Mercury Speciation in the Water Distribution System of Skiatros Island, Greece †

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† Presented at the 3rd EWaS International Conference on “Insights on the Water-Energy-Food Nexus”, Lefkada Island, Greece, 27–30 June 2018.

Published: 2 August 2018

Abstract: In recent years, mercury (Hg) concentration that exceeds the Maximum Contaminant Level Standard set by the World Health Organisation for drinking water has been detected in the groundwater of Skiatros Island in Greece. The island single source of urban water is groundwater; as a result, tap water has been characterised as unsafe for drinking and people rely on bottled water for their everyday needs. The origin and speciation of Hg in the aquifer is investigated with the use of the Pourbaix diagram, while the possible correlation with groundwater salinization due to seawater intrusion is examined.

Keywords: Pourbaix diagram; mercury speciation; groundwater salinisation

1. Introduction

During the last few decades, there has been a growing interest worldwide in mercury and the mechanisms that govern its concentrations in air, soil and water. In many parts of the world, health authorities are becoming increasingly concerned about the effects of heavy metals on the environment and human health [1]. Mercury is one of the most important heavy metal environmental pollutants because of its volatility and accompanying long-range atmospheric transport, its toxicity and its ability to bioaccumulate in organisms [2,3]. Unlike organic contaminants, metals do not undergo microbial or chemical degradation, persisting in their original quantities after their introduction into the environment. Some of them also accumulate in living organisms, causing various diseases and disorders [4]. Mercury has often been used in the chloralkali process, the wood pulping industry, technical instruments (thermometers, barometers), electrical equipment (batteries), dentistry, paints, and military applications, inevitably leading to soil and groundwater contamination [5].

A serious problem that is raised considers the mercury contamination of aquifers used as sources of potable or irrigation water. The subsurface environment may be contaminated either from the mobilization of Hg in geological deposits or from anthropogenic sources [6]. Often, high Hg concentrations in sediments have a natural origin, an example being the Mediterranean Sea, where the basin contains about 65% of the total world Hg mineral resources [7,8]. Mercury enters the environment as either ionic divalent mercury [Hg(II)] or elemental mercury [Hg0] subjected to various biotic and abiotic transformations. As the chemical speciation of mercury greatly affects its toxicity and transport, the fate of mercury in the subsurface is critical to groundwater quality and public health. Mercury sulfide (HgS, known as cinnabar and meta-cinnabar), is a major ore mineral, and one of the largest Hg sinks in contaminated sediments and soils. Dissolution of cinnabar in
aquatic environments is complex and the process could be conceptually simplified in two steps, (a) ionic dissociation of HgS to Hg²⁺ and S²⁻ in water and (b) chemical transformations of the ionic dissociation products [9]. A variety of environmental factors may enhance or inhibit cinnabar dissolution by affecting the aforementioned chemical transformations, most important being the redox tendency (pc or Es) of the subsurface local environment, including groundwater, as well as the presence of Hg binding ligands [10].

Aquifer over exploitation near coastal areas disrupts the hydrostatic equilibria established by hydraulic connections that possibly exist between the water reservoirs and seawater [11]. Hydraulic gradients following intensive withdrawal of freshwater in this type of aquifer can favor salt-water intrusion, which degrades the quality of water. Due to the drinking water standards established by various authorities (EU, USA, Canada), salinity values are required to remain low [12]. In addition, aquifer salinisation is often linked with the presence of Hg, as in Tuscany, Italy and New Jersey, USA [2,13,14].

