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Report

Desalting of Marine Water through Electrodialysis

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1 Introduction and Goal of the Project

The analysis of compounds from seawater usually requires enrichment steps as marine concentrations are usually orders of magnitudes below the detection limits of analytical methods. For the fortification of polar substances from water, such as organic P compounds, solid phase extraction is often utilized, in which the compound of interest is enriched at the solid phase and subsequently eluted through a small volume of solvent.

However, for seawater samples efficient enrichment of the analyte onto the solid phase is often disturbed due to the seawater matrix, i.e, inorganic salts and analyte compete for the binding sites at the solid phase. Therefore, enrichment methods are often limited to water samples with very low salinity and, thus, for a number of polar substances it is not possible to assess the very low marine concentrations.

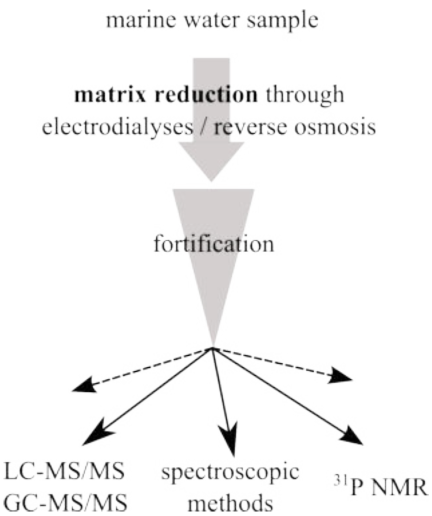

Figure 1: Basic steps during sample preparation for the analysis of polar compounds from marine water including an upstream step for the reduction of the seawater matrix through electrodialysis / reverse osmosis.

Therefore, an upstream step during sample preparation is desirable, in which inorganic salts are reduced to increase the efficiency of subsequent enrichment and purification steps so that current analytical techniques can be more efficiently exploited (Figure 1). In particular, it is a crucial step for the analysis of organic P compounds by GC- and LC-MS/MS which is the overall goal of this research. However, a desalting method might be also of interest for other analytical methods such as for the analysis of the dissolved organic P pool or dissolved organic matter (Vetter et al., 2007; Koprivnjak et al., 2009; Young and Ingall, 2010).

Electrodialysis is a method to reduce the electrolyte concentration from water through the arrangement of cation and anion exchange membranes through which an electrical current is directed. It is often used in combination with reverse osmosis for subsequent concentration of the sample volume and was shown to be successfully applied for the analysis of dissolved organic matter (Vetter et al., 2007; Koprivnjak et al., 2009) or dissolved organic phosphorous from seawater (Young and Ingall, 2010).

The goal of this project was to implement an electrodialysis method for the reduction of inorganic salts in seawater, which can later be expanded to include a reverse osmosis step. Within this project we are aiming to set up a laboratory scale electrodialysis facility and to investigate the influence of pH and salinity of the sample water on the electrodialysis process. Moreover, retention of the bulk paramters dissolved organic phosphorus (DOP), dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) during electrodialysis was investigated. Sufficient retention of compounds during electrodialysis was monitored through analysis of current target compounds, i.e., glyphosate, its metabolite aminomethylphosphonic acid (AMPA) and glufosinate, methyl phosphonic acid (MPhn) as well as a number of organophosphate pesticides.

2 Material and Methods

2.1 Operation of the Electrodialysis Facility

The electrodialysis facility was purchased from the company Deukum Gmbh (Frickenhausen) and was operated as described in Wirth et al., (submitted). During the inital experimental phase, electrodialysis was conducted using artifical sea water to enable preparation of water samples of defined conductivities. In the later stage Baltic Sea coastal water samples were used which were obtained from the Heiligendamm pier (54°08'46.7"N, 11°50'36.1"E) between March and September 2018.

