



Solubility and reactivity of surfactant-enhanced alkaline hydrolysis of organophosphorus pesticide DNAPL

Jens Muff¹ · Leah MacKinnon² · Neal D. Durant³ · Lars Frausing Bennedsen⁴ · Kirsten Rügge⁵ · Morten Bondgaard⁶ · Kurt D. Pennell⁷

Received: 4 April 2019 / Accepted: 21 November 2019 / Published online: 16 December 2019
© Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

The study presented in this paper evaluated the effectiveness of surfactants in enhancing mass removal of organophosphorus pesticides (OPPs) from soil under highly alkaline conditions and potential for enhancing in situ alkaline hydrolysis for treatment of OPPs, particularly parathion (EP3) and methyl parathion (MP3). In control and surfactant experiments, hydrolysis products EP2 acid, MP2 acid, and PNP were formed in non-stoichiometric amounts indicating instability of these compounds. MP3 and malathion were found to have faster hydrolysis rates than EP3 under the conditions studied. All surfactants evaluated increased solubility of OPPs under alkaline conditions with four nonionic alcohol ethoxylate products providing the greater affect over the polyglucosides, sulfonate, and propionate surfactants evaluated. The alcohol ethoxylates were shown to provide substantial mass removal of OPPs from soil. Hydrolysis rates were typically slower in the presence of surfactant, despite the relatively higher aqueous concentrations of OPPs; this was likely due to micellar solubilization of the OPPs which were therefore less accessible for hydrolysis. The results of this study support the use of surfactants for contaminant mass removal from soil, particularly under alkaline conditions, and may have implications for use of some surfactants in combination with other technologies for treatment of OPPs.

Keywords Surfactant · In situ remediation · Alkaline hydrolysis · Organophosphorus pesticides · DNAPL · Parathion

Introduction

Surfactant-enhanced remediation of contaminated sites has been used in clean-up operations targeting nonaqueous phase

liquids (NAPLs) with low aqueous solubility (Pennell et al. 1993; Jafvert and Strathmann 2000; Mulligan et al. 2001; Suchomel et al. 2007). As a stand-alone technology, surfactant flushing for NAPL recovery was based on the prior work in

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11356-019-07152-0>) contains supplementary material, which is available to authorized users.

✉ Jens Muff
jm@bio.aau.dk

¹ Department of Chemistry and Bioscience, Section of Chemical Engineering, Niels Bohrs Vej 8, Aalborg University, DK-6700 Esbjerg, Denmark

² Geosyntec Consultants Inc., 130 Research Lane, Suite 2, Guelph, ON, Canada

³ Geosyntec Consultants Inc., 10220 Old Columbia Road, Suite A, Columbia, USA

⁴ Rambøll, Forurenet jord og grundvand, Lysholt Allé 6, DK-7100 Vejle, Denmark

⁵ COWI A/S, Jord og Grundvand, Parallelvej 2, DK-2800 Kongens Lyngby, Denmark

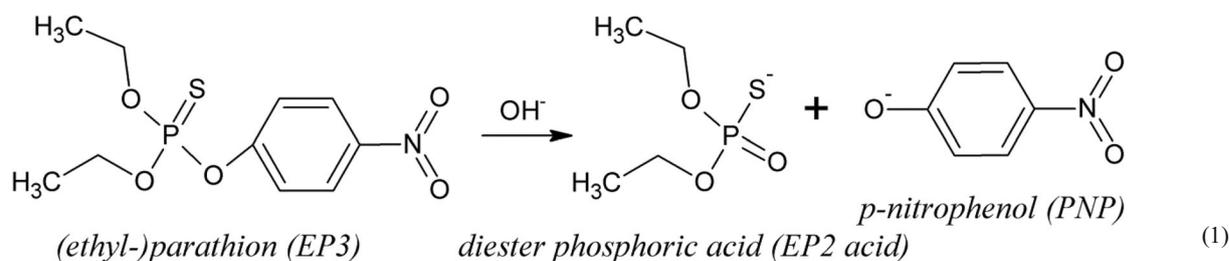
⁶ Central Denmark Region, Environment, Lægårdvej 12, DK-7500 Holstebro, Denmark

⁷ 231 Engineering Research Center, Brown University School of Engineering, 184 Hope Street, Box D, Providence, RI 02912, USA

the field of enhanced oil recovery (EOR). During surfactant flushing, contaminant recovery can be achieved via interfacial tension (IFT) reductions between the organic liquid and aqueous phases (mobilization) and/or increased aqueous solubility due to the formation of surfactant micelles (solubilization) (Dugan et al. 2010; Pennell et al. 2013). Although several field-scale tests have demonstrated the ability of surfactant flushing to recover > 90% of the contaminant mass (e.g., (Hasegawa et al. 2000; Londergan et al. 2001)), recent work has focused on applying surfactants as means to improve the performance of other remediation technologies aimed at in situ contaminant degradation (Menendez-Vega et al. 2007; Dugan et al. 2010; Perelo 2010). Utilization of surfactants in combination with other technologies can be implemented in parallel as an enhancement method or in series as a part of a treatment train approach (Pennell et al. 2013). Many studies have focused on surfactant-enhanced in situ chemical oxidation (S-ISCO) (Tsai et al. 2009; Li and Hanlie 2008; Dugan et al. 2010; Hoag and Collins 2011), where the increased aqueous solubility effect of surfactants has been shown to enhance the performance of chemical oxidants. Additionally, the potential for applying surfactants as an enhancement of other remediation technologies, including electrokinetic remediation (Fan et al. 2014), biodegradation (Ramsburg

et al. 2004; Amos et al. 2007; Dave et al. 2014), and air sparging (Chuan-Yu et al. 2014), has been explored.

The objective of this study was to explore the potential use of surfactants and alkaline hydrolysis as a combined remedy for in situ remediation of organophosphorus pesticides (OPPs). The work was completed using materials from the Groyne 42 site in Denmark to serve as a model site. The Groyne 42 site is a 20,000 m² former disposal site primarily for OPP chemical wastes. After 40 years and two excavation events, about 100 metric tons of OPPs are still present, with the majority existing as sorbed phase and residual dense NAPL (DNAPL) (Bondgaard et al. 2012). Details on the Groyne 42 site and the experiences obtained with in situ alkaline hydrolysis of the OPPs are presented by Bondgaard et al. (Bondgaard et al. 2012). The main contaminants are (ethyl)parathion (EP3: ~50%) and methyl parathion (MP3: ~15%). Both compounds possess low aqueous solubility and high toxicity (Bondgaard et al. 2012). The toxicity of the OPPs can be reduced by hydrolysis at high pH, which results in the formation of water soluble para-nitrophenol (PNP) and organophosphoric acids (EP2 acid and MP2 acid) as hydrolysis products (Eq. 1).



This approach has been demonstrated in a number of studies (Ketelaar 1950; Di Palma 2003), and the process is used by OPP manufacturing companies to transform OPPs in their waste water; however, the technology has not been widely applied for in situ remediation (Bondgaard et al. 2012). The hydrolysis rate is influenced by the low solubility of OPPs and could potentially be enhanced by applying surfactant as a mean to increase the availability of OPPs in aqueous solutions. High pH may in itself promote increased OPP solubility due to hydrolysis of the OPP reactant promoting NAPL solubility. Surfactants and OPP hydrolysis have mainly been studied from a detoxification and potential water treatment perspective using cationic surfactants (Han et al. 2007; Shrivastava and Ghosh 2008; Mirgorodskaya et al. 2012) or to use surfactants as a means to isolate OPPs in sample preparation prior to analysis (Seebunrueng et al.

