

Bioremediation of contaminated mixtures of desert mining soil and sawdust with fuel oil by aerated in-vessel composting in the Atacama Region (Chile)

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Received 30 March 2007; received in revised form 11 June 2007; accepted 11 June 2007

Available online 15 June 2007

Abstract

Since early 1900s, with the beginning of mining operations and especially in the last decade, small, although repetitive spills of fuel oil had occurred frequently in the Chilean mining desert industry during reparation and maintenance of machinery, as well as casual accidents. Normally, soils and sawdust had been used as cheap readily available sorbent materials of spills of fuel oil, consisting of complex mixtures of aliphatic and aromatic hydrocarbons. Chilean legislation considers these fuel oil contaminated mixtures of soil and sawdust as hazardous wastes, and thus they must be contained. It remains unknown whether it would be feasible to clean-up Chilean desert soils with high salinity and metal content, historically polluted with different commercial fuel oil, and contained during years. Thus, this study evaluated the feasibility of aerated in-vessel composting at a laboratory scale as a bioremediation technology to clean-up contaminated desert mining soils (fuel concentration > 50,000 mg kg⁻¹) and sawdust (fuel concentration > 225,000 mg kg⁻¹) in the Atacama Region. The composting reactors were operated using five soil to sawdust ratios (S:SD, 1:0, 3:1, 1:1, 1:3, 0:1, on a dry weight basis) under mesophilic temperatures (30–40 °C), constant moisture content (MC, 50%) and continuous aeration (16 l min⁻¹) during 56 days. Fuel oil concentration and physico-chemical changes in the composting reactors were monitored following standard procedures. The highest (59%) and the lowest (35%) contaminant removals were observed in the contaminated sawdust and contaminated soil reactors after 56 days of treatment, respectively. The S:SD ratio, time of treatment and interaction between both factors had a significant effect ($p < 0.050$) on the contaminant removal. The results of this research indicate that bioremediation of an aged contaminated mixture of desert mining soil and sawdust with fuel oil is feasible. This study recommends a S:SD ratio 1:3 and a correct nutrient balance in order to achieve a maximum overall hydrocarbon removal of fuel oil in the weathered and aged contaminated wastes.

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Keywords: Bioremediation; Composting; Fuel oil; Mining desert soil; Atacama

1. Introduction

There are both commercial and human health justifications to identify and clean up sites that have become heavily contaminated by accidental oil spills around the world. Minera

Escondida Ltd. [1] is a copper mine located in the Atacama region (north of Chile; 170 km SE of Antofagasta; 3100 m above sea level), with the largest production worldwide, representing 8% of the overall world production. The maintenance of machinery and trucks at Minera Escondida Ltd. has resulted in consecutive accidental spills of mixtures of commercial fuel oil (diesel and gasoline), which were normally contained with sawdust and native desert mining soils (used as an economical sorbent material) to avoid dispersion of contaminants. Following, as a common practice, fuel oil contaminated soil and sawdust were disposed in hazardous waste landfills (HWL).

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This common practice in the mining industry has caused a real case environmental problem of current concern, where large amounts of hazardous wastes, comprised mainly by weathered and aged fuel oil contaminated desert mining soil and sawdust, have accumulated over time and need to be cleaned-up. Little literature exists on the degradation and fate of mixtures of commercial products typical in real consecutive accidental spills. The rate of biodegradation of such contaminated wastes depends on biological and physico-chemical factors, such as low numbers of microbes, insufficient oxygen or nutrient availability, temperature and water availability [2–4]. The rate of biodegradation also depends on several physico-chemical properties related to the contaminant (i.e. hydrophobicity, volatility, polarity), solid matrix (i.e. organic matter, porosity) and its bioavailability [5–7]. Additionally, biodegradation of fuel oil following real consecutive accidental spills is a complex process that depends on the nature and amount of contaminants (aliphatic and aromatic hydrocarbon mixtures) present [8].

Current Chilean legislation contemplates bioremediation technologies, such as composting as a valid alternative practice to environmental decontamination [9]. The application of composting as a bioremediation technology to treat hazardous wastes [9], has been shown to be effective in biodegrading PAHs [3,10–12], chlorophenols [13], polychlorinated biphenyls [14], explosives [15] and petroleum hydrocarbons [16,17] at laboratory and/or field-scales. At present, few studies are found on the applicability of composting to contaminated desert mining soils (subject of this study), with a typical low organic matter content, a high mineral content and a high salinity [18,19]. Available literature on bioremediation of desert soils in Kuwait [20,21], refers to open systems where in situ land-farming, bioventing and composting treatment technologies were implemented [22,23] to treat more than 20 Mm³ of oil accumulated in the desert soil following Iraqi invasion of Kuwait in the early 1990s. Research with Kuwait's desert soils indicates that biodegradation of total petroleum hydrocarbons above 60% can be reached following 8 months of compost soil piles treatment. Using a bulking agent (i.e. wood chips), NPK fertilizers and controlling the moisture content of the composting mixture significantly enhanced the biodegradation rate of heavily contaminated desert soils in Kuwait [24].

