

## Assessment of Canadian Regulations and Remediation Methods for Diesel Oil Contaminated Soils

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**Abstract:** Diesel fuel released into the environment can contaminate ground water, degrade potable water supplies and cause the collapse of fisheries. They are toxic to both animals and humans and can affect the liver, lungs, kidneys, and nervous system leading to cancer as well as immunological and reproductive effects. The objectives of this study were to review current Canadian regulations pertaining to diesel fuel and to evaluate the current remediation methods using five criteria: efficiency, applicability, cost, time and cleanliness. PAHs are deemed toxic under the Canadian Environmental Protection Act but no standards have been set for PAHs in diesel. The Canadian Council of Ministers of the Environment (CCME) has developed Canada-Wide Standards for Petroleum Hydrocarbons in Soil (CWS PHCS) while the Atlantic PIRI has implemented a Risk Based Corrective Action (RBCA) for the Atlantic region. The remediation methods included soil washing, landfilling, incineration, thermal desorption, radio frequency heating, chemical addition, landfarming, biopiling, composting, bioventing, liquid delivery and bioreactors. The bioreactors studied included: static bed, continuous mix, horizontal drum, fungal compost, slurry-phase, DITS, biofilters and packed bed bioreactors. The results showed that the biological methods were more effective than nonbiological ones and the bioreactors scored the highest among the biological methods. Eight criteria were then used for the evaluation of bioreactors: efficiency, time, cost, maintenance, simplicity, release of VOCs to the atmosphere, containment of contaminants and control of operating parameters. The results showed that the continuous mix bioreactor was the most effective system.

**Key words:** Diesel fuel, remediation, regulation, ecosystem, physical, chemical, biological, evaluation

### INTRODUCTION

Diesel Fuel is intended for use in compression engines such as those found in trucks, trains and subtrains<sup>[1]</sup>. It is composed of a variety of organic compounds as shown in Table 1<sup>[2]</sup>. As the fuel weathers over time, the concentration of these compounds change due to volatilization and degradation to other compounds<sup>[3]</sup>.

Accidental diesel spills and the leakage of underground storage tanks have far reaching impacts on the environment. A study on marine iguanas on one of the Galapagos Islands in Ecuador has shown that 62 % of the species population has died since the oil tanker spill that occurred 1500 m offshore in 2001<sup>[4]</sup>. There are over 400 000 petroleum hydrocarbon contaminated sites in the USA alone as a result of spillage and leakage of underground tanks located at airports, refineries and farms<sup>[5]</sup>. Pockets of oil on these sites can persist in the environment for many years. The study on

the 700 000 L diesel spill of 1969 (which is only one sixtieth of that spilled by Exxon Valdez) is still going on by Woods Hole Oceanographic Institute of Massachusetts<sup>[6]</sup>.

According to Riser-Roberts<sup>[2]</sup>, hydrocarbons in the soil are considered toxic when they reach concentrations greater than 100 µg/g soil. The soluble compounds of diesel (benzene, toluene, ethyl benzene, and xylenes which are known as BTEX) are toxic to aquatic life as well as animals and humans. Diesel released into the environment can contaminate ground water, degrade potable water supplies and cause the collapse of fisheries<sup>[3]</sup>. Polycyclic aromatic hydrocarbons (PAHs) in diesel (such as naphthalene) have long term effects on soil, ground water and sediments and can act as endocrine disruptors (i.e. interfere with hormone production and function). The PAHs and BTEX affect the liver, lungs, kidneys and nervous system leading to cancer, immunological, reproductive, fetotoxic and genotoxic effects<sup>[1]</sup>.

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CCME<sup>[7]</sup> summarizes the pathways through which humans and wildlife can be exposed to contaminants (Table 2).

Table 1: Composition of Diesel Fuel #2<sup>[2]</sup>

Component	Concentration (% Volume)
C <sub>10</sub> paraffins	0.9
C <sub>10</sub> aromatics	0.4
C <sub>10</sub> cycloparaffins	0.6
C <sub>11</sub> paraffins	2.3
C <sub>11</sub> aromatics	1.0
C <sub>11</sub> cycloparaffins	1.7
C <sub>12</sub> paraffins	3.8
C <sub>12</sub> aromatics	1.6
C <sub>12</sub> cycloparaffins	2.8
C <sub>13</sub> paraffins	6.4
C <sub>13</sub> aromatics	2.8
C <sub>13</sub> cycloparaffins	4.8
C <sub>14</sub> paraffins	8.8
C <sub>14</sub> aromatics	3.8
C <sub>14</sub> cycloparaffins	6.6
C <sub>15</sub> paraffins	7.4
C <sub>15</sub> aromatics	3.2
C <sub>15</sub> cycloparaffins	5.5
C <sub>16</sub> paraffins	5.8
C <sub>16</sub> aromatics	2.5
C <sub>16</sub> cycloparaffins	4.4
C <sub>17</sub> paraffins	5.5
C <sub>17</sub> aromatics	2.4
C <sub>17</sub> cycloparaffins	4.1
C <sub>18</sub> paraffins	4.3
C <sub>18</sub> aromatics	1.8
C <sub>18</sub> cycloparaffins	3.2
C <sub>19</sub> paraffins	0.7
C <sub>19</sub> aromatics	0.3
C <sub>19</sub> cycloparaffins	0.6

