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Terrestrial exposure of oilfield flowline additives diminish soil structural stability and remediative microbial function

S.J. George, J. Sherbone, C. Hinz, M. Tibbett*

Centre for Land Rehabilitation, School of Earth and Environment, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

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ABSTRACT

Onshore oil production pipelines are major installations in the petroleum industry, stretching many thousands of kilometres worldwide which also contain flowline additives. The current study focuses on the effect of the flowline additives on soil physico-chemical and biological properties and quantified the impact using resilience and resistance indices. Our findings are the first to highlight deleterious effect of flowline additives by altering some fundamental soil properties, including a complete loss of structural integrity of the impacted soil and a reduced capacity to degrade hydrocarbons mainly due to: (i) phosphonate salts (in scale inhibitor) prevented accumulation of scale in pipelines but also disrupted soil physical structure; (ii) glutaraldehyde (in biocides) which repressed microbial activity in the pipeline and reduced hydrocarbon degradation in soil upon environmental exposure; (iii) the combinatory effects of these two chemicals synergistically caused severe soil structural collapse and disruption of microbial degradation of petroleum hydrocarbons.

1. Introduction

Oilfield pipelines are essential infrastructure for the petrochemical industry stretching many thousands of kilometres worldwide (Kennedy, 1993). Flowlines contain not only crude oil but also production water which is saline water entrained within reservoir formation co-produced with hydrocarbons as part of petroleum production activities (Burns et al., 1999). The saline water and oil provide conditions within the flowlines conducive to leaks (Papavinasam et al., 2007). For this reason flowline chemical additives such as biocides, corrosion inhibitor and scale inhibitor have become an essential operational tool to maintain these flowline networks.

Corrosion of production and casing tubing, surface equipment and drilling equipment is an acute problem mainly due to the simultaneous presence of mineralized water, carbon dioxide and hydrogen sulphide, with hydrocarbons (Narain et al., 1985). Corrosion inhibitors are used to prevent flowline structural damage. Most of the corrosion inhibitors currently used in flowlines and producing wells are organic nitrogenous compounds e.g. polyoxyalkylated amines, nitrogen quaternaries etc (Foroulis, 2004). Production water contains alkaline earth metal ions which in presence of sulphate and carbonate ions precipitates, resulting in the formation of 'scale' (Papavinasam et al., 2007). Scale inhibitor is continuously added to dissolve mineral deposits in flowlines which can cause progressive flow restrictions leading to large production losses (Gunarathne and Keatch, 1996). Scale inhibitors reduce the tendency of scale formation by inhibiting crystal growth mainly from inorganic di- or higher valent metal ions, particularly alkaline earth metal ions. In oilfields, scale and corrosion inhibitors are extensively used in formation and/or in production lines. Biocide are used mainly to control bacterial contamination of fracturing fluids; if bacterial growth is left unchecked may lead to fouling and/or corrosion (mainly from sulfate-reducing and acid-producing bacteria). Biocides are generically classed based on functional groups into aldehydes, biguanides, isothiazolones and quaternary ammonium, di-amines and amine acetate salts (Rossmoore, 1995). By far the most widely used biocide is a glutaraldehyde/quaternary ammonium compound blend.

Microbial biodegradation is the major pathway through which petroleum hydrocarbons including polycyclic aromatic hydrocarbons (PAH) are removed from the environment (Cho, 1997). Given the complexity of petroleum hydrocarbons, a broader microbial consortium with a suite of enzymatic capabilities will be required to achieve extensive biodegradation (Sepic et al., 1998). The biocides used to control flowline bacterial contamination may interfere with the biodegradation properties of the soil microbial biomass in the event of spill. With such disruption in biodegredational pathways, some of the lower and higher molecular weight PAH of petrogenic origin can lead to serious environmental

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* Corresponding author. Current address: National Soil Resources Institute, Department of Environmental Science and Technology, Cranfield University, Cranfield, Bedfordshire MK43 0AL, England.
E-mail address: m.tibbett@cranfield.ac.uk (M. Tibbett).

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contamination and affecting the health of aquatic, terrestrial and human life through bioaccumulation (Hughes et al., 1997) and are potential carcinogens (Richardson and Gangolli, 1992) if found to persist in the environment.