Due to the limited number of case studies (i.e. Kuwait) available on the use of bioremediation technologies to treat contaminated desert soils and the need to decontaminate large amounts of hazardous wastes in the Atacama region (Chile), this research sought to determine the feasibility of bioremediation by aerated in-vessel composting of mixtures of desert mining soil and sawdust contaminated with fuel oil. The objectives of this research were twofold. Firstly, to determine the effectiveness of different ratios of contaminated soil to contaminated sawdust (S:SD) contained and disposed during 2 years in a HWL on the degradation of fuel oil. Secondly, to find correlations between the percentage of contaminant removal and relevant physico-chemical parameters. This may assist to identify the best conditions for maximum contaminant removal following in-vessel composting treatment of fuel oil contaminated desert

soils. The results of this research are expected to have a major influence in current Chilean legislation.

2. Materials and methods

2.1. Contaminated desert soil and sawdust

Soils in the north of Chile are taxonomically characterized as aridisol (thin A horizon above thin B horizons, often with carbonate accumulation in a K horizon; typical of dry climates), inceptisol (weakly developed soil with recognizable A horizon and incipient B horizon; no iron and aluminium enrichment) and entisol (soil with an incipient A horizon, but generally lacking well-developed compositional horizons) (USDA classification) [25,26]. Main mining activities occur in the Atacama region where the soils present a high salinity (>10 mmhos cm⁻¹, extremely saline) and a high content of metals in comparison to other desert soils (Table 1). Routine maintenance of machinery and trucks at Minera Escondida Ltd. (Chile) has resulted over the years in frequent accidental fuel oil spills, contained using desert mining soil and sawdust as cheap sorbents and disposed in separated sealed vessels in a HWL, as required by current Chilean legislation [9]. For the purpose of the present investigation, Minera Escondida Ltd. provided our laboratory with 80 kg of contaminated desert soil (main contaminant present, diesel fuel, hydrocarbons in the C₁₀–C₁₉ range) and 40 kg of contaminated sawdust (main contaminant present, fuel oil hydrocarbons in the C₄–C₁₃ range), previously kept for 2 years in a HWL. The HWL is normally exposed to environmental conditions typical of desert climate, with daily oscillations of temperature between 0 °C during the night and above 40 °C during the day. Additionally, fuel oil contaminated desert soil and sawdust were not exposed to direct-solar radiation. Contaminated desert soil and contaminated sawdust were air-dried, homogenized by passing them separately through a 5 mm sieve followed by a 2 mm sieve, and stored in the laboratory at room temperature in the dark. Autochthonous microbial communities were assumed to be acclimated to cold and warm temperatures and to the presence of pollutants.

2.2. Reactor's design

Thirty cylindrical (50 cm long, 22 cm i.d.; 51 total capacity) poly-vinyl-chloride aerated composting reactors, were set-up at laboratory-scale and operated continuously during 56 days. It has been previously observed that 56 days of in-vessel composting treatment is sufficient to achieve maximum contaminant removal [3,27]. These reactors each held about 2000 g total composting mixture. The moisture content was adjusted to 50%. In order to investigate the effect of adding contaminated sawdust to contaminated desert soil on the biodegradation of complex mixtures of organic contaminants, the experimental design comprised five ratios of contaminated soil to contaminated sawdust, thus S:SD (wet weight) ratios expanded from of 1:0 (only soil), 3:1, 1:1, 1:3 to 0:1 (only sawdust). These S:SD ratios were selected to investigate whether mixing contaminated wastes offer any advantage on contaminant removal, particularly in

Table 1
Initial physico-chemical characteristics of contaminated soil and soil/sawdust mixtures compared to other soils cited in the literature

