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Integrating chemical imaging of cationic trace metal solutes and pH into a single hydrogel layer

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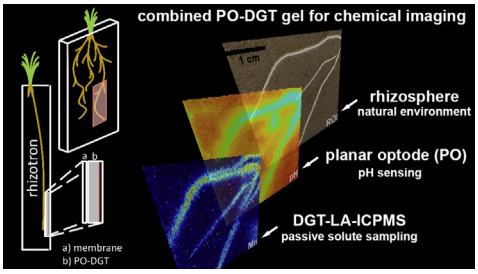
HIGHLIGHTS

- Diffusive gradients in thin films (DGT) and planar optode (PO) imaging is combined.
- A single hydrogel layer contains both, ion binding materials and a pH luminophore.
- DGT is analyzed by laser ablation ICP-MS, PO imaging uses a ratiometric method.
- Anion binding materials interfered with pH sensing, while the cation resin did not.
- Single-layer imaging is easier to handle and offers reduced artifact susceptibility.

GRAPHICAL ABSTRACT



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ABSTRACT

Gel-based, two-dimensional (2D) chemical imaging techniques are versatile methods for investigating biogeochemically active environments at high spatial resolution (sub-mm). State-of-the-art solute imaging techniques, such as diffusive gradients in thin films (DGT) and planar optodes (PO), employ passive solute sampling or sensing. Combining these methods will provide powerful tools for studying the biogeochemistry of biological niches in soils and sediments. In this study we aimed at developing a combined single-layer gel for direct pH imaging using PO and sampling of anionic and cationic solutes by DGT, with subsequent analysis of the bound solutes by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). We tested three ultra-thin (<100 μm) polyurethane-based gels, incorporating anion and cation binding materials and the fluorescent pH indicator DCIFODA (2′,7′-dichloro-5(6)-*N*-octadecyl-carboxamidofluorescein).

Results showed that PO-based pH sensing using DCIFODA was impossible in the presence of the anion binding materials due to interferences with DCIFODA protonation. One gel, containing only a cation binding material and DCIFODA, was fully characterized and showed similar performance characteristics as comparable DGT-only gels (applicable pH range: pH 5–8, applicable ionic strength range: 1–20 mmol L^{-1}, cation binding capacity ~24 μg cm^{-2}). The dynamic range for PO-based pH mapping was between pH 5.5 and 7.5 with t_{90} response time of ~60 min.

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In a case study we demonstrated the gel's suitability for multi-analyte solute imaging and mapped pH gradients and concurrent metal solubility patterns in the rhizosphere of *Salix smithiana*. pH decreases in the rooted soil were co-localized with elevated solute fluxes of Al^{3+}, Co^{2+}, Cu^{2+}, Fe, Mn^{2+}, Ni^{2+} and Pb^{2+}, indicating pH-induced metal solubilisation.

1. Introduction

The investigation of biogeochemical hotspots in soils and sediments has attracted the interest of researchers for decades, as the biological and chemical processes in very small niches may strongly impact biogeochemical cycles even up to the global scale. Traditional methods for investigating spatial solute distributions include soil/sediment slicing [1,2], pore-water sampling [3], the use of micro sensors [4] or bulk extraction procedures, all of which provide point measurements or one-dimensional (1D) profiles. The development of two-dimensional (2D) solute imaging techniques has been a large step towards a more comprehensive understanding of the spatial distribution of sub-mm processes in biogeochemical niches such as the sediment-water interface or the soil-plant root interface (rhizosphere) [5–9].

Planar optodes (PO) represent powerful tools for solute imaging by measuring the fluorescent light emitted by an analyte-sensitive indicator dye immobilized in a thin polymer layer. PO sensors are mainly available for physico-chemical parameters such as pO_2 [8,10], pH [11–14] and pCO_2 [10,15,16], however sensors for other analytes e.g. NH_4^+, NO_3^- have also been reported [17–20]. PO sensors are mostly limited to a single analyte, only few PO for measuring two, three or four analytes simultaneously are available [15,21,22].

Another group of solute imaging techniques is based on diffusive gradients in thin films (DGT), which mainly sample inorganic ions on binding materials finely distributed in a thin hydrogel layer. Common DGT analytes include trace metal cations and oxyanions like phosphate and arsenate. Imaging is performed post sampling by either gel slicing, elution and wet-chemical analysis [2], computer-imaging densitometry (CID) [3,23] or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [24,25], the latter obtaining the highest spatial resolution (~100 μm) and the lowest detection limits (<1–200 ng cm^{-2}) [26,27]. Moreover, LA-ICP-MS imaging of DGT gels facilitates to map a large number of analytes simultaneously, limited mainly by the selectivity of the binding material that is employed.