A prerequisite for proper bioremediation to occur is a fully functional microhabitat and bioremediation may be affected mainly due to: (i) xenobiotics which are toxic to the microbial community and may not allow for an adapted population to develop and (ii) the physical breakdown of the microhabitats disrupting microbial activity in the soil. Even though, soil structural impact following problems such as salinity and sodicity has been highlighted in several comprehensive reviews (Sumner, 1993; Levy, 2000), the obvious carry-over effect on soil microbial and biochemical activity has been poorly researched. It would also be useful to quantity the ecological stability of such affected systems in order to determine the amount of change caused by disturbance and the speed with which a system returns to pre-disturbance levels (Pimm, 1984; Wardle and Parkinson, 1990).

Based on the preliminary observation of impact on soil at flowline leak sites on Barrow Island off the cost of Western Australia (Fig. 1) – Australia's biggest onshore oilfield, a study was initiated primarily to address two research questions: (i) Are soil physico-chemical characteristics affected by waterflood flowline discharge? (ii) Do flowline additives affect microbial activity and hydrocarbon biodegradation in soil? We hypothesised that scale inhibitor, corrosion inhibitor and biocide will affect the soil physical integrity and biological activity. We were also interested to determine whether these additives have synergistic effects when applied in combination.

2. Materials and methods

2.1. General site description

We selected two flowline leak impacted and two uncontaminated field sites on Barrow Island (Fig. 1) off the coast of Western Australia. This region is arid subtropical (Fig. 1) with hot summers and moderate winters (www.bom.gov.au). The leak sites were: H18 leak site resulted from approximately 200 barrels of saline water discharged in January 2002 over 5500 m^2 area and G12A leak site resulted from approximately 60 barrels of saline water discharged in July 2004 over 1620 m^2 area. The pristine sites were: B32A and F13M (soil physico-chemical properties measured; Table 1) with no previous history of oil contamination. Historically, the installation faced risks from leaks in the approximately 1000 km network of the aging carbon-steel flow lines. There is a high priority to layout procedures to mitigate potential impacts to the environment of Barrow Island – a class-A reserve (the highest environmental classification possible in Australia).

The basic soil physico-chemical properties measured (Table 1) at the uncontaminated B32A and F13M sites showed a typical properties of north-western Australian low organic C soils with 5–10% kaolinite; 5% hematite responsible for their red appearance; 5% calcite from parent limestone; and traces of illite and feldspar.

2.2. Application of flowline additives on Barrow Island

Three additives injected into the production system are corrosion, scale inhibitors and a biocide (Table 2). The Corrosion inhibitor is injected constantly at waterflood stations, compressor station, central processing facility (CPF), terminal pit and every production wellhead on the island. Scale inhibitor is injected constantly at waterflood stations and CPF. Biocide is injected once per week for approximately 5 h at 4 separator stations and is also injected once a month at the CPF, terminal pit and waterflood station.

2.3. Field soil sampling strategy

Soils were sampled from 0 to 20 cm depth at the H18 and G12A sites, at 2 m intervals along a 50 m and 30 m north-south disturbance gradient transect from the centre of the contaminated area through to the non-contaminated zone. The soils were analysed for texture (McArthur, 1991); field electrical conductivity (EC) based on a 1:5 soil/water ratio, cation exchange capacity by silver thiourea extraction (Rayment and Higginson, 1992), water repellence using the molarity of ethanol droplet test (King, 1981), and dispersivity of soil aggregates by Emerson's dispersion test (Emerson, 1967). Hydraulic conductivity (determined using the constant hydraulic head method on undisturbed soil cores; Marshall and Holmes, 1992) and bulk density was only determined along the H18 transect.

2.4. Microcosm incubation experiment

Uncontaminated soil collected from 0 to 20 cm depth at from the B32A site was sieved through a 2 mm sieve and stored in cloth bags (to avoid any hydrocarbon cross-contamination from plastics) in field-moist condition at 4 °C (for a maximum of one week).