2.2 Determination of the bulk parameters and target compounds

The experimental procedures for the determination of DOP, DON and DOC, glyphosate, AMPA, glufosinate, MPn and organosphophate pesticides were performed as described in Wirth et al., (submitted). Basically, the analysis of glyphosate and AMPA were conducted as described in Skeff et al. (2015) with modifications; organosphosphate pesticides were determined as described in Habedank et al. (2017) and MPn as described in Lohrer et al., (in preparation).

3 Results and Discussion

3.1 Set up of the system

The basic electrodialysis facility consists of three reservoir tanks which contain the diluate stream, concentrate (ion receiving) stream and electrode rinse (Figure 2), an electrodialysis membrane stack of type quadro, circulation pumps and a voltage regulator. Since November 2017 the system is in use. It was further equipped with conductivity meters for each reservoir and additionally for each reservoir steel sheets were integrated to reduce turbulence and, thus, to allow processing of low volume water samples (2 to 3 l).

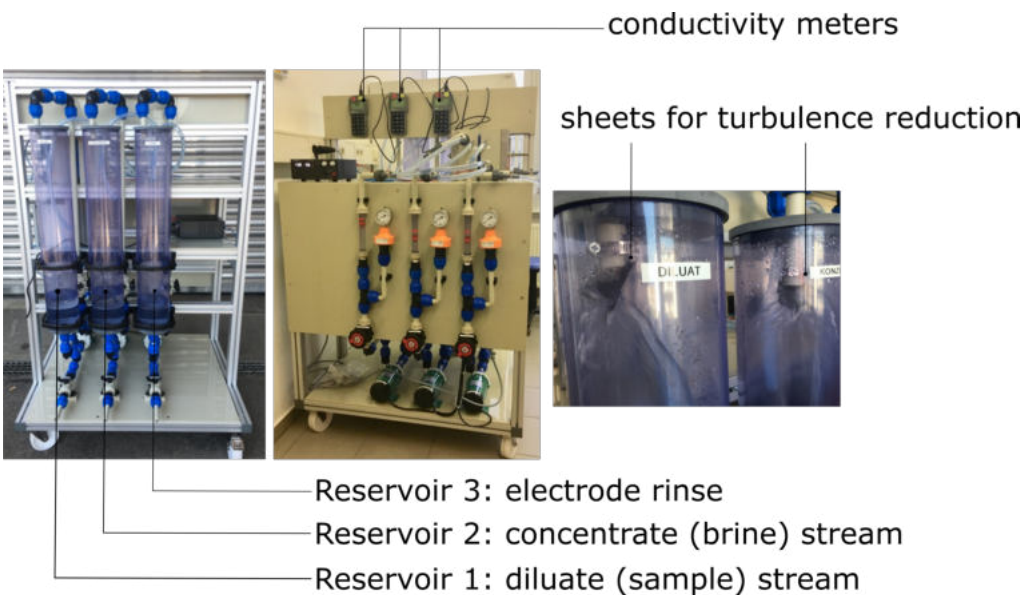

Figure 2: Electrodialysis facility (Deukum GmbH) additionally equipped with conductivity meters and steel sheets to reduce turbulence. Fotograph: M. Sievers/IOW

System parameters such as the limiting current density were experimentally determined (Sievers, 2018). The results presented in the following are obtained from the Master Thesis Sievers (2018) and the manuscript Wirth et al., (submitted) which is submitted for peer review publication.

3.2 Recovery of DOP, DOC and DON

The bulk parameters DOP, DOC and DON were analyzed after conducting electrodialysis of a Baltic Sea coastal water sample (Heiligendamm pier, Figure 3). Basically, DOP recoveries were higher during electrodialysis than those for DOC and DON. DOP was retained by almost 100% until a salinity of about 1.5 and reduced to about 90% recovery at the final salinity of 0.1. However, DOC and DON recoveries reduced yet in the early stage of electrodialysis to a final recovery of about 50% at a salinity of 0.1 (Wirth et al., submitted).