## CANADIAN REGULATIONS

**Federal Regulations:** Many of the regulations that pertain to diesel fuel in Canada relate to its sulphur content<sup>[8]</sup>, since the production of SO<sub>2</sub> during combustion and exhaust is the leading cause of acid rain. However, diesel-powered vehicles are a significant source of aromatic hydrocarbons in urban areas. Human exposure to diesel containing benzene at any concentration will have adverse health effects. Although PAHs (like benzene) are considered toxic under the Canadian Environmental Protection Act (CEPA), there are no standards for PAHs in diesel<sup>[9]</sup>. CEPA regulations apply to quantities greater than 400 m<sup>3</sup> of fuel produced or imported into Canada that contains any additives. The petroleum industry is required to report sulphur content and any additives in the fuel, other than lead, to the Minister of Environment, where the liquid fuel is from crude oils, coal, or bituminous sands.

Many factors affect the cost of the diesel clean-up in Canada including: (a) the accessibility or remoteness

of the spill location, whether the spill is located on land, in a river, or in the ocean, (b) the weather conditions, (c) the quantity spilled, (d) the extent of environmental damage, and (e) the time required for the clean-up. Blondeau<sup>[10]</sup> reported that, based on the data obtained from the Saskatchewan Spill Response Center, the leading causes of spills are equipment failure and accidents during road transport and most of the spills documented were from petroleum, transportation and mining companies.

About 60 % of Canada's contaminated sites involve petroleum hydrocarbons (PHCs) that can cause fires and/or explosions on these sites and impair the quality and uses of land and water. The Canadian Council of Ministers of the Environment (CCME) developed Canada-Wide Standards for Petroleum Hydrocarbons in Soil (CWS PHCS) in 2001<sup>[7]</sup>. These standards separate soil under four different land uses: agricultural, residential/parkland, commercial, and industrial. Table 3 shows the allowable petroleum hydrocarbon (PHC) fractions in soil, depending on the land use. The CWS PHCS specifies the methods and outcomes for the assessment and management of contaminated sites but timelines are left for individual jurisdictions to decide. When assessing a contaminated site, one must also consider ignition hazards, toxicity, odor, appearance of the contaminants, effects on buried infrastructure, and formation of non-aqueous-phase liquids (NAPL). Table 4 shows the required site characterization. All provinces and territories except Quebec have endorsed CWS PHCS and the legislation for its enforcement.

**Regulations in the Atlantic Region:** The Atlantic Provinces (Nova Scotia, New Brunswick, Prince Edward Island, and Newfoundland and Labrador) have a harmonizing partnership agreement called the Risk Based Corrective Action (RBCA) agreement with its own set of PHC guidelines. The Atlantic Partnership in RBCA Implementation (PIRI) ensures that RBCA is effective and serves the needs of Atlantic Canadians by returning more sites to safe use at a reduced cost. The RBCA has been in use since 1999 and it differs from the CWS PHCS with respect to criteria for laboratory procedures for the comparison of site data<sup>[11]</sup>.

RBCA is a 3-tiered approach to risk assessment and risk management. Tier I uses the risk-based screening levels from Table 5 to determine the need for and the extent of removal of any remedial work required after confirmation of site applicability. It identifies the presence of ecological receptors on or adjacent to the site (within 150 m) and the potential for ecological receptors to be exposed to the release of

hydrocarbons. Tier II uses the values from Table 6 to determine the need for and the extent of remedial work required. Tier III is triggered by an ecological risk assessment, even if human health risk is managed under RBCA. RBCA is used in residential and commercial land use settings and adult is the default receptor<sup>[11]</sup>.

### REMEDICATION METHODS

Soil remediation can take place either in-situ or ex-situ using one or more of the current remediation technologies. These include: physical, thermal, chemical and biological processes<sup>[2]</sup>.

**Physical Processes:** Physical remediation technologies include soil washing and landfilling.

**Soil washing:** Soil washing is when a wash solution (water and/or a surfactant) is added to soil to remove contaminants. The contaminant is transferred from the soil to the wash solution, which then must be treated. Residual sludge is often associated with this method. Water alone is not effective in removing PAHs. Haapea and Tuhkanen<sup>[12]</sup> reported that the amount of total PAHs in the soil decreased by about 50% after soil washing as the PAHs were transferred into the washing water. Viglianti et al.<sup>[13]</sup> found the addition of cyclodextrins significantly improved the soil washing process. Rajput et al.<sup>[14]</sup> used soil washing to remove 1,2,4-trichlorobenzene (TCB), aniline, phenol, and 2,4-dichlorophenol (DCP) and found water washing to be suitable for removing all contaminants except TCB which required washing with surfactant first and then rinsing with water. Other solutions such as hydrochloric

acid and sodium hydroxide have also been used in soil washing techniques<sup>[15, 16]</sup>.

**Landfilling:** Landfilling is one of the oldest forms of remediation. Contaminated soil is excavated from the site and transported to a landfill where it remains indefinitely. In cases where the soil is brought to a first generation landfill, there is still the potential for the contaminants to enter groundwater or bedrock. PAHs can contaminate landfill leachate and their presence has been reported<sup>[17, 18]</sup>. However, methods have been devised for the removal of aromatic organics from soil which may help to control these contaminants in landfills<sup>[19]</sup>.