	Soil used in this study, S:SD ratio					Other soils		
	1:0	3:1	1:1	1:3	0:1	Kuwait [22]	Atacama	Agronomic value
pH suspended	7.3	7.5	7.3	7.3	7.4	7.5–8.0	7.0–8.0	NA
EC suspended (mmhos/cm)	10.0	14.0	12.9	15.0	12.5	0.6	>10	4<
TOC	14%	24%	30%	49%	NA	<0.02%	<0.1%	NA
Cultivable heterotrophic bacteria (CFU g ⁻¹)	10 ⁵	10 ⁵	10 ⁶	10 ⁶	10 ⁶	10 ⁵⁻⁶	NA	NA
Soil water holding capacity	NA	NA	NA	NA	NA	6%	4–5%	0–50%
Texture	Sandy Loam	Sandy Loam	Sandy Loam	Sandy Loam	Sandy ^a	Sandy Loam	NA	NA
Minor essential elements (mg kg ⁻¹)								
Total N	1100	1500	2900	3200	4100	NA	NA	NA
Total P	1110	1200	1300	1500	1600	NA	NA	NA
Total K	2110	1330	1720	1110	9800	NA	NA	NA
Total S	3000	2750	3090	3310	3350	NA	NA	NA
Major essential elements (mg kg ⁻¹)								
Ava N (NO ₃ ⁻ , NH ₄ ⁺)	148.3	199.9	234.5	265.9	285.7	NA	NA	300–3000
Ava P (HPO ₄ ⁻ , H ₂ PO ₄ ²⁻)	12.3	22.3	11.2	15.2	16.8	NA	NA	10–100
Ava K (K ⁺)	214.0	252.8	279.2	319.2	340.7	NA	NA	2000–3000
Ava S (SO ₄ ²⁻)	2210.8	2208.5	2233.1	2190.8	2239.1	NA	NA	10–100
Minor essential elements (mg kg ⁻¹)								
Cu (Cu ²⁺ , Cu ⁺)	741.9	544.4	484.5	352.6	248.9	NA	NA	5–100
Fe (Fe ²⁺ , Fe ³⁺)	6.4	6.6	9.0	19.2	22.7	NA	NA	4000–40,000
Mn (Mn ²⁺ , Mn ³⁺)	10.4	13.2	20.1	24.5	30.6	NA	NA	200–4000
Zn (Zn ²⁺)	34.0	120.2	89.0	173.1	150.7	NA	NA	10–300
B (H ₂ BO ₃ ⁻ , HBO ⁻)	25.0	41.5	39.6	40.1	44.2	NA	NA	0.5–100

Note: Ava, available; NA, data not available or not applicable.

^a Sandy with high calcareous materials.

the contaminated soil; and if so, to identify the optimal S:SD ratio to achieve a maximum contaminant removal. The abiotic controls comprised the same contaminated soil to contaminated sawdust ratios, but the mixtures were radiated with Gamma rays of a Cesium 137 source, to 25 kGy doses for three times in an Experimental Nuclear Reactor (Chilean Commission of Nuclear Energy, CCHEN).

Atmospheric air previously warmed at 60 °C was introduced (pump of 1.1 KW and a maximum flow of 550 m³ h⁻¹) to each reactor and circulated through an internal perforated piping to assure a sufficient oxygen concentration in the reactors (Fig. 1). Temperature in the reactors was monitored with thermocouples K type. Recorded temperatures throughout the length of the treatment showed that the composting reactors reached mesophilic temperatures of 30 ± 2 °C at the top surface of the

substrate in contact with the head space, and 40 ± 2 °C at the bottom of the substrate. Additionally, gas streams from the inlet and exhaust were continuously monitored for carbon dioxide production as an evidence of aerobic biodegradation. Each reactor was homogenized on a daily basis to avoid stratification and oxygen content limitations. Sterilized distilled water (SDW) was added when needed to maintain 50% moisture content in all reactors during the treatment.

2.3. Sample analysis

Samples from each reactor were collected in triplicate after 0, 14, 28, 42 and 56 days for analysis, following homogenization. Stratified samples were collected using a core tube (70 cm long, 5 cm i.d.). Then, each sample was separately manually homog-

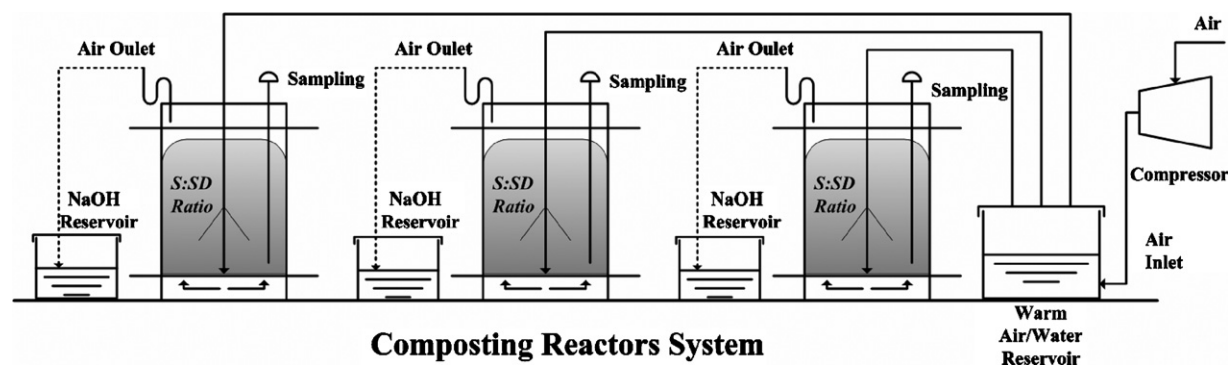


Fig. 1. Schematic laboratory set up of composting reactors.

enized with a stainless steel spatula in a sterile bag and stored in an amber glass flask for further analysis.