2011; Seebunrueng et al. 2012). In aqueous systems, cationic surfactants are the most obvious candidates for OPP hydrolysis, since once OPPs are solubilized in micelles, alkaline hydrolysis requires gradient-driven transport of the reactive hydroxide anions from the aqueous bulk phase to the micellar surfactant phase (Han et al. 2007). According to the pseudophase ion exchange (PPIE) model of micellar catalysis, it is assumed that the micellar surface is saturated with counterions and that the counterion binding is constant for inert counterion surfactants (Han et al. 2007). The inert counterions reduce the rate of micellar-assisted reactions of reactive counterions with nonionic organic substrates as a result of this competition at the micelle surface (Han et al. 2007), and a decrease of hydrolysis rate at increased ionic strength of solution is possible. From a subsurface remediation perspective, cationic surfactants are limited by their potential toxicity and

strong adsorption on soil materials (Mulligan et al. 2001). As a consequence, only few papers have investigated the combination of OPPs and surfactants from a soil washing perspective (Sharma et al. 1985; Zeng et al. 2006; Chu et al. 2006; Wattanaphon et al. 2008; Torres et al. 2012). These papers have primarily focused on nonionic surfactants. For example, Torres et al. 2012 [22] showed that 63% and 85% of MP3 could be removed from artificial contaminated soil by nonionic surfactants Brij 35, Triton X-100, and Tween 80 at near neutral pH. At a low dosage of EP3, Chu et al. [20] demonstrated that 73% to 97% could be extracted from soil using Brij 35 at near neutral pH. Batch experiments indicated that recovery efficiency was independent of soil organic matter content and increased linearly with surfactant dose, yielding a molar solubilization ratio (MSR) of 0.11 mol EP3 per mol of surfactant [20]. However, prior studies have not considered concomitant surfactant-enhanced solubilization and alkaline hydrolysis. Thus, the specific aim of this research was to study the ability of surfactants to increase the solubility of OPP-NAPL contaminants at alkaline pH and their effect on the alkaline hydrolysis of OPPs.

Eight nonionic, one modified anionic, and one amphoteric surfactant were screened at a dose of 30 g L^{-1} in 0.34 M NaOH tap water. The 3 wt% surfactant dosage was chosen based on previous experience from bench and larger scale surfactant flushing systems, since a loss of available surfactant may occur due to soil adsorption (Pennell et al. 2013). Batch reactor studies were performed to measure OPP solubility and hydrolysis product formation. Subsequently, the alcohol ethoxylate group of nonionic surfactants was selected for further remediation tests using contaminated soil from the Groyne 42 site. The remediation tests included dose studies and the influence of mechanical mixing.

Materials and methods

Chemicals

Solid sodium hydroxide (VWR) was mixed with Esbjerg tap water (Denmark) with pH 7.7 and 5.1-mM ionic strength. EP3 (99.9% grade) and MP3 (99.9% grade) were provided by Cheminova A/S (Rønland, Denmark). The NAPL sampled at the Groyne 42 site had a liquid density of 1.16 g mL^{-1} (measured by pycnometer) and a dynamic viscosity of 13.9 cP at 10 °C (measured with Brookfield DV-III). The Groyne 42 NAPL was a complex mixture of the OPP commercial pesticides and all intermediate products, reactants, and solvents used or produced in the synthesis of the OPPs. The chemical composition of the NAPL, determined by gas chromatography as in

accordance with the analytical procedure presented in the Analysis subsection, is shown in Table 1.

The site soil used in the experiments was sampled with an auger from a Groyne 42 hot spot area in accredited soil bags and stored in a cooling box during transportation and at -18 °C during storage. At use, the soil was thawed, homogenized in a borosilicate glass contained with a stainless steel spoon, subsampled into $\sim 500 \text{ g}$, and further homogenized before 80 g was weighed out in blue cap borosilicate glass reactors.

Ten surfactant formulations, which were divided into four groups based on chemical structure, were supplied by three manufacturers: Rhodia, DOW Chemicals, and DeForest (Table 2). These surfactants were preselected for further study based on practical criteria including stability at alkaline conditions (pH 12 or higher) to be compatible with alkaline hydrolysis, acceptability for use in the field (e.g., readily biodegradable in the environment and low toxicity), and limited foaming in aqueous solution.

Experimental setup

The experiments were completed as duplicate batch experiments. The time of reaction for all experiments was fixed at $168 \pm 1 \text{ h}$ (7 days). To establish reference solubility and reactivity, alkaline hydrolysis of the site NAPL and the two most important OPPs EP3 and MP3 were evaluated in tap water only and base-only (0.34 M NaOH in tap water) experiments. In the initial surfactant screening experiments, 0.34 M NaOH in tap water was used as solvent for the 30 g L^{-1} ($3 \text{ w/v} \%$) surfactant formulations. In the case of the modified anionic surfactant DeTERGE NAS, $4.0 \text{ w/v} \%$ NaCl was added to improve performance. The initial pH of the surfactant solutions containing 0.34 M NaOH was in the range of 13.4 to 13.5 measured by a Metrohm NTC pH probe. For all surfactant screening tests, NAPL and aqueous solutions were mixed in 1:10 volumetric ratio (3 ml NAPL and 30 ml solution) in 100 mL borosilicate autoclave flasks. The reactors were sealed and mixed on a temperature-controlled (10 °C) mixing table operated at speed of $170 \text{ revolutions min}^{-1}$. Prior to sampling, the aqueous phase supernatant was transferred to 35 mL borosilicate glass centrifuge tube and separated at 3000 rotations per minute for 15 min. The final pH was measured in a 12-mL aliquot of the aqueous phase that afterward was preserved by freezing (-18 °C) prior to analysis of OPP and hydrolysis products.

For the batch reactor experiment conducted with soil and water, four ethoxylate surfactants were selected based on the screening experiments. In each reactor, 80 g of contaminated site soil and 20 mL of surfactant solution (soil-water ratio of 4 g/mL) were added to the 100 mL borosilicate glass reactors. No additional site NAPL was added. Batch experiments were performed at two surfactant concentrations (30 g L^{-1} and

Table 1 Composition by weight of Groyne 42 NAPL

Compound	Abbreviation	Comp.(wt%)	Aq. sol.(mg L ⁻¹)	Density (kg L ⁻¹)	log K _{ow}
Ethyl-parathion	EP3	40.1	11	1.26	3.83
Methyl parathion	MP3	10.1	55	1.36	2.86
Malathion	Malathion	7.0	145	1.23	2.36
Ethyl-sulfotep	E-sulfotep	6.9	30	1.20	3.99
Solvent naphtha (~n-hexane)	Sol. naph.	6.4	–	–	–
O,O,O-triethyl-thiophosphoric acid	E-OOOPS	2.9	–	–	–
O,O-diethyl-S-methyl-dithiophosphoric acid	EEM-OOSPS	2.0	–	–	–
Xylenes	Xylene	2.0	–	–	–
O,O,S-trimethyl-dithiophosphoric acid	MOOSPS	1.4	–	–	–
4-Cl-3-cresol	4-Cl-Cresol	1.1	–	–	–
Iso-amino-parathion	Iso-Amino-EP3	1.0	–	–	–
2-Cl-3-Cresol	2-Cl-Cresol	0.5	–	–	–
Toluene	Toluene	0.5	–	–	–
Amino-methyl parathion	Amino-MP3	0.5	–	–	–
O,O,S-triethyl-dithiophosphoric acid	EOOSPS	0.4	–	–	–
Amino-ethyl-parathion	Amino-EP3	0.03	–	–	–
Not identified (unknown)		17.2	–	–	–
Total		100.0			

Aqueous solubility and density for compounds are provided at 20 °C unless otherwise mentioned. Data on compound properties are from estimation programs interface by US Environmental Protection Agency (USEPA 2014)