**Thermal Processes:** There are currently three thermal remediation technologies in use: incineration, thermal desorption and radio frequency heating.

**Incineration:** Incineration is the destruction of contaminants by burning contaminated soil. This method can achieve greater than 99.99% success in destroying carbon tetrachloride, chlorinated benzenes and polychlorinated biphenyls but is very expensive<sup>[2]</sup>. Benzene is adequately destructed via thermal incineration at temperatures ranging from 850 to 973 K<sup>[20]</sup>. However, catalytic incineration is more efficient than thermal incineration in destroying aromatic hydrocarbons. CuO/CeO<sub>2</sub> and CuO/γ-Al<sub>2</sub>O<sub>3</sub> were found to be effective catalysts in the incineration of toluene and *p*-xylene<sup>[21-23]</sup>. Arsenijević et al.<sup>[24]</sup> used a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst to incinerate ethylene oxide. Tseng and Chu<sup>[25]</sup> studied the catalytic incineration of styrene (also known as vinyl benzene) using MnO/Fe<sub>2</sub>O<sub>3</sub> as a catalyst.

Table 2: Land uses, key receptors and exposure pathways<sup>[7]</sup>

Exposure Pathway	Agriculture	Residential/ Parkland	Commercial	Industrial
Soil contact	Nutrient cycling	Nutrient cycling	Nutrient cycling	Nutrient cycling
	Soil invertebrates	Invertebrates	Invertebrates	Invertebrates
	Crops (plants)	Plants	Plants	Plants
	Human (child)	Human (child)	Human (child)	Human (adult)
Soil ingestion	Herbivores	Wildlife*	Wildlife*	Wildlife*
	Human (child)	Human (child)	Human (child)	Human (adult)
Groundwater/ Surface water	Aquatic life	Aquatic life	Aquatic life	Aquatic life
	Livestock watering	Human (child)	Human (child)	Human (adult)
	Human (child)			
Vapour inhalation**	Child (indoor)***	Child (indoor)	Child (indoor)	Adult (indoor)
Produce (meat and milk produced on site)**	Child	Child (produce only)	-	-
Off-site (migration of soil/dust)	-	-	-	Human/eco

\* Wildlife dermal contact and ingestion data may be particularly important for PHCs, but there are unlikely to be sufficient data to develop guidelines that address this exposure pathway.

\*\* Humans only

\*\*\* A 30m horizontal offset is assumed between the farm residence and the PHC contamination, consistent with oil and gas development practices. Contamination nearer a farm residence triggers a residential assessment.

Table 3: Tier 1 levels for surface soil

Land Use	Soil Texture	PHC (mg/kg)			
		Fraction 1	Fraction 2	Fraction 3	Fraction 4
Agricultural	Coarse	130	450 (150 <sup>a</sup> )	400	2800
	Fine	260 (180 <sup>b</sup> )	900 (250 <sup>b</sup> )	800	5600
Residential/ Parkland	Coarse	30 <sup>c</sup>	150 <sup>c</sup>	400	2800
	Fine	260 (180 <sup>b</sup> )	900 (250 <sup>b</sup> )	800	5600
Commercial	Coarse	310 (230 <sup>a</sup> )	760 (150 <sup>a</sup> )	1700	3300
	Fine	660 (180 <sup>b</sup> )	1500 (250 <sup>b</sup> )	2500	6600
Industrial	Coarse	310 (230 <sup>a</sup> )	760 (150 <sup>a</sup> )	1700	3300
	Fine	660 (180 <sup>b</sup> )	1500 (250 <sup>b</sup> )	2500	6600

<sup>a</sup>Where applicable, for protection against contaminated groundwater discharge to an adjacent surface water body.

<sup>b</sup>Where applicable, for the protection of potable groundwater. <sup>c</sup>Assumes contamination near residence with slab-on-grade construction.

Table 4: Site characterization

Characteristics	Description
Land use	Historical, existing, intended, and potential land uses at the site and its surroundings, including the presence or absence of any critical wildlife habitat
Proximity	Distance between the site and surface water especially drinking water supplies
Groundwater	Depth of ground water
Human receptors	Children and adults
Ecological receptors	Microorganisms responsible for nutrient cycling, soil invertebrates, plants, wildlife, and aquatic life
Exposure pathways	Soil contact, soil ingestion, groundwater/ surface water, vapor inhalation, produce, meat and milk produced on site, and off-site migration of soil/dust
Stratigraphy	Properties of surficial materials, especially soil texture
Depth to contamination	Distance to points of exposure or compliance
Built environment	The presence and type of buildings, utility corridors, and conduits
Contaminants	Characterization and delineation of contaminants such as toxicity, ignitability, solubility and volatility

Table 5: Tier I TBSL for soil<sup>[11]</sup>

Receptor	Groundwater Use	Soil Type	Compound of concern in soil (mg/kg)						
			Benzene	Toluene	Ethyl Benzene	Xylenes	Modified TPH		
							Gas	Diesel/#2	#6 oil
Residential	Potable	Coarse	0.03	0.38	0.08	11	39	140	690
		Fine	0.01	0.08	0.02	2.3	140	220	970
	Non-potable	Coarse	0.16	14	58	17	39	140	690
		Fine	1.5	120	430	160	330	4400	8300
Commercial	Potable	Coarse	0.03	0.38	0.08	11	450	7400	10000
		Fine	0.01	0.08	0.02	2.3	520	840	4700
	Non-potable	Coarse	1.8	160	430	200	450	7400	10000
		Fine	11	680	430	650	10000	7700	10000

Everaert and Baeyens<sup>[26]</sup> review catalytic oxidation processes for volatile organic contaminants (VOCs).

