, in the exploitation of chelation therapies in metal detoxification, sensors, transport and the efficacy of drugs. Therefore, this kind of investigation can follow the thermodynamic approach necessary to assess the formation constants of the different complex species [1,2], their stability under conditions in which natural fluids are found and the possible applications of complex formation in processes involving removal of toxic metal cations from either physiological fluids or polluted waters. Other studies can be directly conducted on real samples [3–5], such as sea, river, lake waters, and can concern both the speciation of metal cations, i.e., the distribution of an element among defined chemical species, as well as the application of new materials for their removal from natural waters [5]. Similar to other research fields, metal complexation investigations can be carried out via different experimental techniques as well as their combination with advanced computational approaches. Five papers in the field of metal complexation in natural fluids are collected in the current Special Issue.

Foti et al. [1] studied the interactions of As(III), a contaminant present in different environmental compartments, with four carboxylic acids, five amines, and four amino acids, evaluated via experimental methods and quantum–mechanical calculations. The experimental results were also analyzed with those previously obtained for thio-carboxylic ligands, obtaining a rough estimate of the contribution of each functional group to the complexation of As(III). The results of quantum–mechanical calculations confirmed and interpreted the higher binding capabilities of the thiol group on an atomistic basis and indicated the possibility of the simultaneous binding of As(III) via the thiol and carboxylic groups.

Furia et al. [2] studied the acid–base behaviour of a natural antioxidant, coumarin-3-carboxylic acid and its chelating properties towards neodymium(III) and dioxouranium(VI) (uranyl) at 37 °C in an aqueous solution (0.16 mol/L in NaClO₄) using potentiometric and UV–Vis spectrophotometric measurements. The results of this speciation study reveal that coumarinic anions form metal ligand species with stoichiometry 1:1 and 1:2 types with both metal ions. Uranyl ion also forms a polynuclear species with stoichiometry 2:2.

Omanovic et al. [3] reported the results of a study on the concentration and distribution of different trace metals, namely Zn, Cd, Pb, Cu, Ni, Co, Mn, Fe and Al, between five size fractions (5 µm) along the vertical salinity gradient of the Krka River estuary in Croatia, employing syringe filtration, centrifugal ultrafiltration (for metals in the truly dissolved fraction), acid extraction, stripping voltammetry, and high-resolution–inductively coupled plasma–mass spectrometry (HR-ICP-MS).

In the study by Berto et al. [4], the main ionic components in water extracts of atmospheric depositions, collected at eight sites in Antarctica, were quantified using ICP-OES



Citation: Cassone, G.; Foti, C.; Giuffrè, O.; Saija, F. Special Issue on Complexation of Metals in Natural Fluids: Simulations, Experiments and Applications. *Appl. Sci.* **2023**, *13*, 3320. <https://doi.org/10.3390/app13053320>

Received: 17 February 2023

Accepted: 1 March 2023

Published: 6 March 2023



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(inductively coupled plasma–optical emission spectroscopy), HR-ICP-MS (high resolution–inductively coupled plasma–mass spectroscopy) and ionic chromatography. A chemical model with the main components of the samples— Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Mn^{2+} , Zn^{2+} , $\text{Fe}^{2+}/^{3+}$, Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , HCOO^- , and CH_3COO^- —was used to predict the effect of increasing concentrations and modelling the biogeochemical cycles of metal cations.

Fontàs et al. [5] studied the preparation and testing of a polymer inclusion membrane (PIM), made from polymer cellulose triacetate, extractant di-(2-ethylhexyl) phosphoric acid, and a plasticizer 2-nitrophenyloctyl ether, employed as a sensor for Zn and Cu complexes. This PIM sensor has been shown to effectively transport free metal ions, and the accumulation of metals in the receiving phase is greatly influenced by the presence of ligands, such as ethylenediaminetetraacetic acid and humic acid, which form stable complexes with divalent metal cations. The effect of the main ions in natural waters was studied, and it was found that the accumulation of Zn or Cu did not decrease due the presence of calcium. A PIM sensor was also successfully used for a metal complexation assessment in river waters affected by Zn pollution.

Although submissions for this Special Issue are closed, the topic of metal complexes is always important and sparks great enthusiasm among scholars due to all possible applications in environmental, medical, and pharmaceutical fields.

Author Contributions: Conceptualization, G.C., C.F., O.G. and F.S.; writing—original draft preparation, G.C., O.G.; writing—review and editing, G.C., C.F., O.G. and F.S.; supervision, G.C., C.F., O.G. and F.S. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: We thank all the authors of the manuscripts for contributing to this research topic, as well as all peer reviewers for their rigorous and fair feedback. We would also thank all the staff involved in this Special Issue.

Conflicts of Interest: The author declares no conflict of interest.

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