10 g L⁻¹) and at mixing rates up to 170 revolutions min⁻¹. Surfactants included in this experiment were Rhodasurf CET 25 (surf1), Rhodasurf T50 (surf2), Ecosurf EH-9 (surf3), and Tergitol 15-S-12 (surf4). After 7 days of rotary mixing, the reactors were drained through glass wool filters, and the

aqueous phase was analyzed for OPP constituents. No free phase NAPL was observed in any of the aqueous samples. After draining, 10 g of the moist soil from each of the reactors was extracted with 10 mL of toluene that was analyzed for OPPs. For some of the soil samples, the addition of up to

Table 2 Overview of surfactant formulations applied in the study

Surfactant	Type	Active ingredient	CAS no.	Supplier	Surf. ID
<i>Alcohol ethoxylates</i>					
Rhodasurf CET 25	Nonionic	Ethoxylated cetyl-oleyl alcohol	68,920–66-1	Rhodia	surf1
Rhodasurf T50	Nonionic	Ethoxylated oleyl-cetyl alcohol	68,920–66-1	Rhodia	surf2
Ecosurf EH-9	Nonionic	Alcohol ethoxylate, 2-ethyl hexanol EO-PO nonionic surfactant	7732-18-5 64,366–70-7	Dow	surf3
Tergitol 15-S-12	Nonionic	Secondary alcohol ethoxylate	84,133–50-6 25,322–68-3	Dow	surf4
DeTERGE LF-2379	Nonionic	Modified alcohol ethoxylate		DeForest	surf5
<i>Alkyl polyglucoside</i>					
Triton BG-10	Nonionic	C8-C10 alkyl polyglucoside; D-glucopyranose, oligomeric, decyl octyl glycoside	68,515–73-1	Dow	surf6
Triton CG-50	Nonionic	C8-C10 alkyl polyglucoside; D-glucopyranose, oligomeric, decyl octyl glycoside	68,515–73-1	Dow	surf7
DeSULF GOS-P-60WCG	Nonionic	Alkyl polyglucoside (caprylyl/capryl glucoside)	113,976–90-2	DeForest	surf8
<i>Alkane sulfonates</i>					
DeTERGE NAS	Modified Anionic	Octyl sulfonate		DeForest	surf9
<i>Alkyl Amino Acids</i>					
DeTERIC CP-Na-38	Amphoteric	Sodium salt, carboxylated C10–12 Modified propionate		DeForest	surf10

30 mL of toluene was needed in order to obtain a sufficient toluene phase due to formation of a turbid toluene soil mixture. Soil drying was avoided due to risk of contaminant volatilization.

Analysis

This study focused on the most toxic NAPL components: the pesticides EP3, MP3, malathion, and E-sulfotep and their hydrolysis products EP2 acid, MP2 acid, and PNP. For this reason not all compounds present in the NAPL were monitored. Table 3 shows the compounds included in the chemical analysis program, as well as their abbreviation.

OPPs (EP3, MP3, malathion, E-sulfotep) were analyzed by gas chromatography (Agilent 6890) with polar capillary column (J&W Scientific, DB 210) equipped with nitrogen-phosphorous detector (NPD). All samples (10 mL) were treated with 2 mL of isopropyl acetate for organic extraction during 15 min of ultrasonic mixing and subsequent centrifugation (4000 rpm for 3 min), injection volume was 1 μL , and detection limits were reported as 0.01 mg L^{-1} using 5-point standard curve calibration. The remaining compounds of the NAPL characterization were analyzed by the same procedure. The hydrolysis products (EP2 acid, MP2 acid, PNP) were analyzed by liquid chromatography (Agilent 1100 LC) with UV detection (Diode Array; Signal 210 nm bw 4, Reference 550 nm bw 100). The column was a Phenomenex Prodigy ODS 3 (3.2 \times 150 mm, 5 μ with security guard), gradient eluent flow using phosphate buffer (pH 2.5), and acetonitrile applied, and 5-point standard curve calibration gave a detection limit of 0.1 mg L^{-1} in toluene.

Results and discussion

The surfactant-enhanced in situ alkaline hydrolysis (S-ISAH) is a process that combines solubilization of OPPs from the NAPL and/or sorbed phase followed by reaction with hydroxide in the aqueous phase. The performance of this combined process was evaluated based on the concentration of OPPs in the aqueous and soil phase and hydrolysis products in the aqueous phase only. The processes were difficult to study

individually, since solubilization occurs in parallel with hydrolysis. A reaction time of 7 days was used in all tests to allow sufficient time for micellar solubilization of the OPPs. The OPP-NAPL is a complex mixture, with EP3 and MP3 comprising 40% and 10% of the NAPL mass (Table 1). These OPPs yield EP2 acid and MP2 acid, respectively, as well as PNP as hydrolysis products. EP2 acid is also produced by hydrolysis of E-sulfotep, comprised 7% of NAPL mass, and yields two EP2 acid molecules. Finally, malathion (7% of the NAPL mass) also undergoes hydrolysis under alkaline conditions to yield MP2 acid and thiophosphate. The EP2 and MP2 diester phosphoric acids might undergo further hydrolysis that might complicate completion of the mass balance of the reactors. In batch reactors where 0.34 M NaOH was added, the hydrolysis products PNP, EP2 acid, and MP2 acid were dissociated and were therefore detected as their conjugated bases. For the ease of comparison of OPP reactivity between circumneutral and alkaline conditions, these will be referred to as their acidic form.

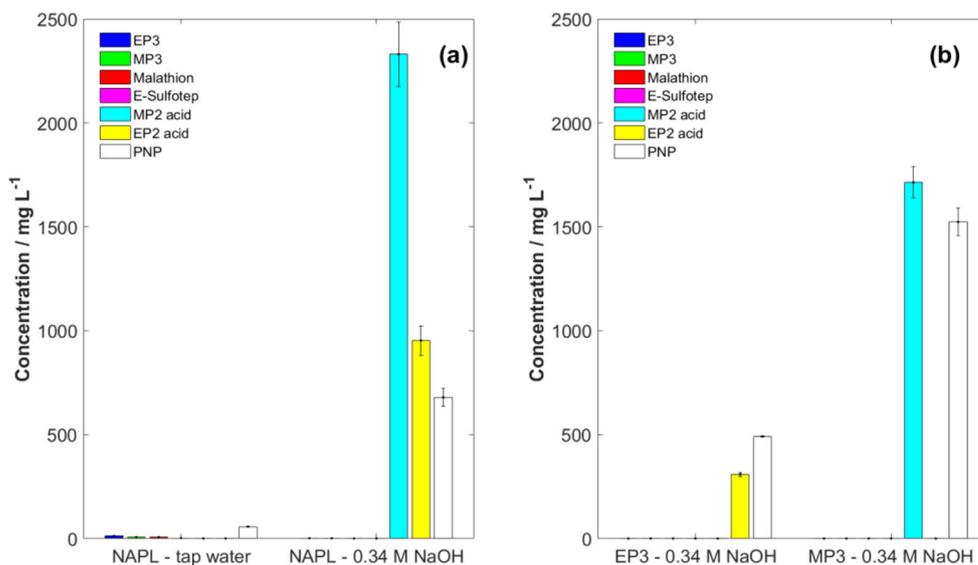
Alkaline hydrolysis of NAPL compounds

The initial batch experiment served to establish reference conditions for surfactant screening based on the alkaline hydrolysis in tap water (initial pH 8.26) and in 0.34 M NaOH (initial pH 13.4) (Fig. 1a). The final pH in the alkaline reactors did not decrease below 13.0 in any of the tests reported in this study, and initial and final pH of all tests is reported as Fig. S1. At pH 8.26, low levels of MP2 acid and PNP were detected after 7 days of rotary mixing, indicating that MP3 and/or malathion undergoes some hydrolysis even at, in consideration of the context of this study, near neutral pH. However, no EP2 acid was found, indicating the absence of EP3 and E-sulfotep hydrolysis. At this pH, the parent OPPs were found at levels comparable to their reported aqueous solubilities (~ 10 to 20 mg L^{-1}) taking into account the approximate mole fraction of the specific OPP in the NAPL. At pH 13.4, much higher rates of alkaline hydrolysis were observed compared to at pH 8.26 as indicated by high concentrations of hydrolysis products, where MP2 acid peaks with a concentration of $2329 \text{ mg L}^{-1} \pm 156 \text{ mg L}^{-1}$. The concentration of EP2 acid was substantially lower ($953 \text{ mg L}^{-1} \pm 71 \text{ mg L}^{-1}$) than that of