**Thermal desorption:** In thermal desorption, soil is heated under an inert atmosphere to increase the vapor pressure of organic contaminants causing the contaminants to volatilize and be released from the soil<sup>[27]</sup>. Merino and Bucala<sup>[28]</sup> reported that hexadecane can be nearly completely removed at 300°C without risk of pyrolysis. Piña et al.<sup>[29]</sup> found that low heating rates practically eliminate gas oil from soil matrices while avoiding significant chemical transformations but higher temperatures were required to achieve optimal removal efficiencies.

**Radio frequency heating:** Radio frequency power has been used in the steam reforming of hydrocarbons. These waves are converted to thermal energy in the soil for heating the contaminants and causing their volatilization. This procedure is very expensive but because the heat can be directed, the treatment is more accurate<sup>[2]</sup>. Al-Mayman and Al-Zahrani<sup>[30]</sup> cracked Saudi light oil into lower olefins using radio frequency heating. Shih et al.<sup>[31]</sup> decomposed benzene (C<sub>6</sub>H<sub>6</sub>) in radio frequency plasma environments and found naphthalene (C<sub>10</sub>H<sub>8</sub>) to be a predominant product.

**Chemical Processes:** Peroxide or an alkaline solution with a pH of 10.5 containing cobalt (III) can be added to contaminated soil to oxidize organic contaminants to

Table 6: Tier II Pathway-Specific Screening Level (PSSL) for soil<sup>[11]</sup>

Receptor	Groundwater Use	Soil Type	Exposure Pathway	Compound of concern in soil (mg/kg)								
				Benzene	Toluene	Ethyl Benzene	Xylenes	Modified TPH				
								Gas	Diesel/#2	#6 oil		
Residential	Potable	Coarse	Soil ingestion	390	12000	7000	120000	8900	5300	8300		
			Soil leaching	0.031	0.38	0.083	11	680	1100	8300		
			Indoor air	1.5	120	>430	160	330	4400	>RES		
		Fine	Soil ingestion	390	12000	7000	120000	8900	5300	8300		
			Soil leaching	0.0071	0.082	0.018	2.3	140	220	970		
			Indoor air	0.16	14	58	17	39	140	690		
	Non-potable	Coarse	Soil ingestion	390	12000	7000	120000	8900	5300	8300		
			Soil leaching	Not applicable for non-potable scenarios			>430	160	330	4400	>RES	
			Indoor air				>430	200	450	7400	>RES	
		Fine	Soil ingestion	390	12000	7000	120000	8900	5300	8300		
			Soil leaching	Not applicable for non-potable scenarios			>430	200	450	7400	>RES	
			Indoor air				>430	200	450	7400	>RES	
Commercial	Potable	Coarse	Soil ingestion	570	18000	10000	180000	13000	7700	12000		
			Soil leaching	0.031	0.38	0.083	11	2500	11000	>RES		
			Indoor air	11	>680	>430	>650	>RES	>RES	>RES		
		Fine	Soil ingestion	570	18000	10000	180000	13000	7700	12000		
			Soil leaching	0.0071	0.082	0.018	2.3	520	840	4700		
			Indoor air	1.8	160	>430	200	450	7400	>RES		
	Non-potable	Coarse	Soil ingestion	570	18000	10000	180000	13000	7700	12000		
			Soil leaching	Not applicable for non-potable scenarios			>680	>430	>650	>RES	>RES	
			Indoor air				>680	>430	>650	>RES	>RES	
		Fine	Soil ingestion	570	18000	10000	180000	13000	7700	12000		
			Soil leaching	Not applicable for non-potable scenarios			14	58	17	39	140	690
			Indoor air				14	58	17	39	140	690

Table 7: Advantages and disadvantages of nonbiological methods<sup>[67]</sup>

Process	Advantages	Disadvantages
Soil Washing	Relatively efficient Quick Uses water	Transfers contaminants to a different phase Surfactants are often necessary Requires infrastructure
Landfilling	Removes contamination from site	Transfers pollution to another site Expensive Land requirement Transportation costs
Incineration	Quick Destroys hydrocarbons	Expensive Can cause air pollution Irreversible soil degradation
Thermal Desorption	Broad applicability High removal efficiencies No excavation required in situ	At high temperatures contaminants may volatilize and are released from the soil into the air Low temperatures do not achieve optimal removal efficiencies Energy use
Radio Frequency Heating	Accurate	Very expensive Products must be disposed of
Chemical Addition	Simple Oxidizes organic contaminants Soil left intact	Extracts must be treated Excavation

CO<sub>2</sub> and CO. Supercritical water can also be used to oxidize hazardous materials<sup>[32-34]</sup>. Acetone, methanol and ethanol solutions can then be used to extract compounds like benzene and pyrene<sup>[2, 35]</sup>.