DGT imaging yields time-averaged images of solute distributions for the chosen sampling time, whereas many PO methods utilize reversible fluorescence indicators that react dynamically to short-term changes in the porewater solute concentration, allowing for time-lapse studies to be conducted. As both PO and DGT are based on analyte diffusion into thin hydrogel layers of similar size (several cm^2) and target complementary sets of analytes, PO-DGT combinations have great potential for investigating the biogeochemistry of soils and sediments at the microscale.

A few researchers already trialed such imaging combinations. Hoefer, *et al.* [28] used DGT and PO in parallel (on different specimen) to map Mn^{2+}, Zn^{2+}, Cd^{2+} and O_2 around willow roots in aerobic, metal-contaminated soil. Stahl, *et al.* [29] investigated Fe^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} release from aquatic worm burrows by combining trace metal DGT sampling with O_2 PO imaging in a gel stack, *i.e.* placing the planar optode layer on top of the DGT gel. Williams, *et al.* [30] used a similar approach in submerged soil for the localization of As, Pb^{2+} and Fe^{2+} fluxes as well as the O_2 and pH distribution around lowland rice roots.

However, the handling of PO-DGT gel stacks is cumbersome and prone to imaging artifacts connected to the entrapment of air bubbles between the gels and to potential displacement of the gel layers during gel installment. Moreover, elongating the diffusive pathways by stacking gels results in increased image blurring due to lateral diffusion of the target analytes [5,29].

In this study, we aimed at combining PO and DGT into a single, self-supporting gel layer. We incorporated well-studied anion and cation binding materials together with the lipophilic pH indicator 2',7'-dichloro-5(6)-*N*-octadecyl-carboxamidofluorescein (DCIFODA) and a reference fluorescent dye into a polyurethane-based hydrogel matrix, based on a recently developed anion-cation binding gel [26] and a ratiometric PO imaging approach [17]. The performance characteristics of this PO-DGT gel were assessed in detail, with special regard to potential interferences between both techniques.

2. Materials and methods

2.1. Materials and reagents

If not stated otherwise, glassware and plastics used for gel preparation and deployment were acid-washed in 5% HNO_3 and rinsed twice with lab water type 1 (≤0.055 μS cm^{-1}, TKAGenPure, Thermo Electron LED GmbH, Niederelbert, Germany). Gel solutions and reagents were prepared with lab water type 1. Gel coating and handling was performed in a biological class II laminar flow bench (Clean Air, EuroFlow EF/S, Telstar Laboratory Equipment B.V., Woerden, The Netherlands). All chemical reagents were of analytical grade and purchased from VWR (Vienna, Austria), Merck (Vienna, Austria) or Sigma Aldrich (Vienna, Austria).

For the combined PO-DGT gels we used a polyurethane-based hydrogel matrix (HydroMed-D4, AdvanSource biomaterials, Massachusetts, US), which had previously been used for both, pH planar optodes [18,31] and DGT gels [26]. The lipophilic pH indicator, 2',7'-dichloro-5(6)carboxyfluorescein (DCIFODA) was prepared according to the procedure of Schröder, *et al.* [31], the reference fluorescent pigment Ziegelrot was acquired from Kremer Pigmente (Aichstetten, Germany). We used suspended particulate reagent-iminodiacetate (SPR-IDA) (CETAC Technologies, Nebraska, US), which is well characterized as a binding material in DGT gels, for binding cationic solutes [26,27,32], and zirconium hydroxide (ZrOH) and the anion resin DOWEX 1 × 8 in the chloride form, milled to a particle size <20 μm, as materials for binding anionic solutes [25,26,33].

2.2. Gel fabrication

All gel solutions were prepared by mixing the components stated in Table 1 into the corresponding HydroMed-D4 matrix in closed 30-mL glass vials overnight using magnetic stirrers while the ZrOH containing gel solution was additionally homogenized using a dispersing device (Ultra-Turrax T10 Basic, IKA-Werke GmbH, Staufen, Germany) [26].

Three PO-DGT gel combinations were prepared: DCIFODA + SPR-IDA (D_S), DCIFODA + SPR-IDA + ZrOH (D_SZ),