Table 3 Chemical compounds included in the monitoring program

Compound	Abbreviation	Origin/class
(Ethyl-)parathion	EP3	OPP
Methyl parathion	MP3	OPP
Malathion	Malathion	OPP
Ethyl-sulfotep	E-sulfotep	OPP
Para-nitrophenol	PNP	Hydrolysis product of EP3 and MP3
O,O-diethyl-thiophosphoric acid	EP2 acid	Hydrolysis product of EP3 and E-sulfotep
O,O-dimethyl-thiophosphoric acid	MP2 acid	Hydrolysis product of EP3 and malathion

Fig. 1 (a) Control experiments for establishing the concentration of OPPs and hydrolysis products in the aqueous phase after 7 days of reaction at 10 °C in tap water (initial pH 8.26) and 0.34 M NaOH (initial pH 13.6). (b) Single component experiments with EP3 in 0.34 M NaOH (initial pH 13.5) and MP3 in 0.34 M NaOH (initial pH 13.5). For ease of comparison, **a** and **b** were formatted in a similar manner despite **b** considered only EP3 and MP3. Standard deviations are shown as error bars



MP2 acid despite the fact that EP3 comprised a larger fraction of the NAPL mass (40% w/w) compared to MP3 (10% w/w). Additional source of MP2 acid was malathion (7.0% w/w) that was not detected in the aqueous phase in significant amounts indicating a fast hydrolysis of this compound contributing to the difference in MP2 and EP2 acid production rates. E-sulfotep (7.0% w/w) served as a source of EP2 acid. This data indicated a slower hydrolysis rate for EP3 and E-sulfotep compared to MP3 and malathion under the experimental conditions. When the reaction products were compared on a molar basis (MP2 acid, 16.4 mM; EP2 acid, 5.6 mM; PNP, 4.9 mM), it was clear that the hydrolysis products were not formed in stoichiometric amounts indicating instability at pH 13.4. The observed difference in hydrolysis rate of EP3 and MP3 was studied further in separate experiments for each of EP3 and MP3 at an initial pH 13.5 (Fig. 1b). The measured production of MP2 acid was 1714 mg L⁻¹ ± 76 mg L⁻¹ compared to 307 mg L⁻¹ ± 11 mg L⁻¹ for EP2 acid, consistent with MP3 having a higher hydrolysis rate as compared to EP3. This finding is in agreement with earlier OPP research that in aqueous alkaline hydrolysis experiments has demonstrated four times faster hydrolysis of MP3 compared to EP3 (Ketelaar 1950). The 1:1 M stoichiometry expected between the P2 acids and the respective concentrations of PNP was not found in any of the batch reactor tests (EP2 acid, 1.8 mM vs. PNP, 3.5 mM and MP2 acid, 12.1 mM vs. PNP 11.0 mM), again indicating instability of the hydrolysis products at pH 13.5.

Screening of surfactant

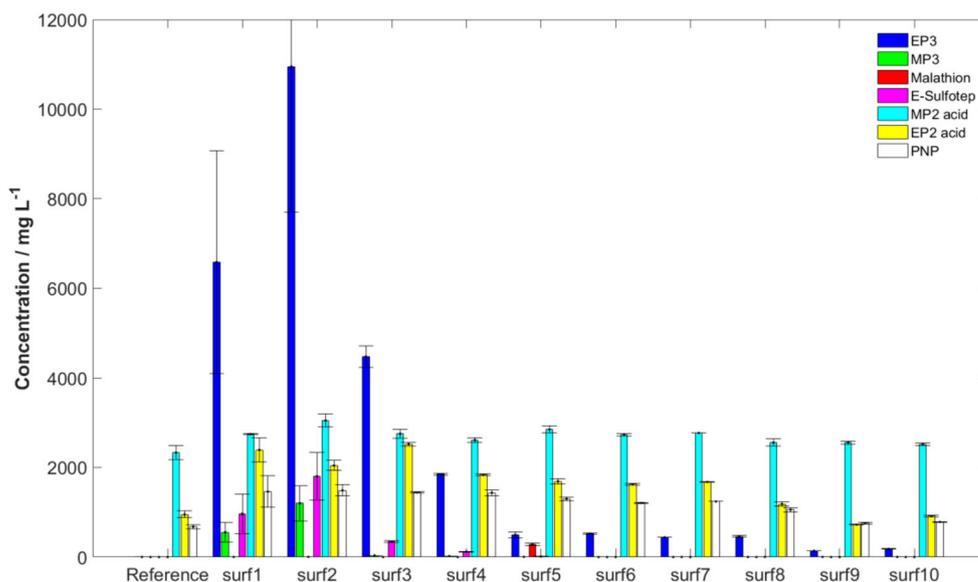
With the baseline performance of OPP alkaline hydrolysis in 0.34 M NaOH established, the next experiment was designed to evaluate the effectiveness of ten surfactants (Table 1) in enhancing OPP alkaline hydrolysis. The surfactants were

evaluated in separate batch experiments used at 30 g L⁻¹ and initial pH in the range of 13.4 to 13.6. The concentrations of OPPs and hydrolysis products after 7 days of mixing are shown in Fig. 2.

These results clearly show differences in the effectiveness of the surfactants to enhance the solubility and hydrolysis of the OPPs. Only minor increases in solubility were observed with the amphoteric alkyl amino acid (surf10), the modified anionic alkane sulfonate (surf9), and nonionic alkyl polyglucoside (surf6 to 8)-type surfactants. In contrast, the alcohol ethoxylate surfactants (surf 1 to 5) did show increased OPP levels. In particular, EP3 concentrations increased above 4000 mg/L in the surf1, surf2, and surf3 tests, which were attributed to micellar solubilization. The OPP concentrations were relatively high as compared to the hydrolysis product concentrations, implying that micellar solubilization may have prevented rapid hydrolysis following dissolution. However, the highest concentrations of EP2 acid were found with these three surfactants showing that an increased aqueous concentration of EP3 did allow for improved EP3 hydrolysis. MP2 acid was the most abundant hydrolysis product, with concentrations in all tests comparable to results obtained in the reference experiment (Fig. 1a).