In New Jersey, potable supply wells were found to yield water in which concentrations of total Hg (unfiltered samples) exceed the State and US Environmental Protection Agency drinking-water maximum contaminant level of 2 μg/L [14,15]. In Tuscany, specifically in the Orbetello-Mt. Argentario area, routine analyses of several wells in the mid-1990s revealed anomalies in Hg concentration, far beyond the upper limit for drinking water standards fixed by Italian law (1 μg/L). This was not an isolated case along the southern Tuscany coast, since about 50 km north, in the Gulf of Follonica, three wells used for drinking water were forced shut in 1995 on account of Hg contamination. Interestingly, in both cases, contamination was coupled with a steep increase in Cl⁻ values related to the intrusion of seawater [13]. Furthermore, along the coast of the province of Grosseto in southern Tuscany, the well water of five areas started to present Hg concentrations above the limit for drinkable water in 1998. In this part of Tuscany, mercury occurs both as ore deposit and as clastic material within shallow alluvial sediments. Grassi and Netti [2] also observed a close relationship between Cl⁻ and Hg in different areas, concluding that higher Cl⁻ contents always correspond to higher Hg concentrations in water.

Overall, in many studies, concerns have been expressed for the increased salt intrusion into the coastal aquifer in regards to the release of heavy metals, such as Hg, to the drinking water supply [16]. For different reasons, such as groundwater over-exploitation, sea-level rise and increased salt applications for winter deicing in northern watersheds, many areas in the US, Europe, and Canada face the same problem, i.e., the contamination of the water supply with Hg [1,2,13–17]. The causes of such elevated heavy metal concentrations in response to the increased salt concentrations have been attributed to cation exchange, complex formation with Cl⁻ and colloidal dispersion [17]. In this paper, a preliminary study for the speciation of Hg in the water system of Skiathos Island, Greece is presented. The possible reasons for the observed Hg contamination are examined and an evaluation of the possible relations to the intrusion of seawater is presented.

2. Materials and Methods

The island of Skiathos is one of the most popular Greek Islands; it has 5000 permanent residents, while island population grows rapidly during the summer tourist season lasting 5 to 6 months and peaking in August. The tourism industry is a key sector of the island’s economy [18]. The island of Skiathos has a small water distribution network with a total of about 3500 water consumption meters; the water demands present high variability and seasonality, while its network has reportedly some of the highest water leakage in Greece. The island faces serious water supply issues, since potable water comes from groundwater of low quality due to aquifer salinization [19]. The entire island water network is mainly supported by a single drilling in the area of Ftelia, while a second smaller one has recently become operational in Ag. Antonios.

According to the water utility company of Skiathos (DEYASK), which is conducting monthly samplings in the water system for quality testing, Hg has been detected above the permitted limit. The concentration of Hg has been measured repeatedly to attain values up to 6 μg/L, while the maximum permitted European limit for total Hg in the drinking water is 1 μg/L [20,21] (appearing
as a red line in Figure 1). According to data from DEYASK, the increase in Hg concentration shows the same periodicity pattern as the water consumption. Increased pumping seems to lead to increased concentrations of Hg in the water, with a hysteresis of 1–4 months as seen in Figure 1.

The increase of Hg concentration in the water system is a cause of concern, particularly from 2008 onwards, without a firmly substantiated explanation. The absence of possible anthropogenic sources of Hg in the vicinity of Skiathos suggests that the observed Hg in groundwater comes from natural sources, in particular Hg-rich underground minerals. The decrease in Hg concentration after February of 2015 that is observed in Figure 1 is artificial since DEYASK started to mix the contaminated water with uncontaminated water from the second supplementary drilling, in order to achieve lower concentrations in the water distribution network [22].

![Figure 1](image-url)

**Figure 1.** Mean daily water consumption (green bars) and Hg concentration (blue line) from 2008 to 2016 for the island of Skiathos. The red line is the Maximum Concentration Limit of Hg for drinking water.

The island’s water problem is aggravated by two key factors: the seasonal sharp increase in water consumption due to tourism and the impact of climate change resulting in a temperature rise and rainfall reduction [23,24]. According to Kofinas et al. [25], the increase in water demand is directly related to tourist arrivals in Skiathos, which results in summer water demand being about 170% higher than that of winter. In order to satisfy the growing needs of the island during the tourist season, groundwater pumping increases, resulting in the influx of sea water that makes the water brackish.

