**Introduction**

Control of contaminant degradation within the unsaturated zone is important for protection of groundwater. One example is for airport management where large amounts of de-icing chemicals, used to remove snow and ice on airplanes and runways every winter, infiltrate the green areas along the runways. Understanding degradation of organic contaminants in the unsaturated zone is highly challenging. Commonly used redox potential sensors provide only point measurements and are error prone. Both redox sensors and destructive sampling can potentially cause contact with air, which will influence the redox state. Hence, assessing redox conditions in soil and groundwater is challenging. Redox sensitive reactions such as degradation of an organic contaminant in a static partly saturated and unsaturated sandy system will change water chemistry and hence geoelectrical properties.

The use of geophysical techniques to monitor hydrogeological (hydrogeophysics) and biological processes (biogeophysics) at the field scale has become more widespread (Hubbard and Rubin, 2000; Vereecken et al., 2006; Atekwana et al., 2006).

In this study, we have explored ERT and SIP geophysical techniques to observe the degradation processes of Propylene Glycol (PG), a de-icing chemical often used at airports.

**Method**

*Propylene Glycol (PG)*
This study focuses on one particular organic contaminant widely used for aircraft de-icing, namely propylene glycol (PG), which has been studied for decades at Oslo international airport, Norway (Laake and Efraismen, 1992). PG is often used in cold climate airports, as it is as effective and less toxic than ethylene glycol (Gooden, 1998). The PG contaminant itself is less problematic to the environment than the degradation products causes. Observations at Oslo airport have shown that under anaerobic conditions, redox reactions release iron and manganese (Table A) in groundwater and even in the unsaturated zone (French et al., 2001; Lissner et al., 2013; Fernandez et al. 2018 and 2019). Reduced iron precipitates with oxygen, and tends to clog water log pumps. High manganese concentrations have been reported to be harmful for aquatic life and people. In the long term, when iron and manganese oxides are exhausted, PG degradation leads to methane formation, which is toxic and flammable in contact with oxygen (by a redox reaction).

**Table A.** Complete PG ($C_3H_8O_2$) degradation depending on the electron acceptor.

| | Reactants | | | | Products | | |
|---|---|---|---|---|---|---|---|
| | PG | + protons | + electron acceptor | => | $CO_2$ | + water | + specific species |
| a. | $C_3H_8O_{2(L)}$ | | + 4 $O_{2(g)}$ | => | 3 $CO_{2(g)}$ + | 4 $H_2O_{(L)}$ | |
| b. | $C_3H_8O_{2(L)} + \frac{16}{5} H^+_{(aq)}$ | | $+ \frac{16}{5} NO_3^-{}_{(aq)}$ | => | 3 $CO_{2(g)} + \frac{28}{5} H_2O_{(L)}$ | | $+ \frac{8}{5} N_{2(g)}$ |
| c. | $C_3H_8O_{2(L)} + 16 H^+_{(aq)}$ | | + 8 $MnO_{2(s)}$ | => | 3 $CO_{2(g)}$ + 12 $H_2O_{(L)}$ | | + 8 $Mn^{2+}{}_{(aq)}$ |
| d. | $C_3H_8O_{2(L)} + 32 H^+_{(aq)}$ | | + 8 $Fe_2O_{3(s)}$ | => | 3 $CO_{2(g)}$ + 20 $H_2O_{(L)}$ | | + 16 $Fe^{2+}{}_{(aq)}$ |
| e. | $C_3H_8O_{2(L)} + 2 H^+_{(aq)}$ | | + 2 $SO_4^{2-}{}_{(aq)}$ | => | 3 $CO_{2(g)}$ + 4 $H_2O_{(L)}$ | | + 2 $HS^-{}_{(aq)}$ |
| f. | $C_3H_8O_{2(L)}$ | | | => | $CO_{2(g)}$ | | + 2 $CH_{4(g)}$ |

*Electrical resistivity technique*
Geophysical techniques can provide continuous maps of the horizontal and vertical distribution of physical properties of larger subsurface volumes than traditional techniques, and is cost-efficient. The resistivity of the subsurface reflects the combination of saturation, soil structure, and pore fluid properties, such as salinity, when applicable (Kemna *et al.*, 2000; Depountis *et al.*, 2001).

Since anaerobic degradation causes the release iron and manganese ions (assuming the corresponding oxides are available), the electrical conductivity of the water phase is increased and therefore electrical

resistivity tomography (ERT) should be an applicable method. Also the release of methane gas (if iron and manganese oxides are unavailable), will reduce the water saturation, another ERT sensitive change.

*Spectral Induced Polarisation technique*
To perform Induced polarisation (IP) an electrical current is injected, the soil responds to an alternating current in two parts: an in-phase component (the real conductivity) when the current is injected and an out-of-phase component (quadrature or imaginary conductivity) when the current is switched off and the system goes back to neutral. Complex conductivity is the sum of the real and imaginary conductivity. As complex conductivity changes may be frequency dependent, IP investigation needs to be done for several frequencies. It is then called Spectral Induced Polarisation (SIP) which might be sensitive to iron reduction (Williams et al., 2009).

Available iron and manganese oxides (solid phase) are used as electron acceptors for anaerobic degradation and become dissolvable cations in pore water. The impact of iron and manganese oxide dissolution caused by degradation of an organic compound, could be observed with SIP technique.