The concentration data for EP3 and its hydrolysis products EP2 acid and PNP as statistically analyzed by box plots are shown in Fig. 3. This analysis clearly demonstrates that the concentrations of EP3 with surf1, surf2, surf3, and surf 4 were significantly greater compared to the other surfactants. Concentrations of EP2 acid and PNP were comparable among the nonionic surfactant and significantly higher than concentrations obtained with the anionic and amphoteric surfactants. The overall indication

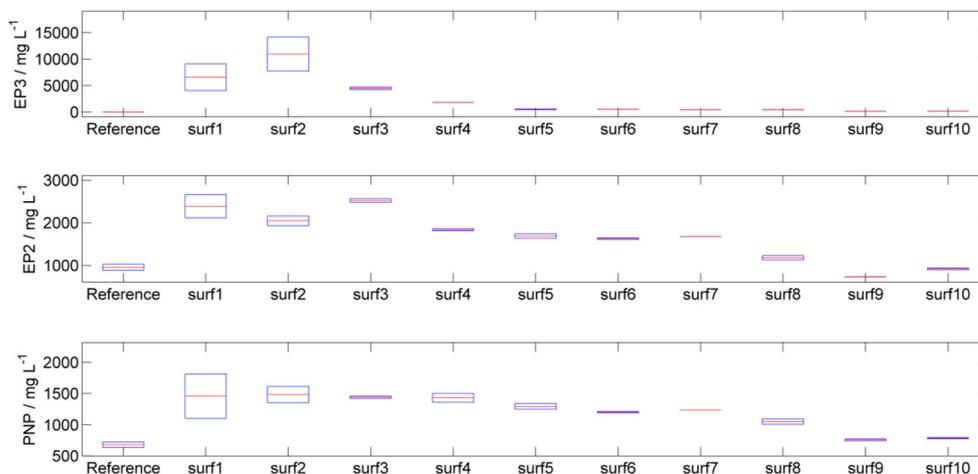
Fig. 2 The concentrations of OPPs and hydrolysis products in the aqueous phase of the surfactant screening experiments (30 g L^{-1}) sampled after 7 days of reaction at 10°C in 0.34 M NaOH (initial pH 13.4–13.6). Standard deviations are shown as error bars



of the data was that although the solubility of OPP increased, especially for the nonionic alcohol ethoxylate surfactants, the production of hydrolysis reaction products was only slightly enhanced. This observation differed from previous referred studies using cationic surfactants, which found a significant increase in hydrolysis rate with surfactant dose (Shrivastava and Ghosh 2008; Mirgorodskaya et al. 2012). The presence of high concentrations of aqueous micellar solubilized OPPs suggests that the hydrolysis process was limited by the mass transfer of OPP from the micelle core to the free aqueous phase. A similar type of phenomena has been observed when surfactants have been used to promote biodegradation of sparingly soluble compounds (Yeh et al. 1999; Amos et al. 2007).

Based on the results obtained with OPP-NAPL systems, (Figs. 2 and 3), surf1 through surf4 were selected for subsequent experiments designed to evaluate the performance of the nonionic alcohol ethoxylate surfactants in the presence of OPP-contaminated soil.

Fig. 3 A box plot showing the variations in EP3, EP2 acid, and PNP concentrations through their quartiles. The bottom and top of the box are the first (25%) and third quartiles (75%), and the band inside the box is the second quartile (the median)



Contaminated soil and nonionic surfactant systems

The performance of surfactants can be strongly influenced by adsorption of the active ingredients to the solid phase (Jafvert and Strathmann 2000; Mulligan et al. 2001). For this reason, the alkaline hydrolysis enhancement of four alcohol ethoxylate formulations was tested with contaminated site soil at two different dosages. Also, the influence of mechanical mixing of the batch reactors was studied to provide information on a potential gain of hydrolysis efficiency by induced subsurface mixing due to well injection and recirculation of site groundwater. All experiments were completed with a $4:1 \text{ g mL}^{-1}$ soil to water ratio to resemble subsurface conditions. The initial concentration of OPP in the contaminated site soil is presented in Table 4. No additional NAPL was added.

In Fig. 4, the OPP and reaction product concentration data obtained in the aqueous supernatant of the reactors after 7 days of mixing are shown. The increase in aqueous EP3 in the

Table 4 Initial concentrations of OPP in the site soil and the estimated contaminant composition in mass percentage

OPP	Comp. (wt%)*	Concentration ± std. (mg kg ⁻¹)
EP3	51.8	934.5 ± 6.5
MP3	7.6	137.5 ± 0.5
Malathion	8.5	152.5 ± 2.5
E-sulfotep	4.9	89.0 ± 1.0
Other compounds	9.9	–
Not identified (Unknowns)	17.2	–
Total	100	

*The composition in mass percentage (wt%) is calculated based on soil concentrations of OPP and other compounds and assuming the same mass percentage of not identified (unknowns) as in the NAPL (Table 1)

presence of surfactants compared to the 20 mg L⁻¹ found in the 0.34 M NaOH reference was evident. Surf3 yielded the highest concentrations of aqueous EP3 when comparing among the four surfactants at both dosages (219 ± 8.5 mg L⁻¹ at 10 g L⁻¹ and 633 ± 36 mg L⁻¹ 30 g L⁻¹). In comparison to the data obtained for NAPL water systems (Fig. 2), experiments conducted in the presence of contaminated soil resulted in lower aqueous phase OPP concentrations, due to less contaminant mass available in the reactor (i.e., NAPL versus contaminated soil). In the NAPL water systems, surf1 and surf2 showed the best performance in terms of EP3 solubilization, whereas the best performance for EP3 solubilization in the soil-water systems was found by surf 3 and surf 4. For all surfactants tested, concentrations of EP3 in the aqueous phase increased when the applied surfactant concentration was increased from the reference control (water only) to 10 and 30 g L⁻¹, consistent with micellar solubilization behavior (Pennell et al. 2013). Relatively small changes in aqueous concentrations were observed for the other OPPs, indicating a fast rate of hydrolysis of MP3, malathion, and E-sulfotep.

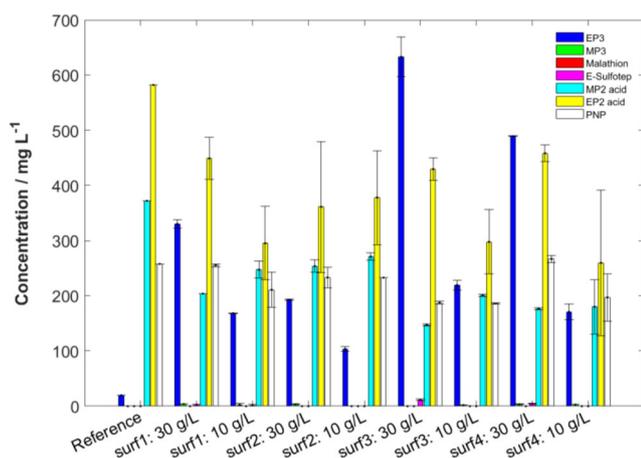


Fig. 4 Concentrations of OPPs and hydrolysis products in the water samples of the soil experiments. All of these reactors were placed on the shaker table for the 7 days of reaction at 10 °C. Two surfactant dosages (30 g L⁻¹ and 10 g L⁻¹) in 0.34 M NaOH were used for all four surfactants

An interesting observation was that EP2 acid was the most abundant of the hydrolysis products in all of the tests. This can be explained by the change in contaminant source from site NAPL to contaminated site soil, which had a different OPP composition, with EP3 being even more prevalent (51.8 wt%, Table 4). However, concentrations of the hydrolysis products in the reference sample (0.34 M NaOH alone) were similar to those observed in the surfactant solutions indicating that the hydrolysis was not improved in the presence of the selected surfactants. These data did again suggest that the solubilized form of EP3 was not readily available for hydrolysis. A box plot of the EP3, EP2 acid, and PNP data in Fig. 4 is for ease of comparison provided in Supporting Information (Fig. 2).

