## 6.10 Eze, M. Effect of ethanol on the vertical migration of diesel fuel: implications for phytoremediation

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Crude oil and fuel spillages are the most persistent environmental menace resulting from oil and gas exploration, production and utilisation. Diesel spills are difficult to remediate because they have less volatile and less biodegradable characteristics compared to petrol (gasoline) spills (Kuo et al., 2012; Silva-Castro et al., 2015). Traditional solutions for remediation such as excavation and off-site treatments are expensive and usually impractical because of the amount of soil involved. Consequently, more cost-effective remediation technologies are being investigated.

One of the emerging strategies is the use of plants to extract, mitigate, and stabilise contaminants, which is known as “phytoremediation”, and which can assist in reforestation (Cunningham et al., 1995; Macek et al., 2000; Pilon-Smits and Freeman, 2006; Weyens et al., 2009). However, the increasing shift from unblended petroleum-derived diesel to ethanol-blended diesel may pose significant challenges to the success of phytoremediation and rehabilitation of contaminated sites. This is due to the co-solvency of petroleum hydrocarbons with ethanol, which may cause them to leach beyond the rooting zones of plants. Ethanol-fuel mixtures have an “E” number, which describe the percentage of ethanol fuel by volume in the mixture. For example, “E10” refers to a 10% ethanol and 90% diesel mixture. While these additives are beneficial in reducing diesel particulate matter and $CO_2$ emissions, the co-solvency created by them can make the spilled hydrocarbons inaccessible to phytoremediation. Therefore, the environmental implications of ethanol additives to diesel fuel must be thoroughly investigated.

The movement of diesel fuel was followed in a lab-based study of a 90 cm soil column packed in a polyethylene column of 15 cm diameter, and the effect of ethanol addition on this movement investigated. Three columns representing E0, E5 and E10 were set up and eluted with deionised water. The results reveal that ethanol addition significantly enhances the leaching potential of petroleum hydrocarbons. More significant was the percentage of diesel fuel fraction eluted from the entire column into the leachate fraction. While the E0 leachate contained only 0.02% of the total diesel fuel introduced on top of the column, the E10 leachate contained 10%.

To better understand the effect of ethanol on the movement of petroleum hydrocarbons, molecular analysis of the leachates was carried out using gas chromatography-mass spectrometry (GC-MS). Firstly, pure diesel was analysed to determine its molecular composition. Then the molecular compositions of the leachates from each column were compared.

The GC-MS results for the E0 and E10 leachates for just one group of aromatic hydrocarbons commonly found in diesel fuel (alkylnaphthalenes) show that alkylnaphthalenes were not detected in the leachate from the unblended diesel fuel column (Figure 1). In contrast, 10% by volume ethanol addition resulted in a considerable amount of alkylnaphthalenes eluting all the way down the 90 cm column (Figure 1). This indicates co-solvency of alkylnaphthalenes in ethanol. Overall, while 5% by volume ethanol addition caused minimal enhancement of leaching potentials of petroleum hydrocarbons, 10% ethanol addition enhanced the leaching potentials of almost all hydrocarbons investigated.

Since most grasses employed in the phytoremediation process have rooting depths of about 90 cm, our results reveal that diesel fuel ethanol addition will significantly limit the effectiveness of phytotechnology as a remediation strategy for ethanol-blended diesel spills. In addition, since the majority of soil microbes (including hydrocarbon-degrading bacteria) depend on root exudates for nutrients and thus often remain within the rhizosphere (Weyens et al., 2009), diesel fuel ethanol addition may also impact on the successes of microbial-mediated phytoremediation.

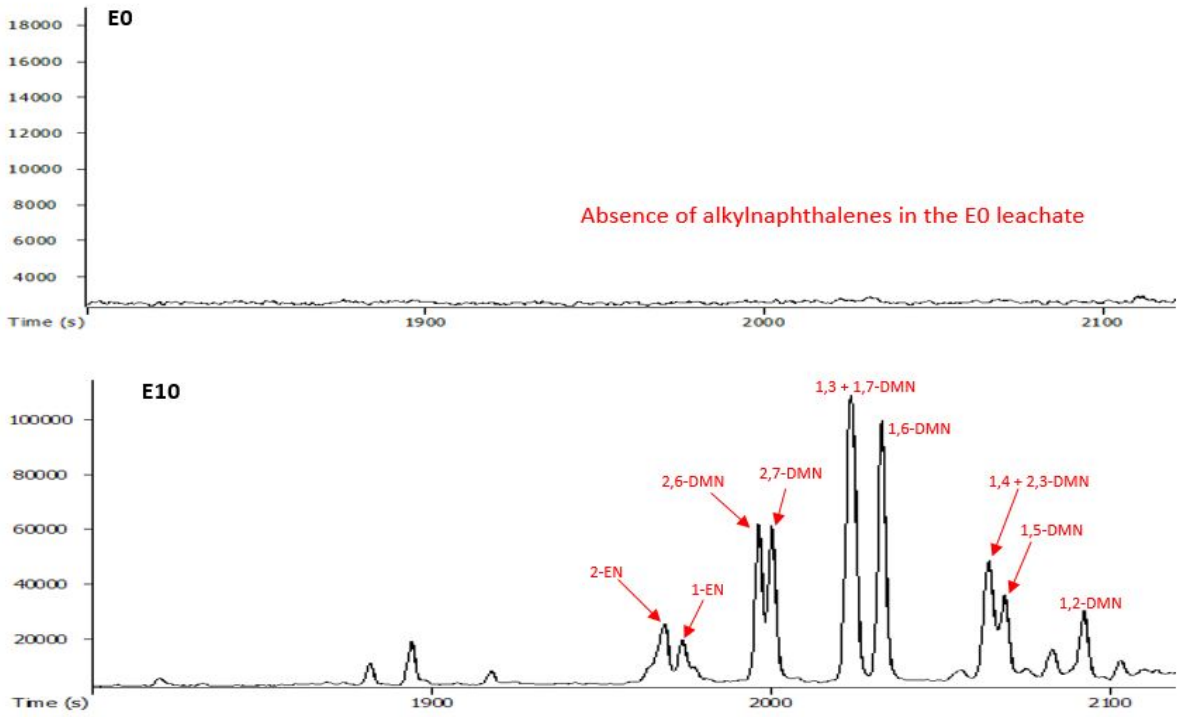


**Figure 1**: Partial m/z 156 chromatograms of the E0 and the E10 leachates showing that alkylnaphthalenes were eluted from the E10 diesel but retained in the E0 column, indicating co-solvency of alkylnaphthalenes with ethanol. EN: Ethylnaphthalene; DMN: Dimethylnaphthalene.

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