2.3.1. Soil and sawdust analyses

Chemical analyses including pH, electrical conductivity (E.C.), total organic carbon (TOC) and nitrogen (N), were performed using standard procedures [28]. Granulometric properties were determined by the Bouyoucos densitometric method [29]. Trace elements were determined by atomic absorption spectrometry (GBC 920; Victoria, Australia) and heavy metals were determined by atomic absorption spectrometry as well (Perkin-Elmer; model 2380, USA). Moisture content was maintained using SDW when necessary.

Cultivable heterotrophic bacteria were determined using the dilution and spread-plate method. Briefly, 5 g of soil were collected in triplicate from pooled samples and re-suspended in 15 ml SDW in an Erlenmeyer flask, then shaken for 5 h (200 rpm) and gently centrifuged for separation. One milliliters of the top layer was serially diluted (10^{-1} to 10^{-6}) and incubated in Luria Agar plates at 28 °C for 5 days for determination of colony forming units (CFU). The presence of anaerobes was determined using an oxidizing marker in sealed tubes with Luria broth and inoculum.

2.3.2. Organic contaminant analyses for fuel oil content determination

Sampling and quantification of organic contaminants were conducted following USEPA SW-846 method (including QA/QC procedures) by ANAM accredited laboratory for environmental analysis in Chile [30]. Briefly, three samples of 5 g were collected from each bioreactor, homogenized and placed in 10 ml sealed amber glass flasks for organic contaminant analysis. Hexane solvent and a Soxhlet apparatus were used for the extraction of fuel oil in samples from experimental and abiotic controls. The solvent in the extracts was then evaporated and the mass of extracted material was determined by gravimetric measurement.

2.4. Statistical data and multivariate analysis

A two-factor ANOVA test (factor 1, treatment (sawdust percentage); factor 2, time) was applied for each degradation curve to elucidate the effect of S:SD ratio treatment and time on the removal of fuel oil. *T*-test was applied to investigate possible differences between initial and final values of fuel oil content in each treatment and final fuel oil content following different treatments. Principal components analysis (PCA) and linear correlations (*r*) within groups of physico-chemical parameters and removal percentage in different reactors were also investigated (assuming a Gaussian population) to study correlations between treatments.

3. Results and discussion

Laboratory scale bioreactors were used to investigate the feasibility of applying composting as a bioremediation treatment to fuel oil contaminated desert soils and contaminated

sawdust, seeking for correlations between removal of organic contaminants (aliphatic and aromatic hydrocarbons) and relevant physico-chemical parameters.

3.1. Chemical composition of the contaminated desert soil and sawdust

The initial chemical composition of contaminated desert soil and contaminated sawdust at different S:SD ratios, as well as typical desert soil chemical compositions in Atacama and Kuwait's regions are presented in Table 1. This table also summarises typical values of the various chemical properties in soils with an agronomic value [26].

Since the pH is one of the key factors for microbial metabolism, pH was monitored in the composting substrates every 14 days. In the conditions of excess of nutrients and oxygen, pH values are expected to drop following aerobic microbial degradation [31]. Before treatment, all reactors presented a pH range close to neutrality (pH 7.0–7.5) and no statistical differences were found between reactors (Fig. 2a). Once the treatment started, pH changes were observed in the reactors. Significant lower pH values were observed in the reactors with low S:SD ratios and in the reactor with only contaminated sawdust. Additionally, statistical significant differences were found between initial and final pH values ($p < 0.05$, *t*-test) in the majority of the reactors. Only the pH values in the reactors with S:SD ratios 1:1 and 3:1 presented no statistical differences at the end of the treatment (Table 2). No pH changes were observed in the abiotic controls (data not shown).

Lower pH values in the composting reactors with low S:SD ratios could be explained due to the formation of channelizations facilitated by the presence of sawdust, which may have facilitated the aeration of the contaminated mixture promoting aerobic biodegradation with subsequent CO₂ production and acidification of the mixtures. On the contrary, in the reactor with only contaminated desert soil (S:SD ratio 1:0) the pH tendency was to rise over time (Fig. 2a). Desert soils are similar in composition to the mother rock due to their low exposition to erosion by pluvial waters. Water entering in contact with minerals that constitute the desert soil may hydrolyse present cations and form hydroxides (Ca, Mg, K, Na hydroxides mainly). These hydroxides may have favoured a temporal pH increase in the contaminated soil under aerobic conditions.