Since mercury is naturally found on the earth’s crust mainly in the form of the mineral cinnabar (HgS), it would be reasonable to assume that the same form is present in the subsurface minerals of the Skiathos island, conforming to the relatively high abundance of mercury in the underlying crustal bed of the Mediterranean [7,8]. However, since HgS is practically insoluble in water with an extremely low solubility product $K_{sp}$ of $1.4 \times 10^{-45}$ [26], we postulate that due to groundwater salinisation, the increase in chloride ion concentration shifts the reaction equilibria towards a higher degree of mercury solubilization by complexation with $Cl^-$ anions, resulting in the appearance of Hg in the water, as emerged by the chemical analyses carried out by DEYASK. By this process, a part of Hg contained in the minerals escapes to the water and consequently to the main network of the island. A first step for the investigation of the contamination with Hg in the Skiathos water system is to identify the speciation of Hg in groundwater.

Under certain conditions, when a solid mineral is exposed to an aqueous solution of inorganic species, chemical reactions may occur on the mineral surface, yielding products which may enter the aqueous phase if sufficiently soluble or remaining on the surface as secondary solid phases. These mineral transformation reactions may be studied by $pc$-$pH$ or $Eh$-$pH$ diagrams ($pc$ and $Eh$ represent the oxidation-reduction tendency of the water medium and $pH$ represents the activity of the
hydrogen ion H\(^+\)), also known as Pourbaix or stability diagrams. Since kinetic bottlenecks are neglected by the assumption of sufficient time available for the reactions completion, these diagrams have been proven to be very useful in geochemistry [27], and are collected in the Pourbaix Atlas [28,29].

In general, a Pourbaix diagram is a kind of phase diagram that shows the stability boundaries for an interaction system consisting of several compounds of a chemical element in water within a range of redox conditions and pH. The diagrams are divided into areas, each of which represents a locally predominant species. A \(p\varepsilon\)-pH diagram can describe not only the effects of potential and pH but also of chemical complexation, temperature and pressure. By convention, \(p\varepsilon\)-pH diagrams always show the thermodynamically stable area of water with different marked lines [30] (Figure 2). An aqueous solution phase is always present in such a system. At a given pH and \(p\varepsilon\), the stability of a particular chemical form of an element may be immediately judged by the knowledge of the pH and the redox intensity of the solution (\(p\varepsilon\)), and thus, the most likely chemical form of the element at the specified conditions can be determined [31,32].

In the present study, the Pourbaix diagrams were applied for the identification of dissolved Hg in the water system of Skiathos, using available data from DEYASK. For the construction of Pourbaix diagrams, the values of pH and \(p\varepsilon\) are necessary. However, a direct measurement of the redox conditions of groundwater is difficult to perform. It is therefore generally preferable to evaluate it through the use of redox couples [33]. Considering the redox couples of \(\frac{NO_3^-}{NO_2^-}\) and \(\frac{NO_3^-}{NH_4^+}\), whereas the concentrations of nitrogen species have been measured analytically in Skiathos, Equations (1) and (2) are obtained which enable an estimation to be made for the redox intensity of the groundwater.

\[
p\varepsilon_1 = \frac{1}{2} \log_{10}(K_1) - pH + \frac{1}{2} \log_{10}\left(\frac{[NO_3^-]}{[NO_2^-]}\right) \quad (1)
\]

\[
p\varepsilon_2 = \frac{1}{8} \log_{10}(K_2) - \frac{10}{8} pH + \frac{1}{8} \log_{10}\left(\frac{[NO_3^-]}{[NH_4^+]}\right) \quad (2)
\]

The values \(p\varepsilon_1^o = \left(\frac{1}{2}\right) \log_{10}(K_1)\) and \(p\varepsilon_2^o = \left(\frac{1}{8}\right) \log_{10}(K_2)\) are known from literature to be 14.5 and 14.90, respectively [34], where \(K_1\) and \(K_2\) are the equilibrium constants of the reduction half-reactions. The value of the dimensionless quantity \(p\varepsilon\) represents an indicator of the redox condition of the subsoil from which the water is pumped.