The corresponding initial and final OPP soil concentration data from the batch reactors is shown in Fig. 5. The solid phase concentration of EP3, which was the most predominant OPP, decreased from an initial concentration of 935 ± 6.5 mg kg⁻¹ to levels of 461 ± 129 mg kg⁻¹ (surf1) and 469 ± 67 mg kg⁻¹ (surf3) at 30 g L⁻¹ as the lowest concentrations observed. Benefits regarding the performance of increased surfactant dosage were seen for all surfactants. For example, an additional 171 mg kg⁻¹ EP3 was removed when the applied

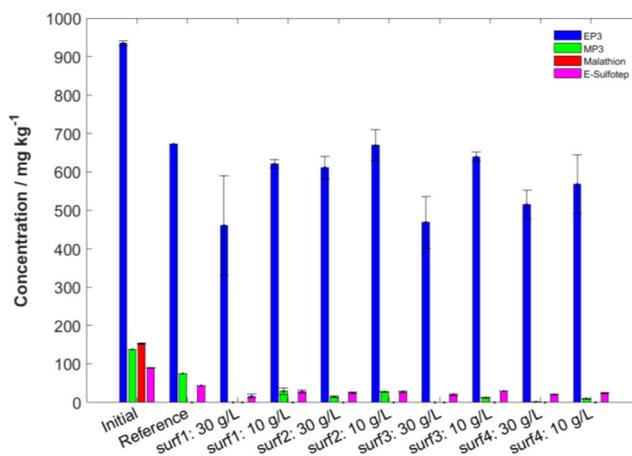


Fig. 5 Soil data of OPP concentrations from the soil experiments. All of these reactors were placed on the shaker table for the 7 days of mixing at 10 °C

concentration of surf3 was increased by 20 g L^{-1} . A box plot of the EP3 data in Fig. 5 is for ease of comparison shown in Supporting Information (Fig. 3).

The mass balances of the reactors are shown in Fig. 8 that present comparisons between the absolute mass (in gram) of OPPs removed from the soil and the mass found in the aqueous phase. It is evident that the balances did not match well and the sum of OPPs removed from the soil in all reactors was higher than the sum of OPPs and hydrolysis products found in the aqueous phase. The reason is very likely instability and further hydrolysis of the EP2 and MP2 acid hydrolysis products that may release ethanol and methanol through further hydrolysis of ester bonds.

Influence of mechanical mixing

Mechanical mixing of the soil-water reactors did not result in consistent trends in change of aqueous concentrations of OPPs (Fig. 6). For surf3 and surf4, EP3 concentration increased slightly when mechanical mixing was applied, but for surf1 and surf2 EP3, concentrations decreased. However, the standard deviations of the reported mean values overlap or nearly overlap, and the box plot of EP3 variations in Fig. S4 also shows overlap. These data suggest that mechanical mixing on a shaker table had minimal impacts on aqueous phase solubilization and hydrolysis of OPP-contaminated soil.

In contrast to the aqueous phase data of Fig. 6, the soil data presented in Fig. 7 indicated that the quiescent reactors consistently resulted in lower final soil concentrations of EP3. The lowest final concentrations of EP3 was obtained with surf3 and surf1 following 7 days of quiescent reaction, reaching a value of $306 \pm 29 \text{ mg kg}^{-1}$ (surf3) and $310 \pm 25 \text{ mg kg}^{-1}$ (surf1), respectively, equal to 67% removal of OPP when compared to the initial concentration of $935 \pm 7 \text{ mg kg}^{-1}$.

Mixing concerns promoting contact between species, so the outcome was quite opposite to expectations of reduced solubility and reactivity in the quiescent reactors. The effects of mixing were likely complex, complicating the interpretation of the outcome of the mixing tests. Several factors may play a role: (1) variability in total mass of OPPs between reactors, (2) increasing sorption of surfactants to soil, (3) enhanced hydrolysis rates through increased contact of hydroxide with OPP mass, (4) enhanced solubilization of NAPL/sorbed mass with more contact with surfactant, and (5) decreased local hydrolysis rates as hydroxide is consumed by contact / reaction with OPPs. With these complex processes ongoing, it seems reasonable that there may have been a high degree of variability between reactors based on slight differences in OPP presence, surfactant, soil mass, mixing, and surfactant type.

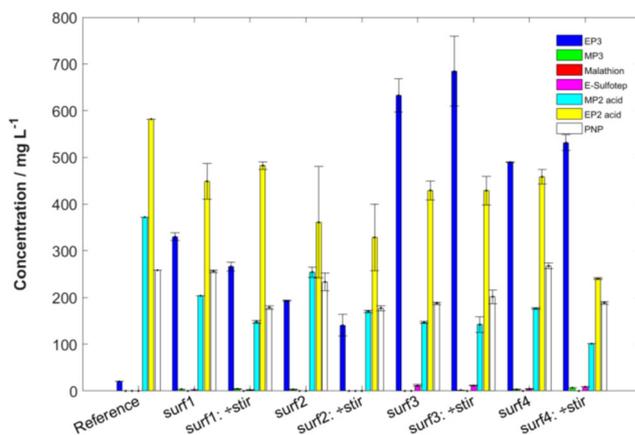


Fig. 6 Concentrations of OPPs and hydrolysis products in the water samples from the soil water mechanical mixing tests. All of these reactors (except the reference) had a surfactant dosage of 30 g L^{-1} , and all were in 0.34 M NaOH . Mixing occurred at 170 revolutions per min at 10°C for 7 days. The mixed reactors are labeled Reference, surf1, surf2, surf3, and surf4, and the quiescent reactors are labeled surf1, +stir; surf2, +stir; surf3, +stir; surf4, +stir

Mass balances and OPP removal

When considering the mass balances of the soil-water/surfactant reactors presented in Fig. 8, some observations may be highlighted. As touched upon earlier in the manuscript, the OPP mass removed from the soil could not be found in the aqueous phase indicating instability of the hydrolysis products. The closest match was in the reference 0.34 M NaOH reactor indicating that the presence of surfactant did influence the distribution and behavior of species in the reactors. Except for surf3, where the mass removed vs. aqueous mass was similar, the overall trend was that the quiescent reactors showed the largest deviations when comparing the mass balances between stirred or not stirred reactors at the dosage of 30 g L^{-1} . This might indicate that mixing promoted further

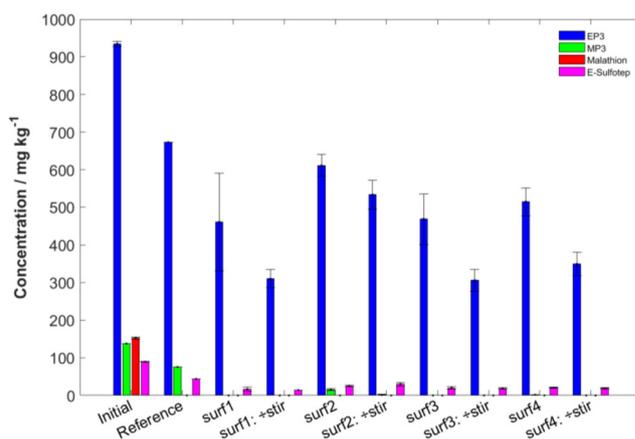
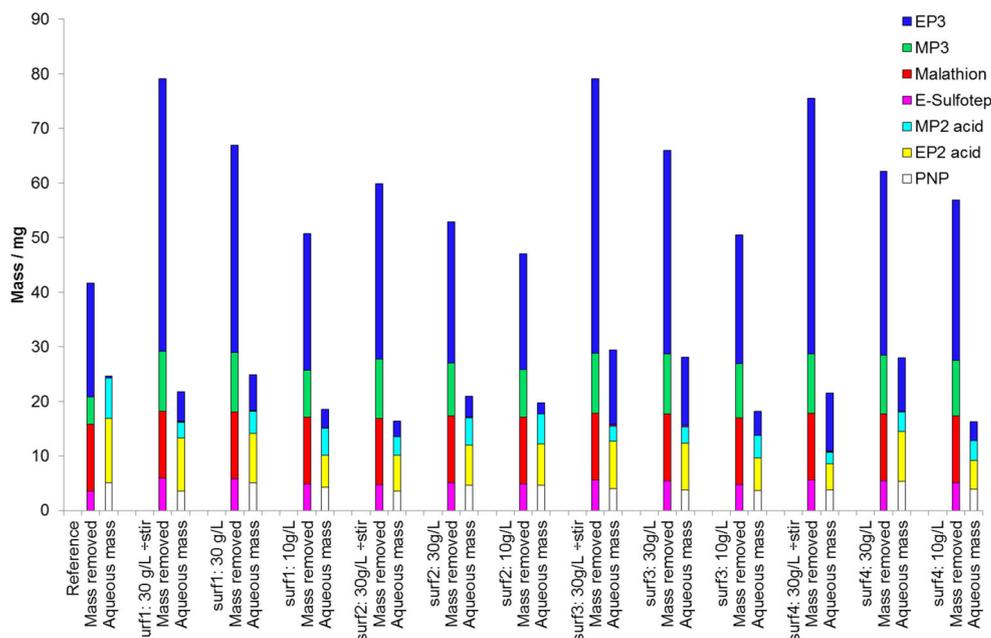