In the North of Chile, at Atacama region, the soils are hypersaline (E.C. > 10.0 mmhos cm⁻¹), which has been one of the main reasons to dedicate these soils to mining activities. Increasing levels of salinity, measured as E.C., in the composting reactors were observed over time (data not shown), which suggested a higher content of free ions in the composting mixtures over time. In the reactors with only sawdust, the E.C. remained at constant levels (≈12 mmhos cm⁻¹). However, in the reactor with S:SD: 1:0 the E.C. progressively decreased during the treatment to values closer to 7 mmhos cm⁻¹. Nevertheless, differences in salinity during time and between treatments were not significantly different in the various composting treatments ($p > 0.05$, correlation index and PCA) in this study. Previous studies reported in the literature indicate that microorganisms

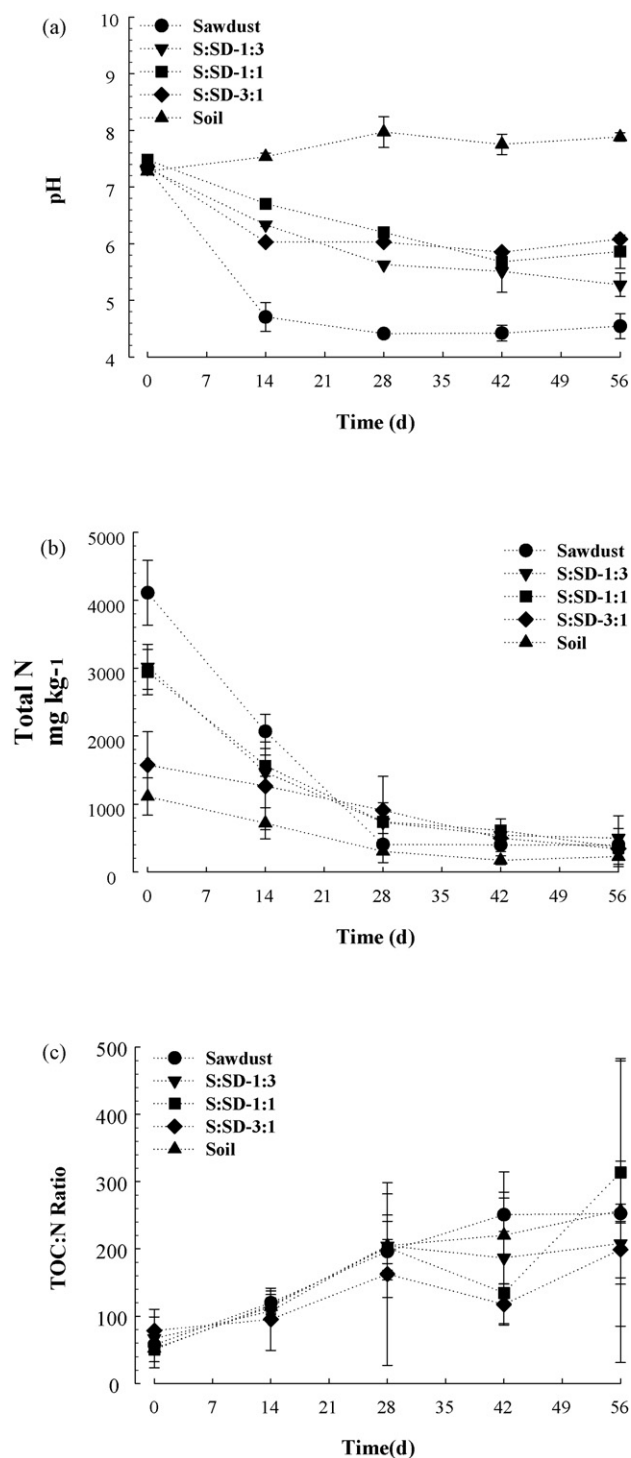


Fig. 2. Temporal changes of: (a) pH, (b) total N, (c) TOC/N ratio in soil and mixtures S:SD during the length of the composting treatment.

present in fuel diesel contaminated sediments and exposed to high salinities can metabolize fuel diesel [32]. Additionally, the bioremediation of motor-oil in soil may be reduced by salinity and also this effect may be different in different soils [19].

Regarding the coupled effect of metal and hydrocarbon in aged contaminated soils on the diversity of microbial communities, it has been reported that the variation of the catabolic diversity of an indigenous microbial community in soils with a

30 year history of Pb, Cr and hydrocarbon contamination was attributed to the concentration of hydrocarbons present more than to Pb and Cr [33]. Nevertheless, previous studies have not considered the possible acclimation of microorganism present in hyper-saline soils (halotolerants) to the coupled effect of metal's content and a high salinity [32,33].