Grassi and Netti [2] identify the source of Hg in well waters using its Pourbaix diagram in the Mediterranean area of Grosseto, Tuscany during the summer of 1998. The areas of Grosseto and Skiathos have many similarities, both located near the coast with groundwater salinisation due to seawater intrusion and a comparable seasonal variability due to tourism; furthermore, cinnabar may exist in both areas. Considering that the pH of groundwater was found to vary within the range 6.3 to 8.0, it was concluded that HgS could be stable only in significantly reducing conditions. On the other hand, Hgl has a wider stability field, remaining stable under both reducing and oxidizing conditions (Figure 2). Due to the similarities of Grosseto and Skiathos, the former Pourbaix diagram [2] is used here for the identification of dissolved Hg speciation.
3. Results and Discussion

By using the DEYASK monthly data for pH and the concentrations of NO\textsubscript{3}, NO\textsubscript{2}, NO\textsubscript{4}, the values of $p_{\varepsilon_1}$, $p_{\varepsilon_2}$ were calculated by equations 1 and 2 on a monthly basis; they were then averaged on a yearly basis from 2003 to 2017, and they are presented in Table 1.

Table 1. Yearly Average of $p_{\varepsilon_1}$, $p_{\varepsilon_2}$ from 2003–2017 based on pH values for Skiathos water system.

| Year | pH  | Yearly Average $p_{\varepsilon_1}$ | Yearly Average $p_{\varepsilon_2}$ |
|------|-----|------------------------------------|------------------------------------|
| 2003 | 7.55| 6.93                               | 5.31                               |
| 2004 | 7.73| 7.08                               | 4.99                               |
| 2005 | 7.64| 7.23                               | 5.28                               |
| 2006 | 7.90| 6.89                               | 5.04                               |
| 2007 | 8.29| 6.11                               | 4.64                               |
| 2008 | 7.65| 7.64                               | 5.45                               |
| 2009 | 8.08| 7.32                               | 4.93                               |
| 2010 | 8.04| 7.25                               | 4.93                               |
| 2011 | 7.96| 7.39                               | 5.02                               |
| 2012 | 8.02| 7.24                               | 4.92                               |
| 2013 | 7.94| 7.38                               | 5.06                               |
| 2014 | 8.33| 6.83                               | 4.53                               |
| 2015 | 8.07| 7.18                               | 4.87                               |
| 2016 | 8.05| 7.29                               | 4.87                               |
| 2017 | 7.44| 7.58                               | 5.54                               |

Considering the Pourbaix diagram shown in Figure 2 and the Skiathos average pH value range (7.44 to 8.33), the resultant values of $p_{\varepsilon_1}$ span the range 6.11 to 7.64 (Table 1), whereas the values of $p_{\varepsilon_2}$ are even lower in the range 4.53—5.54 (Table 1). Both indicators suggest that Hg is predominantly in the form of elemental (metallic) Hg\text{I} and possibly small amounts of solid Hg\text{II}Cl\text{I} (calomel). Compared with the results of Grassi and Netti [2], it appears that the underground environment, from which water in Skiathos is pumped, is less oxidizing. According to data for the period 2003–2017, the approximate average chloride ion concentration in the water was 800 mg/L while that for the sulphate anions was 90 mg/L.

In the Pourbaix diagram constructed by Grassi and Netti [2], it was assumed that Cl\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} concentrations are $10^{-3}$ M, which is not fully applicable in the case of Skiathos, where Cl\textsuperscript{−} concentration was measured to be 20 times higher (~0.023 M). The higher Cl\textsuperscript{−} content of the Skiathos...
groundwater is expected to result in the presence of chlorine-containing Hg species in the form of water-soluble HgCl₂ and HgCl₂⁻ complexes.