Fig. 7 Soil data on OPP concentrations of the mechanical mixing tests. All of these reactors (except the 0.34 M NaOH reference) had a surfactant dosage of 30 g L^{-1} , and all were in 0.34 M NaOH . Mixing for half of the surfactant reactors occurred at 170 revolutions per min at 10°C for 7 days

Fig. 8 Mass balances of the soil surfactant solution reactors comparing the absolute mass of OPPs removed from the 80 g of soil in the reactors and the mass of the OPPs and hydrolysis products found in the 20 mL aqueous phase of the reactors. Soil to water ratio was thus 4:1 g mL⁻¹



hydrolysis of the hydrolysis products and explaining some of the deviations observed between the soil and water data.

Finally, the percentage of OPP removal from the contaminated site soil at the 30 g L⁻¹ dosage is shown in Fig. 9. Surf1, surf3, and surf4 performed comparable with overlapping propagated uncertainty intervals and mean removal values of 75 ± 2%, 75 ± 2%, and 72 ± 2% respectively.

The data obtained in this study demonstrated that by using the ethoxylated alcohol surfactant as surf3 with ethoxylated propoxylated 2-ethyl-1-haxanol as active ingredients (CAS 64366–70-7), up to 30% better performance with respect to removal of OPPs from the soil may be achieved if the surfactant is applied in a dosage of 30 g L⁻¹. Considering the soil concentrations after treatment, not all OPPs was equally removed; malathion was not found in any of the alkaline treated reactors including the reference 0.34 M NaOH, MP3, and E-sulfotep which were significantly reduced in all reactors, and EP3 comprised the major remaining fraction in the soil. A concurrent enhancement of the alkaline hydrolysis reactivity was not observed, and the data showed that the production of hydrolysis products was lower in the presence of surfactant within a fixed reaction time indicating overall decreased hydrolysis rates. The increased soil remediation was mainly attributed to increased aqueous phase concentrations of OPP due to increased micellar solubilization meaning that prolonged reaction times to reach the ambitions of toxicity neutralization is needed. None of the tests completed in the current study experienced problems with maintaining pH above 13, so this should not be limiting with hydroxide present in great excess. Due to the concurrent processes of solubilization and hydrolysis, kinetic calculations are complex, and developing a kinetic model of the process is scope of

further work with in situ S-ISAH. Instability of hydrolysis products meant that matching mass balanced could not be obtained in the present study. Published data on potential alkaline hydrolysis of EP2 acid, MP2 acid, and PNP has not been found by the authors and will be the aim of further work to improve the overall understanding of this remediation technology.

Conclusion

The study presented in this paper evaluated the effectiveness of surfactants in enhancing mass removal of OPPs from soil under highly alkaline conditions and potential for enhancing

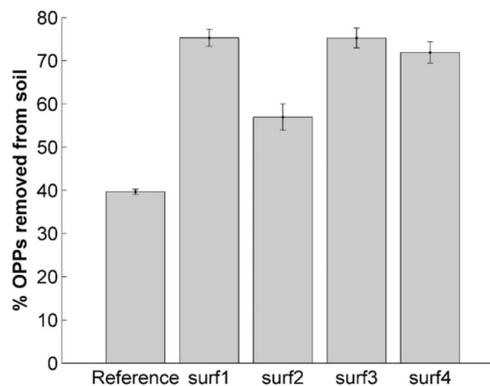


Fig. 9 Removal percentages of OPP from the site soil by the four alcohol ethoxylate surfactant formulations applied at 30 g L⁻¹ dosage in 0.34 M NaOH without mixing and diffusion only as mixing process. The error bars represent the calculated propagated uncertainty of the removal percentages based in the standard deviations of the individual concentrations

ISAH for treatment of OPPs, particularly EP3 and MP3. In control and surfactant experiments, hydrolysis products EP2 acid, MP2 acid, and PNP were formed in non-stoichiometric amounts indicating instability of these compounds. MP3 and malathion were found to have faster hydrolysis rates than EP3 under the conditions studied. All surfactants evaluated increased solubility of OPPs under alkaline conditions with four nonionic alcohol ethoxylate products providing the greater affect over the polyglucosides, sulfonate, and propionate surfactants evaluated. The alcohol ethoxylates were shown to provide substantial mass removal of OPPs from soil. Hydrolysis rates were typically slower in the presence of surfactant, despite the relatively higher aqueous concentrations of OPPs; this was likely due to micellar solubilization of the OPPs, which therefore were less accessible for hydrolysis. The increased solubilization of OPPs does support the use of surfactants for contaminant mass removal from soil by surfactant soil flushing technologies, also under alkaline conditions, but surfactants were not seen to promote the hydrolysis and thus degradation of OPPs during ISAH.

Acknowledgments Acknowledgments go to the NorthPestClean project team for funding and fruitful discussions of the study. In addition to the authors of this paper, it includes Anja Melvej Hermansen, Børge Hvidbjerg, Kaspar Røegg, and Lars Ernst from Region Midtjylland. From Meijer, Erik Petrovskis is acknowledged. Bo Breinbjerg from Cheminova A/S is gratefully acknowledged for help with the chemical analysis of soil and water samples.