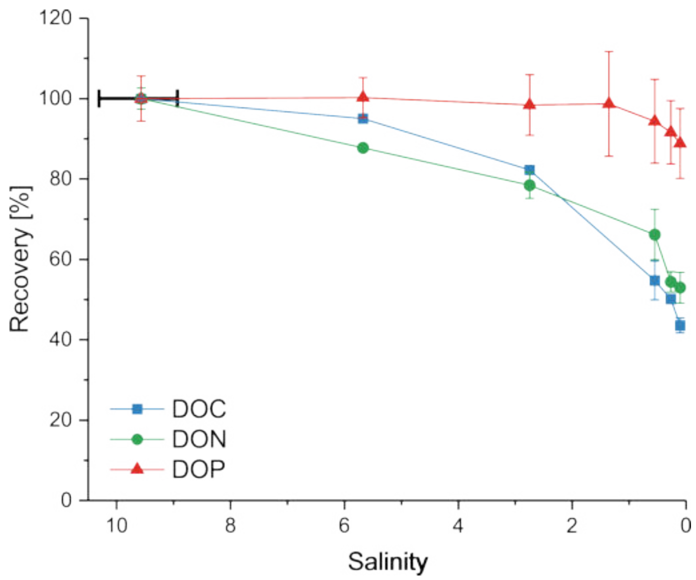

Figure 3: Recoveries of the bulk parameters DOP, DOC and DON after electrodialysis of a Baltic Sea coastal water sample from the Heiligendamm pier (Wirth et al., submitted).

Analysis of the influence of sample salinity, electric current (data not shown) and pH on the recovery of DOP, DOC and DON revealed that, overall, the degree of desalination and, thus, final conductivity of the diluate stream in the first place determines the retention of the bulk organic matter. Therefore, higher recoveries can be obtained if electrodialysis is terminated at higher conductivities. Surprisingly, pH adjustment to pH 4 and pH 10 did not influence DOC and DON recoveries; for DOP the obtained results are not valid (data not shown) (Sievers, 2018).

3.3 Retention of target analytes

A number of compounds were tested to study if their retention in the utilized electrodialysis system is determined by their chemical properties, such as the $\log K_{OW}$. Therefore, the chosen analytes cover a broad range of $\log K_{OW}$ and, moreover, comprise compounds which are in current research focus such as glyphosate, its metabolite AMPA and glufosinate, MPhn and organophosphate pesticides (Figure 4).

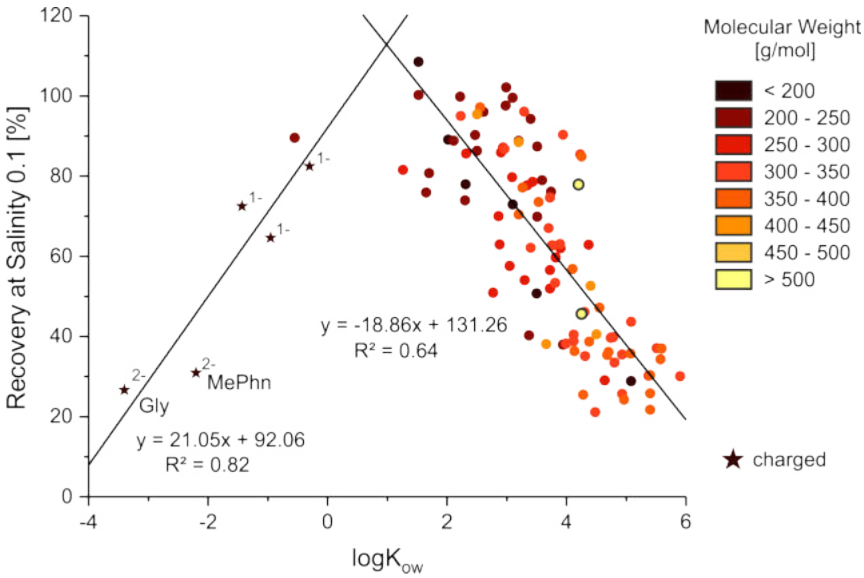

Figure 4: Recoveries of target analytes during electrodialysis until salinity of 0.1 of a Baltic Sea coastal water sample (Heiligendamm pier) *versus* their $\log K_{OW}$. Gly: glyphosate, MePhn: methyl phosphonic acid (Wirth et al., submitted).