The solubility of metallic Hg in water is 45 μg/L [33], which corresponds to a concentration of 2.24 × 10⁻⁷ M at a temperature of 20 °C. The solubility of Hg₂Cl₂ in pure water is determined by the solubility product of K_{sp,Hg₂Cl₂} = [Hg₂⁺][Cl⁻]² = 1.43 × 10⁻¹⁸ at 20 °C, therefore the concentration of a saturated solution of Hg₂Cl₂ is 8 × 10⁻⁸ M, which corresponds to 3.8 × 10⁻⁶ mg/L Hg₂Cl₂ or 7.7 mg/L Hg. Considering the relatively high average concentration of Cl⁻ of approximately 0.023 M in water and its “common-ion effect” on the solubility product, the solubility of Hg₂Cl₂ decreases dramatically, with a final value of [Hg₂⁺] = 2.7 × 10⁻¹⁵ M corresponding to 2 pg/L Hg. This approach suggests that Hg at such Cl⁻ concentrations is not expected to be found as a dilute solution of calomel (Hg₂Cl₂).

Consequently, a first estimate of the speciation of dissolved Hg in Skiathos water system is the presence of mostly metallic Hg, followed by traces of Hg₂Cl₂ and chlorine-containing complexes of Hg(II) without being able to exclude organic forms, such as methylmercury (CH₃Hg⁺). Moreover, concentrations in the order of 1.5 μg/L for the total Hg measured in Skiathos groundwater are consistent with mercury being predominantly in the form of dissolved metal (Hg⁰) whose water solubility is appreciably higher (45 μg/L).

4. Conclusions

The water system in Skiathos has been impacted by high Hg concentrations in the last two decades, rendering water in the island unsafe to be consumed. The island faces water scarcity problems especially during the summer when the number of island residents is rapidly increasing due to tourism. In the study area, the presence of Hg is due to natural causes since the mineral HgS most likely exists in the bedrock of Skiathos. However, concentrations of Hg exceeding the Maximum Concentration Level Standard are being observed only since 2003.

A preliminary investigation of the Hg speciation in the water system of Skiathos is presented in this article, by utilizing the Pourbaix diagram for Hg as constructed by Grassi and Netti [2] and the concentrations of nitrogen species (NO₃⁻, NO₂⁻ and NH₄⁺) for the estimation of the redox indicator (ψc) of groundwater. The latter suggests that metallic Hg is the dominant form of mercury present in the groundwater of Skiathos. A comparison of the ψc values between the two case studies (Skiathos and Grosseto, Tuscany) suggests that in Skiathos the subsurface environment appears to possess a lower oxidative tendency, resulting in lower ψc values in the Pourbaix diagram.

In coastal areas, aquifer overexploitation due to increased summer demands leads to groundwater salinisation. In turn, high concentrations of Cl⁻ appear to correlate with the presence of Hg in Skiathos, which is in agreement with other relevant studies on different study areas [2,13–15]. Thus, it appears that the role of increased Cl⁻ concentration in the aquifer is directly linked to the mobilization of Hg. These preliminary results warrant further investigation and must be supported with a monitoring regime and relevant data, in order to reach conclusive results about the speciation of Hg and finally, to develop a strategic plan for its mitigation.

Author Contributions: Y.L. contributed in the development of the methodology. A.S. wrote the paper with input from Y.L. and C.L. Both C.L. and Y.L. reviewed the paper.

Acknowledgments: Funding for this research is provided by the Stavros Niarchos Foundation, as part of the Post-Doctoral Fellowship Program. The authors wish to acknowledge the General Director of DEYASK, Ioannis Sarris, for providing data and access to the site and for his flawless collaboration with the authors.

References

1. Kozyatnyk, I.; Lövgren, L.; Haglund, P. On the leaching of mercury by brackish seawater from permeable barriers materials and soil. J. Environ. Chem. Eng. 2015, 3, 1200–1206, doi:10.1016/j.jece.2015.04.017.
2. Grassi, S.; Netti, R. Sea water intrusion and mercury pollution of some coastal aquifers in the province of Grosseto (Southern Tuscany—Italy). J. Hydrol. 2000, 237, 198–211, doi:10.1016/S0022-1694(00)00307-3.
Proceedings 2018, 2, 668

3. Nriagu, J.O. A global assessment of natural sources of atmospheric trace metals. Nature 1989, 338, 47, doi:10.1038/338047a0.