In this study weathered and aged contaminated wastes were exposed to a high salinity and metal content as well as hydrocarbon contamination. Levels of heterotrophic bacteria at 10^5 – 10^6 CFU g^{-1} and presence of anaerobes (data not shown) were observed in all reactors, which is in agreement with bacterial levels observed in Kuwait's contaminated soils. On the other hand, presence of viable bacteria in native soils was not observed using the same microbial analysis. Thus, it is suggested that microbial communities present in fuel oil contaminated soil and sawdust in this study were able to grow and acclimate to hyper-saline environments and high metal content and also partially metabolise the hydrocarbons present.

Fuel oil degradation and biomass production depend directly on an accurate balance of nutrients since they are essential for the catabolic activity of microorganisms. Thus, major and minor elements were monitored (Table 1). Levels of Mn and available N, P, K were higher (range between 1000 and 10,000 ppm) than levels of B and Zn (30–180 ppm, respectively) in the fuel oil contaminated soil and sawdust. Levels of S and Cu were considerable higher in the fuel oil contaminated soil and sawdust than those normally encountered in typical desert mining soils (3000 and over 200 mg kg^{-1} , respectively). Levels of S and Cu in this study did not present a significant effect on the removal of hydrocarbons in the soil and sawdust mixtures following treatment in this study ($p > 0.05$, correlation index) and thus, it was assumed that autochthonous microbial communities were adapted to the presence of S and Cu in the contaminated wastes.

Nevertheless, available N, P and K concentration values were low in all reactors as compared to values reported in soils with an agronomic value (Table 1). Initial N content was different in the composting reactors depending on the S:SD ratio, being the total N concentration in sawdust four times higher than in soil. Total N concentration decreased in all reactors under treatment, but the highest decrease of total N was observed in the reactor with only sawdust during the first 28 days (Fig. 2b). Furthermore, total N concentration in all reactors after 56 days of treatment reached a similar minimum steady state concentration value ($p > 0.05$), which may be indicative of nutrient limitations. Total N did not change in the abiotic controls during treatment (data not shown). These results further indicated that microbial communities in the composting reactors demanded nutrients to sustain a metabolic activity required to metabolise, at least partially the hydrocarbons present in the contaminated wastes.

In the present study, it was assumed that indigenous soil microbial populations were adapted to the fuel oil present in the contaminated wastes and to the environmental conditions. Values of available nutrients in this study were lower than those values typically reported in composting processes, which was not surprising because desert soils are mainly composed of mineral surfaces with low organic matter contents. With respect to organic matter content, the composting reactors with mixtures of

Table 2

Statistical analysis of fuel oil removal in abiotic and experimental reactors following 56 days continuous composting treatment

Two-way repeated measures ANOVA (comparison between removal curves, all reactors)				
Source of variation	Control reactors		Experimental reactors	
	Contribution to variation (%)	<i>P</i> -value	Contribution to variation (%)	<i>P</i> -value
Factor time	9.7	0.0078*	73.3	<0.0001*
Factor treatment	8.3	0.7584	10.3	0.0165*
Interaction	13.4	0.1981	7.2	<0.0001*

One-way repeated measures ANOVA (comparison between Experimental removal curves, reactor vs. reactor)			
Reactor vs. reactor	Effect	Variation (%)	<i>P</i> -value
Soil vs. S:SD-3:1	Treatment	47.3	0.0005*
Soil vs. S:SD-1:1		63.2	<0.0001*
Soil vs. S:SD-1:3		62.9	<0.0001*
Soil vs. Sawdust		64.6	<0.0001*
S:SD-3:1 vs. S:SD-1:1		25.4	0.0004*
S:SD-3:1 vs. S:SD-1:3		23.6	0.0008*
S:SD-3:1 vs. Sawdust		44.3	<0.0001*
S:SD-1:1 vs. S:SD-1:3		0.1	0.1830
S:SD-1:1 vs. Sawdust		16.9	<0.0001*
S:SD-1:3 vs. Sawdust		18.9	<0.0001*

* Note: $p < 0.050$.

contaminated desert soil and contaminated sawdust presented a higher organic matter content (24%, 30% and 49% in composting reactors with a S:SD ratio of 3:1, 1:1 and 1:3, respectively) as compared to the composting reactors with only contaminated desert soil (14%) due to the presence of sawdust, which probably enhanced the sorption of organic contaminants reducing their bioavailability [5]. Furthermore, the organic carbon content in the contaminated wastes in this study was significantly higher than that typical of non-contaminated desert soils (Atacama and Kuwait's region, organic matter content <1%).

TOC/N ratios in the composting reactors were initially within the range 50:1–100:1 (Fig. 2c), while TOC/N ratios normally encountered in a composting process are around 75:1 [23]. In general, similar temporal increases in TOC/N ratios in all reactors following composting treatment were observed. The concentration of TOC in the composting reactors decreased during the length of the treatment, thus an increase of TOC/N ratios was indicative of a faster temporal decrease of total N as compared to TOC decrease (Fig. 2c). Further experiments are required to understand a temporal decrease of TOC/N ratios observed from day 28 to 42 in the reactors with S:SD ratios 3:1 and 1:1. Temporal trends of total N and TOC/N ratios in the composting reactors (Fig. 2b and c) suggested nutrient limitations which may have resulted in a limited removal of hydrocarbons presented in the contaminated soil and contaminated sawdust.