**Biological Processes:** There are a number of biological technologies currently in use: landfarming, biopiling, composting, bioventing and liquid delivery. It should be noted that hydrocarbon concentrations of less than 10 µg/l do not usually stimulate microbial growth<sup>[2]</sup> and hydrocarbons with rings or many branches are slower to

biodegrade<sup>[36]</sup>. Ghaly and Pyke<sup>[37]</sup> reported that hydrocarbons with heavy molecular weight (C<sub>12</sub>H<sub>12</sub>-C<sub>31</sub>-C<sub>64</sub>) are slower to biodegrade.

**Landfarming:** Millions of tons of contaminated soil are treated by landfarming annually in the USA and Canada and more than half of which is associated with petrochemical contaminants. The processes involved with this method of treatment include: leaching, adsorption, desorption, photodecomposition, oxidation, hydrolysis, and biological metabolism<sup>[2]</sup>. Aeration and

Table 8: Advantages and disadvantages of land based biological methods

Process	Advantages	Disadvantages
Landfarming	Least expensive, can be performed ex-situ or in-situ	Long residence time, unsuitable in towns (large land area required), potential for contaminating water, air, soil, sensitive to weather, limited capability in degrading complex compounds, possibility of contaminant transport, requires less than 2% grade slope
Biopiling	Effective nutrient supplementation, second least expensive	Biodegradation occurs during summer months unless steam is supplied, soil must be accessible, land requirement is relatively large, requires infrastructure
Composting	High microbial diversity, low capital and operating costs, simple operation and design, high treatment efficiency, moisture, nutrient, and pH levels can be controlled, less threat than incineration, no mixing with surface, shorter treatment time than landfarming, can treat high concentrations of organic compounds	Large land requirement, difficulty siting, time required, possible groundwater contamination, difficult to capture off-gasses
Bioventing	Can be low cost, high efficiency	Not suitable for VOCs, water table should be >10ft from surface, not used for surficial soils, site may need to be capped, adversely affected when hydraulic conductivity <10 <sup>-4</sup> cm/s, off-gases may need further treatment, should not be used near buildings (explosion hazard), can be difficult to add nutrients, can take years, requires underground infrastructure
Liquid Delivery System	Good for fractured rock aquifers, good for shallow water tables	Requires extensive site characterization, H <sub>2</sub> O <sub>2</sub> can be toxic at high concentrations, longer timeframe

Table 9: Advantages and disadvantages of bioreactors

Advantages	Disadvantages
Shorter timeframe (70 times faster than landfarming), less space required, can be cheap, can capture VOCs, can have aerobic conditions for recalcitrant compounds, simple, work on concentrated residues, can be coupled with other techniques, various sizes (several liters to millions of liters), economic and technical advantage for saturated soils	Some reactors can be expensive, soil sometimes has to be pretreated, require constant mixing, transportation costs, off-gases likely require further treatment

Table 10: Evaluation criteria for remediation methods

Criteria	Definition	Score
Applicability	Used under various situations with no or little modification	25
Efficiency	99% removal warrants 25 but <50% warrants 0	25
Time	Removes contaminants within three months	20
Cost	Inexpensive	15
Cleanliness	Pollutants are not transferred to other locations	15
Total score		100

nutrients are provided by tilling the soil regularly<sup>[3]</sup>. There are several disadvantages to this form of treatment: (a) it requires a large amount of land area which can be difficult to find in populated areas, (b) it has the potential to contaminate groundwater, (c) it is sensitive to the weather, (d) it has limited capability for degrading heavier components of petroleum oils, (e) there is a chance of contaminant transport (f) it has a slow detention time and (g) it is not suitable when volatile organic compounds (VOCs) are present because they will be released to the atmosphere<sup>[2, 38,39]</sup>. However, researchers have tried this technique under wide conditions. Marin et al.<sup>[40]</sup> used landfarming to reduce the total hydrocarbon content in an oil refinery sludge by 80 % in 11 months under semiarid

conditions. McCarthy et al.<sup>[41]</sup> treated soil in Alaska contaminated with petroleum hydrocarbons (such as diesel-range organics, trimethylbenzenes, gasoline-range organics and BTEX compounds) in 55 days using landfarming. Landfarming has also been used in the degradation of oil in the desert<sup>[42]</sup>.

**Biopiling:** Biopiling is an ex-situ remediation method that is very effective in nutrient supplementation<sup>[38]</sup>. Biopiles require accessible contaminated soils and sufficient land area. It has been found that contaminants in biopiles show the greatest reduction in concentration over the summer months<sup>[43]</sup>. While treating diesel contaminated soil, Nano et al.<sup>[44]</sup> found that sand improved pile porosity (and subsequently oxygen

diffusion) and surfactants were effective in increasing contaminant bioavailability. Jørgensen et al.<sup>[45]</sup> mixed nutrients (N, P, K) and microbes in soil biopiles and found mineral oil degradation rates to be the highest in the first months, following a standard first order degradation curve.