4. King, J.K.; Harmon, S.M.; Fu, T.T.; Gladden, J.B. Mercury removal, methylmercury formation, and sulfate-reducing bacteria profiles in wetland mesocosms. Chemosphere 2002, 46, 859–870, doi:10.1016/S0045-6535(01)00135-7.

5. Bolan, N.; Kunhi Krishnan, A.; Thangarajan, R.; Kumpiene, J.; Park, J.; Makino, T.; Kirkham, M.B.; Scheckel, K. Remediation of heavy metal(loid)s contaminated soils—To mobilize or to immobilize? J. Hazard. Mater. 2014, 266, 141–166, doi:10.1016/j.jhazmat.2013.12.018.

6. Wiatrowski, H.A.; Paula, M.W.; Barkay, T. Novel reduction of mercury (II) by mercury-sensitive dissimilatory metal reducing bacteria. Environ. Sci. Tech. 2006, 40, 6690–6696, doi:10.1021/es061046g.

7. Aston, S.R.; Fowler, S.W. Mercury in the open Mediterranean: Evidence of contamination? Sci. Total Environ. 1985, 43, 13–26, doi:10.1016/0048-9697(85)90028-2.

8. Buffoni, G.M.; Bernhard, M.; Renzoni, A. Mercury in the Mediterranean tuna. Why is their level higher than in Atlantic tuna? A model. Thalass. Jugosl. 1982, 18, 231–243.

9. Kozin, L.F.; Hansen, S.C. Chemical Properties of Mercury. In Mercury Handbook: Chemistry, Applications and Environmental Impact; Royal Society of Chemistry: Cambridge, UK, 2013; pp. 81–127.

10. Benoit, J.M.; Gilmour, C.C.; Mason, R.P.; Heyes, A. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environ. Sci. Tech. 1999, 33, 951–957, doi:10.1021/es9808200.

11. Jiang, P.; Yanbin, L.; Guaugiang, L.; Yang, G.; Lagos, L.; Yongguang, Y.; Gu, B.; Jiang, G.; Cai, Y. Evaluating the role of re-adsorption of dissolved Hg\textsuperscript{2+} during cinnabar dissolution using isotope tracer technique. J. Hazard. Mater. 2016, 317, 466–447, doi:10.1016/j.jhazmat.2016.05.084.

12. Van Dam, J.C. Salt water intrusion analysis research needs and opportunities. In Proceedings of the 14th Salt Water Intrusion Meeting, Uppsala, Sweden, 16–21 June 1996.

13. WHO. Guidelines for Drinking-Water Quality, Vol. 1 Recommendations; World Health Organisation: Geneva, Sweden, 1993.

14. Protano, G.F.; Riccobono, F.; Sabatini, G. Does salt water intrusion constitute a mercury contamination risk for coastal freshwater aquifers? Environ. Pollut. 2000, 110, 451–458, doi:10.1016/S0269-7491(99)00317-6.

15. Barringer, J.L.; Szabo, Z.; Reilly, P.A.; Riskin, M.L. Variable contributions of mercury from groundwater to a first-order urban coastal plain stream in New Jersey, USA. Water Air Soil Pollut. 2013, 224, 1475, doi:10.1007/s11270-013-1475-7.

16. Barringer, J.L.; Szabo, Z. Overview of investigations into mercury in ground water, soils, and septage, New Jersey Coastal Plain. Water Air Soil Pollut. 2006, 175, 193–221, doi:10.1007/s11270-006-9130-1.

17. Sun, H.; Alexander, J.; Gove, B.; Koch, M. Mobilization of arsenic, lead, and mercury under conditions of sea water intrusion and road deicing salt application. J. Contam. Hydrol. 2015, 180, 12–24, doi:10.1016/j.jconhyd.2015.07.002.