3.2. Biodegradation of fuel oil

In order to follow the biodegradation of fuel oil present in the contaminated soil and contaminated sawdust mixtures, total hydrocarbon concentration was monitored. Different initial concentrations of fuel oil were observed in the reactors with higher initial hydrocarbon concentrations present in sawdust (Fig. 3a).

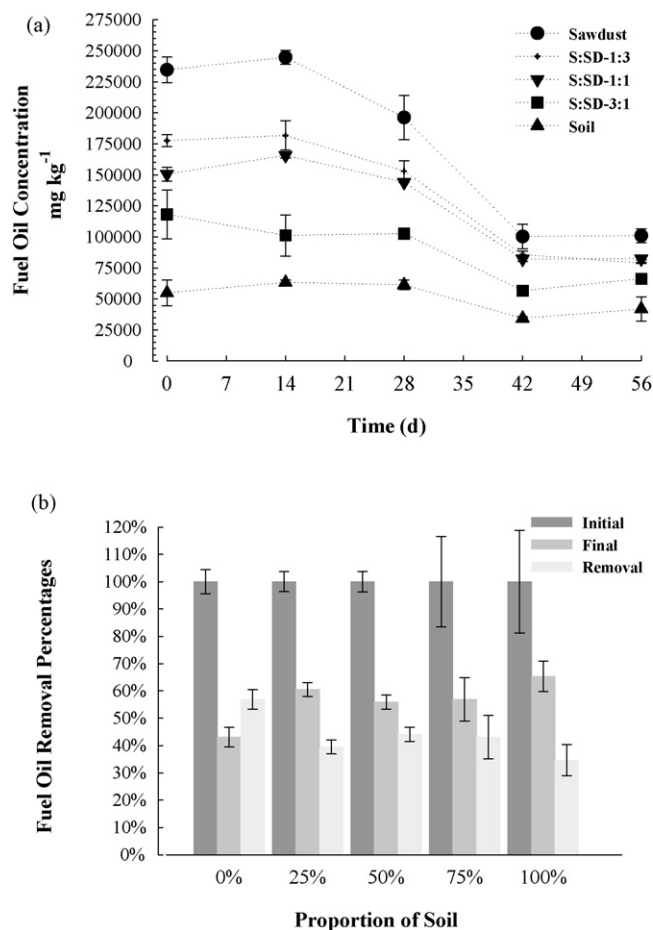


Fig. 3. Temporal changes of: (a) fuel oil concentration in experimental reactors and (b) removal rates in the experimental reactors.

The initial concentration of fuel oil in the mixtures corroborated the higher sorbing capacity of sawdust. Biodegradation curves obtained from each composting reactor indicated that most of the biodegradation occurred during the first 42 days of treatment, with higher hydrocarbon removal rates observed in the reactors with lower S:SW ratios (higher amounts of sawdust and nutrients) (Fig. 3a). Following 56 days of composting treatment a residual concentration of hydrocarbons remained in all the reactors, which may have occurred due to nutrient limitations and also limited bioavailability [7,34].

Reactors with a S:SD ratio 0:1 presented the highest hydrocarbon removal (>55%) as compared to the rest of the reactors, where the reactor with only soil presented the lowest hydrocarbon removal (<30%). Reactors with S:SD ratios 1:3, 1:1 and 3:1 presented similar hydrocarbon final removals (ca. 40%). On the contrary, the concentration of fuel oil remained unchanged in the abiotic controls (data not shown). These removal percentages are similar and concordant with those reported by Marchal et al. [35] and commercial diesel oil as main contaminant in desert mining soil operations. Nevertheless, a higher hydrocarbon's removal (60–80%) was obtained when an aged coal-tar contaminated soil (100 mg kg⁻¹) mixed with green waste was treated under in-vessel composting conditions and a correct balance of nutrients was facilitated in the composting mixture [3]. Additionally, previous studies on the effect of temperature (10 and 25 °C) and addition of inorganic fertilizers (C:N ratios of 10:1 and 50:1) on the bioremediation of soil from a diesel oil contaminated waste disposal site (5580 mg kg⁻¹) reported that the highest diesel-oil decontamination removal were 43% at 10 °C and 55% at 25 °C after 30 days, and that the biodegradation activity of the indigenous soil microorganisms was highly increased by the use of fertilizers [36].