**Composting:** Contaminated soil is mixed with a bulking agent such as manure or wood chips, and heaped in a large pile. Manure or sewage sludge are also used for inoculation of the pile to provide high microbial diversity, specifically mesophilic and thermophilic microbes<sup>[46]</sup>. Jørgensen et al.<sup>[45]</sup> used bark chips as a bulking agent while composting a hydrocarbon contaminated soil in biopiles. Composting can be carried out in-situ or ex-situ to treat highly contaminated soils. Machinery is used to turn the pile (aerating it). Moisture, nutrient and pH levels are also controlled<sup>[2]</sup>. Composting has a shorter detention time than landfarming and the final product can be used for landscaping. The contaminated soil is also not worked into the land so there is less potential for contaminants to enter groundwater than with landfarming. There is also less threat to air than that associated with incineration<sup>[2]</sup>. Namkoong et al.<sup>[46]</sup> treated diesel oil contaminated soil by composting and only 2% of the total petroleum hydrocarbons were lost by volatilization.

**Bioventing:** Bioventing is suitable for less volatile contaminants that are biodegradable under aerobic conditions<sup>[3]</sup>. When volatile compounds are present, off-gases need to be treated, thereby increasing the cost of the operation. This process is most applicable where the water table is greater than 3 m deep from the surface. The site must be capped if the soil and water table are shallow<sup>[43]</sup>. Bioventing should not be used near buildings because there is the potential for an explosion. Moisture levels of 40 %-60 % of field saturation must be maintained in order for the operation to be successful. Major costs are incurred in installing wells, blowers, controllers, infrastructure and other equipment. Österreicher-Cunha et al.<sup>[47]</sup> reported that bioventing may be a valuable tool in treating gasoline-ethanol contaminated soil as the process appeared to accelerate soil detoxification. While treating toluene and decane contaminated soil, Malina et al.<sup>[48]</sup> found bioventing efficiency to be dependent on temperature with respect to remediation time.

**Liquid delivery systems:** Liquid delivery systems require extensive site characterization and are best for sites with fractured rock aquifers, shallow water tables,

formations with narrow saturated intervals, or when control of plume migration is mandated. The cost of the operation depends on the type of contaminants present, the amount and extent of contamination, sediment characteristics and source of oxygen. For example, low numbers of microbes are associated with clay soils and the addition of 100 mg/l of hydrogen peroxide as an oxygen source can be toxic to biota<sup>[43]</sup>. Flores et al.<sup>[49]</sup> reported that hydrogen peroxide is a major source of OH radicals which are oxidative agents in the decomposition of hydrocarbons in the soil. Ghassemi<sup>[50]</sup> demonstrated the in situ delivery of liquid and other treatment agents into hydrocarbon contaminated soil for the purpose of its remediation.

## BIOREACTORS

There are many different types and sizes of bioreactors ranging from a vessel of a few liters to large systems that can hold millions of liters<sup>[43]</sup>. Bioreactors have a shorter detention time, lower costs than traditional physical, thermal and chemical reactors, take up less space, are simple to use, and offer an economic and technical advantage for contaminated soils having high moisture content<sup>[2, 39, 51]</sup>. They are divided into three categories based on the state of the medium: solid, liquid and gas bioreactors. Solid reactors can handle contaminated soil and they include static bed reactors, continuous mix reactors, horizontal drum reactors and fungal compost reactors. Liquid reactors are designed for liquid medium or slurry and they include slurry-phase reactors and dual injection turbulent suspension reactors. Gas bioreactors are usually used in a combination with solid or liquid reactors to remove volatile organic contaminants from the exhaust gas of those reactors and they include a variety of biofilters and packed bed reactors.

**Static Bed Reactors:** A static bed reactor consists of a clay or synthetic liner, overhead irrigation system to spray water and nutrients onto the bed of excavated contaminated soil and pipes embedded in sand to collect leachate. It is a closed loop system, preventing contamination from being released to the environment. Soils contaminated with PAH compounds (naphthalene, phenanthrene, and pyrene) and pentachlorophenol were remediated using this system<sup>[52]</sup>. Diesel fuel was reduced from 683 ppm to 81 ppm in four months using this system<sup>[2]</sup>.

**Continuous Mix Reactors:** Continuous mix reactors allow for enhanced diesel fuel turnover in a soil mixture. They are similar to in-vessel composting systems and as such, the moisture levels should be at 50

% of the maximum water capacity. The temperature, pH, moisture content and aeration level can be effectively controlled in these reactors. However, this type of reactors have the potential to form pellets which reduce microbial activity and the degradation of contaminants and are associated with high equipment and operating costs<sup>[2]</sup>. Antizar-Ladislao et al.<sup>[53]</sup> used this system to remove 16 U.S. Environmental Protection Agency listed PAHs. Truax et al.<sup>[54]</sup> used a continuous flow reactor to treat a diesel contaminated sandy soil.

**Horizontal Drum Reactors:** These are horizontal drums that rotate around on their axis like cement mixers thereby keeping soil loosely packed. Temperature, oxygen content and nutrient supply are all controlled. The advantage of these reactors is that they can be used for solid material or slurry<sup>[2]</sup>. They provide a means for performing chemical processes using high temperatures at near atmospheric pressures. However, their complexity has merely led to practical and expensive designs<sup>[55]</sup>. A Canadian consulting company (UMATAC Industrial Processes, a division of UMA Engineering Ltd) designed a horizontal drum reactor to pyrolyse oil shale into vapors<sup>[56]</sup>.