18. Nelson, S.S.; Yonge, D.R.; Barber, M.E. Effects of road salts on heavy metal mobility in two eastern Washington soils. J. Environ. Eng. 2009, 135, 505–510.

19. Mellios, N.; Kofinas, D.; Papageorgiou, E.; Laspidou, C. A multivariate analysis of the daily water demand of Skiathos Island, Greece, implementing the artificial neuro-fuzzy inference system (anfis). In Proceedings of the 36th IAHR World Congress, The Hague, The Netherlands, 28 June–3 July 2015.

20. Kofinas, D.; Mellios, N.; Papageorgiou, E.; Laspidou, C. Urban water demand forecasting for the island of Skiathos. Proc. Eng. 2014, 89, 1023–1030, doi:10.1016/j.proeng.2014.11.220.

21. WHO. Guidelines for Drinking-Water Quality, 3rd ed.; World Health Organization: Geneva, Switzerland, 2004. Available online: http://www.who.int/water_sanitation_health/dwq/GDWQ2004web.pdf (accessed on 22 January 2018).

22. WHO Mercury and Health. Fact Sheet No. 361. 2012. Available online: http://www.who.int/mediacentre/factsheets/fs361/en/index.html (accessed on: January 22, 2018).

23. Director of DEYASK, Ioannis Sarris, Skiathos Island, Greece. Personal communication, 2017.

24. Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averty, K.B.; Tignor, M.; Miller, H.L. Working Group I: The Physical Science Basis. Chapter 5: Observations: Oceanic Climate Change and Sea Level. Contribution of Working Group I to Fourth Assessment Report of the Intergovernmental Panel on Climate Change; IPCC AR4; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2007; p. 996.
25. Giorgi, F.; Piero, L. Climate change projections for the Mediterranean region. *Glob. Planet. Chang.* **2008**, *63*, 90–104, doi:10.1016/j.gloplacha.2007.09.005.

26. Kofinas, D.; Papageorgiou; E.; Laspidou, C.; Mellios, N.; Kokkinos, K. Daily multivariate forecasting of water demand in a touristic island with the use of artificial neural network and adaptive neuro-fuzzy inference system. In *Cyber-Physical Systems for Smart Water Networks (CySWater)*; International Workshop on IEEE: Piscataway Township, NJ, USA, 2016.

27. Brookins, D.G. *Eh-pH Diagrams for Geochemistry*; Springer Science & Business Media: Berlin/Heidelberg, Germany, 2012.

28. Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solution*, 1st ed.; Pergamon Press: Bristol, UK, 1966.

29. Garrels, R.M.; Christ, C.L. *Eh-pH. Chapter 7: In Solutions, Minerals, and Equilibria*; Freeman; Cooper and Company: New York, NY, USA, 1975; pp. 172–277.

30. Huang, H.H. The Eh-pH diagram and its advances. *Metals* **2016**, *6*, 23.

31. Thompson, W.T.; Kaye, M.H.; Bale. C.W.; Pelton, A.D. Pourbaix diagrams for multielement systems. In *Uhlig’s Corrosion Handbook*, 3rd ed.; The Electrochemical Society and Jon Wiley and Sons: Hoboken, NJ, USA, 2011.

32. Verink, E.D. Simplified procedure for constructing Pourbaix diagrams. In *Uhlig’s Corrosion Handbook*, 3rd ed.; The Electrochemical Society and Jon Wiley & Sons: Hoboken, NJ, USA, 2011.

33. Stumm, W.; Morgan, J.J. An Introduction Emphasizing Chemical Equilibria in Natural Water. In *Aquatic Chemistry*, 2nd ed.; Wiley: New York, NY, USA, 1981; p. 780.

34. Stumm, W.; Morgan, J.J. Oxidation and reduction; equilibria and microbial mediation. In *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed.; John Wiley & Sons: New York, NY, USA, 2012; p. 126.

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