As a result highest recovery of target analytes can be expected in the $\log K_{OW}$ range from about 0 to 2.5. Retention of analytes with higher $\log K_{OW}$, thus hydrophobic compounds, is reduced presumably due to their adsorption in the electrodialysis system; retention of substances with $\log K_{OW}$ below 0, thus hydrophilic and ionic compounds, reduced due to their loss over the electrodialysis membrane during deionization. Detailed and further discussion on this can be obtained from Wirth et al., (submitted).

Retention of the target analytes glyphosate, AMPA, glufosinate and MPhn were analyzed in more detail as those are in current focus of further method development for their analysis in seawater. Glyphosate, AMPA and glufosinate were largely retained until a salinity of about 2 with recoveries ranging from 80 to 90% which then exponentially reduced to about 20 to 60% at the final salinity of 0.1 (Figure 5). This is discussed in more detail in Wirth et al., (submitted). The results for MPhn are currently compiled for publication (Lohrer et al., in preparation).

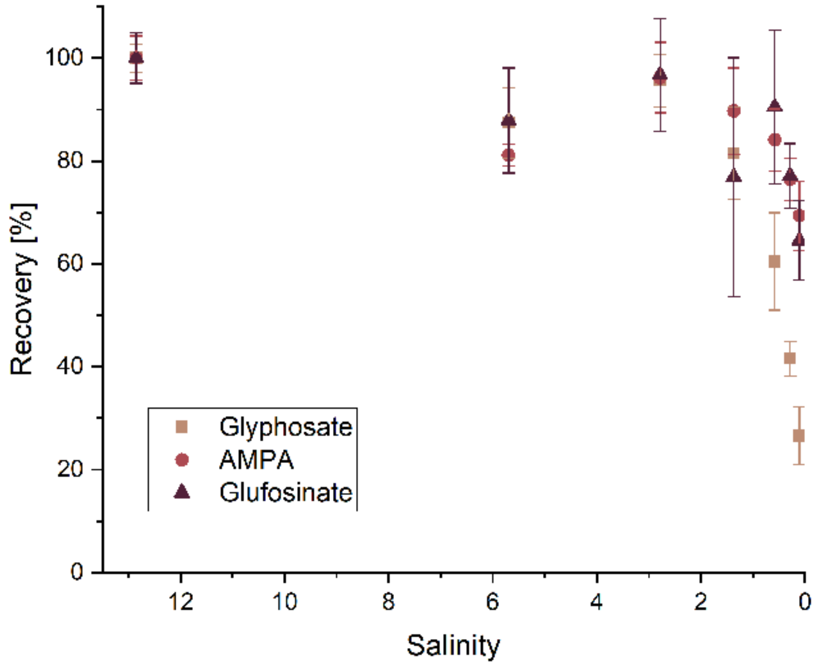

Figure 5: Recovery of glyphosate, AMPA and glufosinate after electrodialysis of a Baltic Sea coastal water sample (Heiligendamm pier, Wirth et al., submitted).

Finally, highest recovery for glyphosate, AMPA and glufosinate in the sample water is obtained if electrodialysis is terminated at a final salinity of 2. For the overall experimental procedure for their analysis, which includes subsequent experimental steps after electrodialysis, this implies that high recovery of these analytes and thus, low detection limits can be assumed if the following experimental steps, i.e., solid phase extraction, are non-sensitive to a sample salinity of 2.

4 Acknowledgements

The project partners are grateful to Monika Nausch, Christoph Kamper, Joachim Kuss, Birgit Sadkowiak, Lars Kreuzer and Jenny Jescheck for their support during analysis of DOP, DON and DOC.