References

- Amos BK, Daprato RC, Hughes JB, Pennell KD, Löffler FE (2007) Effects of the nonionic surfactant tween 80 on microbial reductive dechlorination of chlorinated ethenes. *Environ Sci Technol* 41: 1710–1716
- Bondgaard M, Hvidbjerg B, Ramsay L (2012) Remediation of pesticide contamination by in situ alkaline hydrolysis - a new soil remediation technology. In: Proceedings of the eight international conference on remediation of chlorinated and recalcitrant compounds. Battelle Memorial Institute, Monterey, California
- Chu W, Chan KH, Choy WK (2006) The partitioning and modelling of pesticide parathion in a surfactant-assisted soil-washing system. *Chemosphere* 64:711–716. <https://doi.org/10.1016/j.chemosphere.2005.11.028>
- Chuan-Yu Q, Yong-Sheng Z, Wei Z (2014) The influence zone of surfactant-enhanced air sparging in different media. *Environ Technol* 35(9–12):1190–1198. <https://doi.org/10.1080/09593330.2013.865060>
- Dave BP, Ghevariya CM, Bhatt JK, Dudhagara DR, Rajpara RK (2014) Enhanced biodegradation of total polycyclic aromatic hydrocarbons (TPAHs) by marine halotolerant *Achromobacter xylosoxidans* using Triton X-100 and β -cyclodextrin—a microcosm approach. *Mar Pollut Bull* 79:123–129. <https://doi.org/10.1016/j.marpolbul.2013.12.027>
- Di Palma L (2003) Experimental assessment of a process for the remediation of organophosphorous pesticides contaminated soils through in situ soil flushing and hydrolysis. *Water Air Soil Pollut* 143:301–314. <https://doi.org/10.1023/A:1022890529765>
- Dugan PJ, Siegrist RL, Crimi ML (2010) Coupling surfactants/cosolvents with oxidants for enhanced DNAPL removal: a review. *Remediat J* 20:27–49. <https://doi.org/10.1002/rem>
- Fan G, Cang L, Fang G, Zhou D (2014) Surfactant and oxidant enhanced electrokinetic remediation of a PCBs polluted soil. *Sep Purif Technol* 123:106–113. <https://doi.org/10.1016/j.seppur.2013.12.035>
- Han X, Balakrishnan VK, Buncl E (2007) Alkaline degradation of the organophosphorus pesticide fenitrothion as mediated by cationic C12, C14, C16, and C 18 surfactants. *Langmuir* 23:6519–6525. <https://doi.org/10.1021/la063521u>
- Hasegawa M, Shau B, Sabatini D et al (2000) Surfactant-enhanced subsurface remediation of DNAPLs at the former naval air station alameda, California. In: Wickramanayake G, Gavaskar A, Gupta N (eds) Treating dense nonaqueous-phase liquids (DNAPLs): remediation of chlorinated and recalcitrant compounds. Battelle Press, Columbus, OH, pp 219–226
- Hoag G, Collins J (2011) Soil remediation method and composition
- Jafvert CT, Strathmann J (2000) Innovative surfactant/cosolvent technologies for removal of NAPL and sorbed contaminants from aquifers. In: Tedder DW, Pohland F (eds) EMERGING TECHNOLOGIES IN HAZARDOUS WASTE MANAGEMENT 8. KLUWER ACADEMIC/PLENUM PUBL, 233 SPRING ST, NEW YORK, NY 10013 USA, pp 93–108
- Ketelaar JAA (1950) Chemical studies on insecticides II - the hydrolysis of OO'-diethyl- and -dimethyl-O"-p-nitrophenyl thiophosphonate (parathion and dimethylparathion (E 605)). *Recl des Trav Chim des Pays-Bas* 69:649–658
- Li Z, Hanlie H (2008) Combination of surfactant solubilization with permanganate oxidation for DNAPL remediation. *Water Res* 42: 605–614. <https://doi.org/10.1016/j.watres.2007.08.010>
- Londergan J, Meinardus H, Mariner P et al (2001) DNAPL removal from a heterogeneous alluvial aquifer by surfactant-enhanced aquifer remediation. *Gr Water Monit Remediat* 21:57–67
- Menendez-Vega D, Gallego JLR, Pelaez AI et al (2007) Engineered in situ bioremediation of soil and groundwater polluted with weathered hydrocarbons. *Eur J Soil Biol* 43:310–321. <https://doi.org/10.1016/j.ejsobi.2007.03.005>
- Mirgorodskaya AB, Valeeva FG, Lukashenko SS et al (2012) Dicationic surfactant based catalytic systems for alkaline hydrolysis of phosphonic acid esters. *Kinet Catal* 53:206–213
- Mulligan C, Yong R, Gibbs B (2001) Surfactant-enhanced remediation of contaminated soil: a review. *Eng Geol* 60:371–380. [https://doi.org/10.1016/S0013-7952\(00\)00117-4](https://doi.org/10.1016/S0013-7952(00)00117-4)
- Pennell KD, Abriola LM, Weber WJ (1993) Surfactant-enhanced solubilization of residual dodecane in soil columns. 1. *Exper Inves* 27: 2332–2340
- Pennell KD, Cápiro NL, Walker DI (2013) Surfactant and cosolvent flushing. In: Kueper B, Stroo HF, Ward H (eds) Chlorinated solvent source zone remediation. Springer, New York, NY, pp 353–394
- Perelo LW (2010) Review: in situ and bioremediation of organic pollutants in aquatic sediments. *J Hazard Mater* 177:81–89. <https://doi.org/10.1016/j.jhazmat.2009.12.090>
- Ramsburg C, Abriola L, Pennell K, Löffler FE, Gamache M, Amos BK, Petrovskis EA (2004) Stimulated microbial reductive dechlorination following surfactant treatment at the bachman road site. *Environ Sci Technol* 38:5902–5914
- Seebunrueng K, Santaladchaiyakit Y, Soisungnoen P, Srijaranai S (2011) Catanionic surfactant ambient cloud point extraction and high-performance liquid chromatography for simultaneous analysis of organophosphorus pesticide residues in water and fruit juice samples. *Anal Bioanal Chem* 401:1703–1712. <https://doi.org/10.1007/s00216-011-5214-x>
- Seebunrueng K, Santaladchaiyakit Y, Srijaranai S (2012) Study on the effect of chain-length compatibility of mixed anionic-cationic surfactants on the cloud-point extraction of selected organophosphorus

- pesticides. *Anal Bioanal Chem* 404:1539–1548. <https://doi.org/10.1007/s00216-012-6209-y>
- Sharma SR, Singh RP, Ahmed SR (1985) Effect of different saline, alkaline salts, fertilizers, and surfactants on the movement of some phosphorus-containing pesticides in soils. *Ecotoxicol Environ Saf* 10:339–350. [https://doi.org/10.1016/0147-6513\(85\)90080-6](https://doi.org/10.1016/0147-6513(85)90080-6)
- Shrivastava A, Ghosh KK (2008) Micellar effects on hydrolysis of parathion. *J Dispers Sci Technol* 29:1381–1384. <https://doi.org/10.1080/01932690802313063>
- Suchomel EJ, Ramsburg CA, Pennell KD (2007) Evaluation of trichloroethene recovery processes in heterogeneous aquifer cells flushed with biodegradable surfactants. *J Contam Hydrol* 94:195–214. <https://doi.org/10.1016/j.jconhyd.2007.05.011>
- Torres LG, Ramos F, Avila Ma, Ortiz I (2012) Removal of methyl parathion by surfactant-assisted soil washing and subsequent wastewater biological treatment. *Journal of Pesticide Science* 37(3):240–246. <https://doi.org/10.1584/jpestics.D11-024>
- Tsai T, Kao C, Yeh T, Liang S, Chien H (2009) Application of surfactant enhanced permanganate oxidation and biodegradation of trichloroethylene in groundwater. *J Hazard Mater* 161(1):111–119. <https://doi.org/10.1016/j.jhazmat.2008.03.061>
- USEPA (2014) Estimation programs interface (EPI). In: <http://www.epa.gov/oppt/exposure/pubs/episuite.htm>
- Wattanaphon HT, Kerdsin A, Thammacharoen C et al (2008) A biosurfactant from *Burkholderia cenocepacia* BSP3 and its enhancement of pesticide solubilization. *J Appl Microbiol* 105:416–423. <https://doi.org/10.1111/j.1365-2672.2008.03755.x>
- Yeh DH, Pennell KD, Pavlostathis SG (1999) EFFECT OF TWEEN SURFACTANTS ON METHANOGENESIS AND MICROBIAL REDUCTIVE DECHLORINATION OF HEXACHLOROBENZENE. *Environ Toxicol Chem* 18:1408. [https://doi.org/10.1897/1551-5028\(1999\)018<1408:EOTSOM>2.3.CO;2](https://doi.org/10.1897/1551-5028(1999)018<1408:EOTSOM>2.3.CO;2)
- Zeng Q, Tang H, Liao B, Zhong T, Tang C (2006) Solubilization and desorption of methyl-parathion from porous media: a comparison of hydroxypropyl-beta-cyclodextrin and two nonionic surfactants. *Water Res* 40:1351–1358. <https://doi.org/10.1016/j.watres.2006.01.036>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.