**Fungal Compost Reactors:** Fungal compost reactors work on the principle of bound residue formation. Indigenous peroxidase enzymes are stimulated to enhance the rate of bound residue formation. Although this form of treatment is low cost, the reactor can become carbon limited and a supplementary carbon source should be used<sup>[2]</sup>. McFarland and Qiu<sup>[57]</sup> removed benzo( $\alpha$ )pyrene from soil using *Phanerochaete chrysosporium* and corn cobs as a supplementary carbon source in a fungal compost reactor. Eggen<sup>[58]</sup> used white rot fungi (*Pleurotus ostreatus*) for creosote contaminated soil. This process removed 86% of the total 16 PAHs listed by the U.S. Environmental Protection Agency.

**Slurry Phase Reactors:** A slurry-phase bioreactor contains soil that is suspended in water by utilizing a mechanical stirrer. In these reactors, soil and water are mixed with air, nutrients and microbes. These reactors have been used in the bioremediation of soils contaminated with petroleum and its derivative PAHs. The treating time is in the order of days or weeks<sup>[44]</sup>. Saponaro et al.<sup>[59]</sup> reported a high removal efficiency for all PAHs from soil after 23 days using a slurry system reactor. Boopathy<sup>[60]</sup> reported that diesel biodegradation rates in a slurry reactor operating under anaerobic conditions were highest using mixed electron acceptor

groups followed by sulfate reducing, nitrate reducing and methanogenic groups. Wang<sup>[61]</sup> reported that biodegradation of naphthalene in a continuously stirred batch slurry reactor was successful.

**Dual Injection Turbulent Suspension Reactors:** The dual injection turbulent suspension reactor (DITS) is a modification of the slurry reactor. It has a combined air-liquid injector at the bottom. Residence time is approximately 100 hours, which means that the degradation time is 70 times faster than that of landfarming<sup>[2]</sup>. Geerdink et al.<sup>[62]</sup> found that after treatment in a DITS reactor, oil was slowly released from the contaminated soil and treatment by another method was required for a further 10 weeks to reach minimal contamination levels.

**Biofilters:** Biofilters are bioreactors used to remove volatile compounds from contaminated air streams. They are made from biologically active material to which the microbes can be attached such as compost or peat<sup>[2]</sup>. Because this process relies upon an established microbial population within the filter, it can be difficult to operate when mixtures vary over a short period of time<sup>[3]</sup>. Leson and Smith<sup>[63]</sup> reported that biofilters remove major petroleum hydrocarbon classes (aromatics, aliphatics) to varying degrees. Maestre et al.<sup>[64]</sup> reported that fungal biofilters are an excellent choice to treat high loads of toluene.

**Packed Bed Reactors:** These types of reactors are packed with growth supporting medium such as amberlite and are used to treat gas currents. A helical feed reactor optimizes conditions due to its continuous operation and long residence time. As such, treatment is rapid and the reactor is small. The process is sealed so there is no uncontrolled release of VOCs. This type of reactor allows for a quantitative estimation of the oxygen diffusion through the compacted soil<sup>[2]</sup>. Ogata et al.<sup>[65]</sup> used a conventional packed bed reactor with ferroelectric materials to decompose benzene. Takaki et al.<sup>[66]</sup> also used a packed bed reactor with ferroelectric pellets to remove perfluoroethane (C<sub>2</sub>F<sub>6</sub>).

## COMPARATIVE ANALYSES

**Remediation Methods:** The advantages and disadvantages of the various nonbiological and biological remediation methods are listed in Tables 7-9 were used as the basis for the comparative analysis performed on these remediation methods. Five criteria were used to evaluate these methods: efficiency, applicability, cost, time and cleanliness. Table 10 shows

Table 11: Assessment of nonbiological remediation methods

Criteria	Land Filling	Soil Washing	Incineration	Thermal Desorption	Radio Frequency Heating	Chemical Addition
Applicability	25	16	25	20	15	17
Efficiency	25	20	25	15	15	15
Time	0	25	25	15	15	15
Cost	10	6	0	10	8	10
Cleanliness	0	0	10	10	10	5
<b>TOTAL SCORE</b>	<b>60</b>	<b>67</b>	<b>85</b>	<b>70</b>	<b>63</b>	<b>62</b>

Table 12: Assessment of biological remediation methods

Criteria	Land Farming	Biopiling	Composting	Bioventing	Liquid Delivery	Bioreactors
Applicability	15	15	23	15	10	25
Efficiency	15	23	25	25	23	25
Time	12	12	20	10	8	25
Cost	10	12	10	10	3	12
Cleanliness	3	12	5	10	5	10
<b>TOTAL SCORE</b>	<b>55</b>	<b>74</b>	<b>83</b>	<b>70</b>	<b>49</b>	<b>97</b>

Table 13: Advantages and disadvantages of specific solid bioreactors<sup>[68, 69]</sup>