The experimental design consists of a series of treatments replicated six times with three individual (corrosion, scale and biocide) and two combinations of flowline additives (Table 3) in conjunction with crude oil added to soil. The inclusion of the two combination treatments (corrosion + scale and corrosion + scale + biocide) in the experimental design was based on the premise that corrosion and scale inhibitors are omnipresent in the flowlines and biocide, if present, will always be present in conjunction with these two additives (Table 3). Basal respiration from control treatment not spiked with crude oil was used to factor out CO_2 evolution originating from native organic matter sources.

The stored soils were initially pre-incubated for 48 h and then 100 g soil was weighed into 390 ml glass jars used as incubation vessels. The flowline additives (supplied by Baker Petrolite Ltd.; www.bakerhughesdirect.com) and saline water (34,400 mg L^{-1} in DI water and adjusted to 50% soil water holding capacity, Dibble and Bartha, 1979; Tibbett et al., 2011) were added at the same concentration as present within flowlines on Barrow Island (Table 1). The final solution was surface trickled for even distribution of chemicals in the microcosm. Barrow Island crude oil was sprayed across the soil surface at 50 mL kg^{-1} soil (oil concentration evidenced to produce highest microbial response; Tibbett et al., 2011). Microcosm vessels were maintained at a constant temperature of 25 °C which is close to the mean average Barrow Island temperature and also is in the ideal temperature range of mesanthropic microbes. The timeframe selected for the microcosm experiment (40 days) was aimed at achieving a low level response on the molecular biodegradation scale of Peters et al. (2005). The measurement of microbial CO_2 respiration has been correlated directly to the extent of hydrocarbon degradation (Baptista et al., 2005). Daily measurement of microbial CO_2 was used to monitor biological activity as detailed in Tibbett et al., 2011.

2.5. Flowline additive response ratio, resistance and resilience index

A response ratio metric (ln (treatment response/control); Elser et al. (1996)) was generated comparing cumulative CO_2 evolved during the course of the microcosm experiment for the suite of flowline additives and crude oil spiked samples to sole crude oil spiked controls. An advantage of this metric is that it scales the treatment response against the control treatment and elucidates the direction of the treatment response (Ostertag, 2010).

Based on the daily CO_2 evolved for various flowline additive treatments during the course of the incubation, the stability - resistance and resilience to disturbance - was compared using a relative quantitative measure of both the resistance and resilience developed by Orwin and Wardle (2004). The resistance index (Orwin and Wardle, 2004) signifies resistance to change following disturbance:

$$\mathrm{RS}(t_0) = 1 - \frac{2|D_0|}{(C_0 + |D_0|)} \tag{1}$$

where D_0 is the difference between the crude oil spiked control (C_0) and the disturbance at the end of the disturbance (t_0). This index is standardised by the control, as this takes into account differences in the amount of change that a disturbance could cause (Orwin and Wardle, 2004). This resistance index is bounded by −1 and +1, with a value of +1 showing that the disturbance had no effect (maximal resistance), and lower values showing stronger effects (less resistance). The resilience index (RL, Orwin and Wardle, 2004) at time x is

$$\mathrm{RL}(t_x) = 1 - \frac{2|D_0|}{(|D_0| + |D_x|)} - 1 \tag{2}$$

where D_0 is as above and D_x is the difference between the control (C_x) and the disturbed soil at the time point (t_x) chosen to measure resilience. This index is standardised by the amount of change initially caused by the disturbance (D_0), as this determines the state from which it has to recover. This index of resilience is also bounded by −1 and +1. A value of 1 at the time of measurement indicates full recovery (maximal resilience), and lower values indicate a slower rate of recovery.

2.6. Recoverable hydrocarbon analysis

For determining hydrocarbon biodegradation during the time course of the incubation experiment, C10–C36 hydrocarbon composition of the solvent (dichloromethane and acetone) extractable fraction; poly-aromatic hydrocarbons (PAH); benzene, toluene, ethylene and xylene (BTEX) and C6–C9 levels were determined for pooled samples from each treatment both at the beginning and completion of the incubation experiment (M.D.E.P, 1995; U.S. E.P.A., 1992).

2.7. Statistical analysis

The difference between treatments in basic physico-chemical properties and response ratio was statistically interrogated using one-way analysis of variance