5 Appendix

Presentations

Marisa Wirth, Moritz Sievers, Udo Kragl, Detlef E. Schulz-Bull, Marion Kanwischer: Electrodialysis of marine water for the measurement of organophorsphorus compounds. Symposium of the Leibniz ScienceCampus Phosphorus Research Rostock, Nov 2018, Talk

Marisa Wirth, Marion Abraham, Udo Kragl, Detlef E. Schulz-Bull: Desalting of marine water through electrodialysis. Symposium of the Leibniz Science-Campus Phosphorus Research Rostock, Nov 2017, Talk

Marisa Wirth, Moritz Sievers, Friederike Habedank, Detlef E. Schulz-Bull. Udo Kragl, Marion Kanwischer: How Phosphorus Analysis can benefit from Electrodialysis, in preparation for IPW9

Resulting Publications (to date)

M. A. Wirth, M. Sievers, F. Habedank, D. E. Schulz-Bull. U. Kragl, M. Kanwischer: Electrodialysis as a Sample Processing Tool for Bulk and Target Analysis of Baltic Sea Water. Marine Chemistry, submitted

C. Lohrer, P.P. Cwierz, M. A. Wirth, D. E. Schulz-Bull, M. Kanwischer: Methodological Aspects of Methylphosphonic Acid Analysis: Determinatio in river and coastal water samples. Talanta, submitted

Theses

Moritz Sievers: Untersuchungen zur Wiederfindung von Bulk Parametern (DOC, DOP, DON) nach Elektrodialyse von Meerwasser. University of Rostock, Master Thesis, 2018

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Habedank, F., M. Abraham, H. Tardel, F. Feldhusen, and D.E. Schulz-Bull (2017). "Determination of organophosphate pesticides in sea and surface water with ultrasound-assisted dispersive liquid–liquid micro-extraction coupled to GC-MS/MS analysis". In: *International Journal of Environmental Analytical Chemistry* 97.9, pp. 819–830. ISSN: 10290397. DOI: 10.1080/03067319.2017.1361944.

Koprivnjak, J.-F., P.H. Pfromm, E. Ingall, T.A. Vetter, P. Schmitt-Kopplin, N. Hertkorn, M. Frommberger, H. Knicker, and E.M. Perdue (July 2009). "Chemical and spectroscopic characterization of marine dissolved organic matter isolated using coupled reverse osmosis–electrodialysis". In: *Geochimica et Cosmochimica Acta* 73.14, pp. 4215–4231. ISSN: 00167037. DOI: 10.1016/j.gca.2009.04.010.

Sievers, M. (2018). "Untersuchungen zur Wiederfindung von Bulk Parametern (DOC, DOP, DON) nach Elektrodialyse von Meerwasser". PhD thesis. University of Rostock.

Skeff, Wael, Christine Neumann, and Detlef E Schulz-Bull (Nov. 2015). "Glyphosate and AMPA in the estuaries of the Baltic Sea method optimization and field study". In: *Marine Pollution Bulletin* 100.1, pp. 577–585. DOI: 10.1016/j.marpolbul.2015.08.015.

Vetter, T, E Perdue, E Ingall, J KoprivnjakK, and P Pfromm (Sept. 2007). "Combining reverse osmosis and electrodialysis for more complete recovery of dissolved organic matter from seawater". In: *Separation and Purification Technology* 56.3, pp. 383–387. ISSN: 13835866. DOI: 10.1016/j.seppur.2007.04.012.

Young, Cindy L and Ellery D Ingall (2010). "Marine Dissolved Organic Phosphorus Composition: Insights from Samples Recovered Using Combined Electrodialysis/Reverse Osmosis". In: *Aquatic Geochemistry* 16.4, pp. 563–574. ISSN: 1573-1421. DOI: 10.1007/s10498-009-9087-y.