*Laboratory experiments*
1. Degradation of PG near the water table in four sand tanks with constant water table, one tank rich in iron and manganese oxides and 3 with little oxides, was monitored with 3D ERT time-lapse measurements due to changes in electrical properties caused by the degradation process (Fernandez et al., submitted 2019).
2. The same degradation of PG was monitored in a column set-up with twenty-six vertical columns (30cm high, inner diameter 4.6cm) filled with a sand rich in oxides with a static water table in the middle. In half of the columns, a 2cm high contaminated layer was installed just above the water table. Every three days over a period of one month, SIP (twenty-two frequencies between 5mHz and 45kHz) data was collected in six columns: three contaminated replicas and three control replicas. Chemical analysis was done on twenty columns meant assigned for destructive water sampling, ten contaminated columns and ten control. (Fernandez et al., 2018).
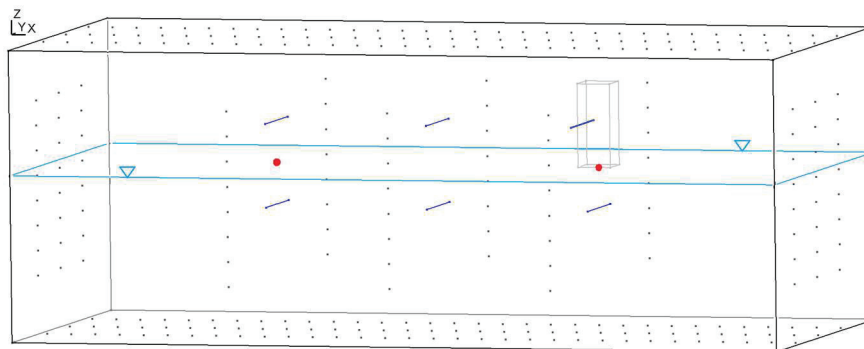
Figure 1. The tank is 96 cm long, 42 cm wide and the sand 35 cm, the saturated part is 20 cm. The red dots indicate where PG is added. of

Figure 2 The SIP columns are 30 cm long, with current electrodes at either ends, and 5 potential electrodes (non polarizable) in between (4 cm separation).

**Results**

With the ERT we observed that when iron and manganese oxides were available, degradation reduced the bulk resistivity, because of cation release in pore water. While, when iron and manganese oxides were unavailable, the electrical resistivity increased, most likely due to methane production that reduced water saturation.
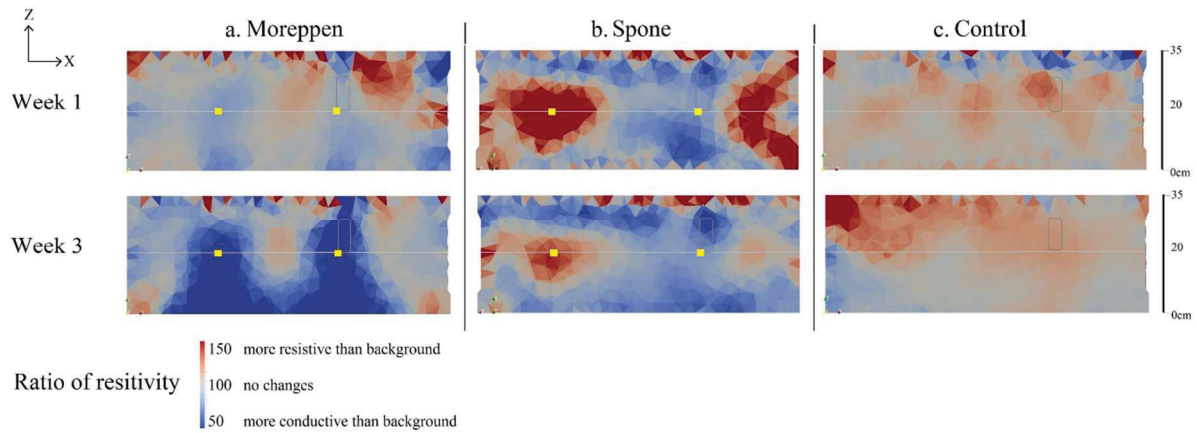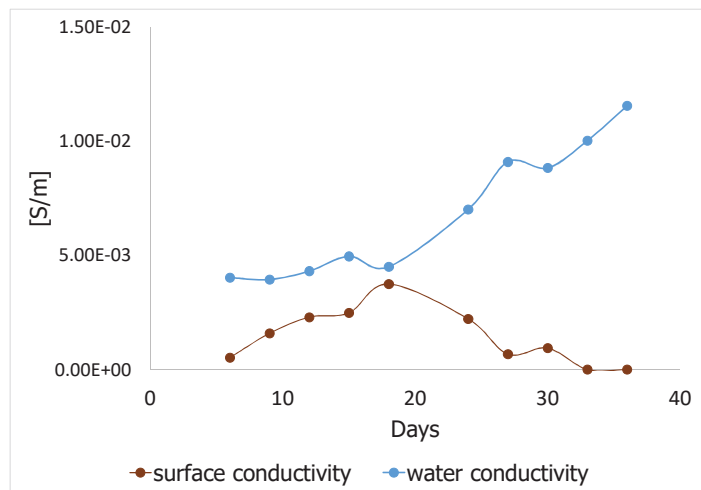


Figure 3 Ratio electrical resistivity inversion results observed in the Moreppen (oxide rich sand), Spone (oxide poor sand) and the control without added PG at week 1 and 3

Figure 4. The water conductivity observed in the water samples and the surface conductivity observed with SIP during the course of the PG degradation.



With the SIP method (Fig 4) we observed that an increase of the real conductivity (also reflected in the water conductivity shown in the figure) associated with the metal ions release but independent of the frequency. While the surface conductivity increased as soon as PG degradation is started, and is then reduced again, indicating that the iron and manganese reduction is occurring step wise (first still adsorbed to the soil surface, and then released into solution).

**Conclusions**

The detailed laboratory study demonstrated that ERT is a powerful tool for mapping the location of redox affected degradation processes. SIP is promising to investigate iron and manganese oxidation, particularly the solid phase that precede the release of cations, but remained for now more suitable for laboratory investigation.

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