Ozone as a remediation technique for the treatment of petroleum hydrocarbons in unsaturated soils

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Aims of the project
The study is designed to examine the feasibility of using ozone as a remediation technique to treat soils contaminated with hydrocarbons within the West Coast of Scotland environment.
Ozone remediation is becoming a key tool within the range of processes used to remediate contaminated soils, particularly since extraction and offsite disposal of contaminated soils is no longer viable.
The key benefits of ozone remediation are:
- In-situ destruction of targeted pollutants
- Rapid reaction - process allows for a quick turn around compared to some traditional in-situ processes
- Contaminants are destroyed rather than transferred from one phase to another
- Clean reaction - no hazardous by-products produced, and
- Micro-bubbles act to extract pollutants from both groundwater and soil pores, so acting across the total soil body.
There are a range of studies into the use of ozone to treat TPH that show it to be successful, for example Schwartz et al. (2006), Masten & Davies (1997) and Manhart & Chaney (2005). However, these are US based studies conducted in warm, sandy environments, conditions which differ widely from those found in Scotland.

The site
A 30-acre site, a former oil refinery closed since the mid-80s, has been identified for remediation and redevelopment.
The final Development is planned to be composed of:
- 400 new homes
- Offices, restaurants and shopping
- The creation of new public parkland on the sea front, and
- An extension to the existing marina.

Expected pollutants
It is believed the pollutants onsite are 80% to 90% aliphatic with the remainder being aromatic compounds, presenting varying degrees of environmental and health risks if left untreated prior to site reuse.
Primary pollutants include:
- n-hexane and derivatives
- benzene
- toluene
- xylenes
- naphthalene, and
- fluorine.

Methodology
To investigate the effectiveness of ozone as a means of treating petroleum hydrocarbons in clay-based soils, samples were taken from the site and treated with ozone over a range of treatment times, from zero treatment to 24 hours. Samples were then divided up and used to support the analysis of the chemical, microbial and physical properties of the treated soils.

Chemical Analysis
Levels of PAHs in the soils were measured both prior to and after treatment with ozone. Chemical extraction was carried out using ASE® extraction using hexane and toluene as solvents. Extracts were then analysed using gas chromatography (GC) and integrated flame ionisation detection (FID).

Microbial Analysis
Soil extraction was carried out to recover any viable bacteria. Samples were then serially diluted between 10⁻¹ and 10⁻³, then plated using a general purpose agar and allowed to germinate for 48 hours. Colonies were then counted.

Soil Properties
Moisture content and total organic content were then measured for each sample. Samples were heated initially at 110°C to measure moisture content and then to 410°C to burn off the organic content.

Results
Ozone is effective at reducing the concentrations of the PAHs in clay-based soils. Figure 2 shows a clear reduction in the levels of PAHs over the treatment time, with a 48% reduction in the average levels of PAHs over 12 hours. With regards the microbial populations, ozone in low levels stimulates the microbial populations as shown in Figure 3. As concentrations of ozone increase, the populations reduce and then at the 12 hour treatment point the populations again recover. This has some interesting implications for bioremediation in that there is a potential role for the use of low-level ozone treatment as a means of increasing microbial activity.

That the cost of ozone when compared to other remediation technologies has the potential to put it a disadvantage to other technologies is not unexpected (Figure 4). However, with changes in legislation and attitudes towards one of the more traditional techniques used, i.e. excavation and off-site disposal, new technologies or older technologies when used in combination may offer new ways to address older issues.

Conclusion
This study shows that:
1. Ozone is effective for remediating PAHs in clay soils such as found in central Scotland
2. Ozone has the potential to be a beneficial part of an integrated, multi-approach solution where bioremediation is a key component, including its ability to support and influence microbial populations in a positive manner.
3. Ozonation as a site-wide approach may in most circumstances be an expensive and over engineered solution. However, its use as a solution for localised hotspots as part of a broader multi-technique approach is more appropriate.