3.3. Optimal conditions for in-vessel composting of fuel oil contaminated desert soil and sawdust

Statistical analysis using all different treatments indicated that two factors could explain 83.6% of the total variance (Table 2). Factor time explained 73.3% of the total variance, and factor treatment (S:SD ratio) explained 10.3% of the total

variance. These results were confirmed with PCA analysis. Comparing the results of the abiotic and experimental reactors, all treatments presented significant differences, indicating that the main mechanism of removal during fuel oil contaminated soil and sawdust composting treatment was biodegradation. The temperature used in this experiment (mesophilic range) was lower than that required for volatilization [37], which further supported biodegradation as the main hydrocarbon removal mechanism in the weathered and aged contaminated wastes.

A linear correlation analysis including the various physico-chemical parameters monitored in this study during treatment indicated that the removal of fuel oil was significantly influenced by pH, TOC/N ratio and total N (Table 3). The reactor with only soil presented a significant correlation of fuel oil removal with TOC:N ratio, which may further indicate that N was a limiting factor for fuel oil biodegradation during treatment. Additionally, the reactor with a S:SD 1:3 presented a significant correlation of fuel oil removal with the total N present, which may also further indicate nutrient limitations during treatment. The rest of reactors presented no significant correlations with the monitored physico-chemical parameters.

The major difference between treatments was observed for treatments with only soil (S:SD 1:0) and mixtures of contaminated soil and contaminated sawdust (Table 2). No statistical difference was observed between treatments with a S:SD 1:1 and 1:3, and both were statistically different from treatments with S:SD ratios 0:1 and 3:1. Furthermore, the reactors with S:SD ratios 0:1 and 1:3 presented a significant difference between the initial and final fuel oil concentration ($p < 0.005$). These results may suggest a lower biodegradation capability of residential microorganisms to biodegrade fuel oil present in the contaminated soil and thus the importance of mixing both, soil and sawdust, to achieve a maximum overall hydrocarbon removal of fuel oil in the weathered and aged contaminated wastes. Additionally diesel fuel initially present in the contaminated soil could be more recalcitrant (C₁₀–C₁₉) than fuel oil initially present in the contaminated sawdust (C₄–C₁₃). Thus, this study indicates that Treatment (or S:SD ratio) is the factor that more strongly affects the removal of fuel oil under in-vessel composting conditions of mixtures of aged fuel oil contaminated soil and

Table 3
Linear correlations (r) of fuel oil removal and physico-chemical parameters in each experimental reactor during treatment

Weekly (%)	pH	Ratio TOCs:N	Total N	Available N	Available P	Total S	Total K
Soil							
Removal	0.5	-0.9*	0.7	NA	NA	NA	NA
Soil:Sawdust—S:SD-3:1							
Removal	0.5	-0.5	0.4	0.5	0.2	-0.6	-0.0
Soil:Sawdust—S:SD-1:1							
Removal	0.7	-0.6	0.6	0.6	0.6	-0.5	0.3
Soil:Sawdust—S:SD-1:3							
Removal	0.7	-0.5	0.9*	0.8	0.8	0.1	0.3
Sawdust							
Removal	-0.2	-0.5	0.5	0.4	0.6	-0.2	-0.7

Note: NA, data not available or not applicable.

* $p < 0.050$.

sawdust. These results corroborate previous studies that indicated that soil to organic amendment ratios have a significant effect for in-vessel composting optimisation [3]. Finally, for an elevated operation yield (i.e. higher amount of contaminated mixture treated), a low S:SD ratio will be advantageous, since a high S:SD ratio may show inhibitory effects on the residential microbial populations.

4. Conclusions

The bioremediation of aged fuel oil contaminated desert mining soils and sawdust is feasible by aerated in-vessel composting. The percentages of removal were in the range 30–55%, and the reactor with a S:SD ratio 0:1 presented the highest hydrocarbon removal. Two principal factors, time and sawdust percentage, explained the removal of pollutants. The optimisation of time, soil to sawdust ratio and a correct balance of nutrients are required for a maximum contaminant removal. The optimisation of time is required for the time management of the process which will result in an economic benefit. This study recommends a S:SD ratio 1:3 and a correct nutrient balance in order to achieve a maximum overall hydrocarbon removal of fuel oil in the weathered and aged contaminated wastes. Finally, this study supports the use of in-vessel composting to treat weathered and aged fuel oil contaminated desert mining soils and sawdust.

Acknowledgments

This research was funded by Minera Escondida Ltd. through donations to G.-F.A. The authors thank CONICYT (Comisión Nacional de Ciencia y Tecnología) for a doctoral fellowship to G.-F.A. Dr. B. Antizar-Ladislao thanks the Spanish Ministry of Education and Science for a Ramón y Cajal senior research fellowship. Many thanks also to M.D. Paul Harris for his support and continuous advice and the equipment and instruments that he made available for the purpose of this research.

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