Bioreactor	Advantages	Disadvantages
Static Bed	Environmentally friendly, contaminants contained, temperature and gas flow control, simple; easy to operate, efficiency increases with temperature	Slow, no pH/moisture control, gases may leak during cleaning or maintenance, other equipment used to capture volatile off gases, relatively costly
Continuous Mix	Enhanced turnover, consistent aeration, temperature, pH, moisture content and aeration effectively controlled, simple hardware; easy to operate, would not have to be cleaned as often as a batch reactor which could reduce some costs, VOCs stored	Expensive, can form pellets that reduce microbial activity
Horizontal Drum	Can use high temperatures at atmospheric pressures, feed can be dry or in slurry, soil stays loosely packed, aiding efficiency, contaminants contained, VOCs housed in the drum	Expensive, complex, difficult to control thermal reactions inside drum, may be difficult to operate based on design, biofilms on the inside of the drum would be difficult to clean
Fungal compost	Low cost, can treat a wide range of contaminants, fast and efficient, contaminants contained, temperature and other variables can be controlled, VOC traps	Carbon supplementation required, cleaning, fast in terms of bioreactors but will take many weeks

Table 14: Advantages and disadvantages of specific liquid and gas bioreactors<sup>[70-72]</sup>

Bioreactor	Advantages	Disadvantages
Slurry Phase	Well stirred, efficient, used in situ or ex situ, contaminants contained, conditions controlled, lab microcosms are cheap, easy to clean and operate	Will need to separate solids and liquids, volatile off gases must be controlled, expenses reasonable; depend on pollutant concentration
DITS	70 times faster than landfarming, two zones; separates light material from heavily polluted material - both contained, off gases captured, bed easily removed for maintenance, parameters can be controlled, simple	Extract must be further treated for upwards of 10 weeks slow, simply a modified slurry reactor, cost depends on the outlet concentration of the pollutant
Biofilters	Remove VOCs, simple; easy to operate, low cost, minimal maintenance, efficient, contaminants contained, temperature, pH, and moisture controlled	Rely on microbes, slow
Packed Bed	Rapid treatment, VOCs not released, parameters controlled, easy to operate, minimal labor, contaminants contained, low cost	Small, localized high temperature regions (hot zones) could cause serious environmental or safety incidents

Table 15: Evaluation criteria for bioreactors

Criteria	Definition	Score
Efficiency	95-99% removal warrants 20	20
Time	Removes contaminants within weeks	15
Cost	Relatively inexpensive	15
Maintenance	Easy to maintain	10
Simplicity	Easy to operate	10
Release of VOCs	Non degraded VOCs are not released to the atmosphere	10
Containment of contaminants	Pollutants are not leaked out of the reactor	10
Control	Need for pH, temperature or moisture control	10
<b>TOTAL SCORE</b>		<b>100</b>

Table 16: Assessment of specific bioreactors

Criteria	Static Bed	Continuous Mix	Horizontal Drum	Fungal Compost	Slurry Phase	DITS	Biofilters	Packed Bed
Efficiency	10	15	12	10	10	10	10	5
Time	5	15	12	5	10	10	5	12
Cost	8	5	5	12	10	0	8	5
Maintenance	10	10	5	5	10	10	10	10
Simplicity	10	10	5	10	10	8	10	10
Release of VOCs	5	10	10	10	0	10	10	10
Containment	8	10	10	10	10	10	10	10
Control	5	10	2	10	5	8	5	0
<b>TOTAL SCORE</b>	<b>61</b>	<b>85</b>	<b>61</b>	<b>72</b>	<b>65</b>	<b>66</b>	<b>68</b>	<b>62</b>

the definition and scores assigned to these criteria. The final results of the comparative analysis are shown in Tables 11 and 12. Among the nonbiological remediation methods, incineration scored the highest (85) followed by thermal desorption (70). The other nonbiological remediation methods had much lower scores (67, 63, 62 and 60 for soil washing, radio frequency, chemical addition and landfilling, respectively). The analysis performed on the bioremediation methods showed that with the exception of liquid delivery and landfarming (which are used under special circumstances), they are more effective than nonbiological remediation methods (except incineration). Bioreactors scored the highest (97) followed by composting (83), biopiling (74) and bioventing (70). Bioreactors have the advantages of: (a) shorter treatment time, (b) minimum space for operation, (c) ability to capture VOCs, (d) operate under aerobic conditions for recalcitrant compounds, (e) work on very concentrated residues, (f) can be operated at various sizes, and (g) can be coupled with other techniques if so needed.

**Bioreactors:** The advantages and disadvantages of the various bioreactors listed in Tables 13 and 14 were used as a basis for the comparative analysis performed on the bioreactors. Eight criteria were used to evaluate these reactors: efficiency, residence time, cost, maintenance, simplicity of operation, release of VOCs to the atmosphere, containment of contaminants and control of operating parameters such as pH, temperature and

moisture control. Table 15 shows the definition and scores assigned to these criteria. The final results of the comparative analysis are shown in Table 16. Among the solid bioreactors evaluated, the continuous mix bioreactor scored the highest (85) followed by the fungal compost bioreactor (72). Both, the static bed bioreactor and the horizontal drum bioreactor scored 61, the first suffered from the release of VOCs and the long residence time while the second had a high cost and difficulties associated with maintenance and control. The Liquid and gas bioreactors, which are usually used for specific cases, scored much lower than the continuous mix bioreactor, 62 for the packed bed reactor, 65 for the slurry-phase bioreactor, 66 for the DITS bioreactor and 68 for the biofilters.

### CONCLUSION

Many of the current Canadian regulations relate to sulphur content in diesel fuel because of acid rain. Although PAHs are considered toxic under the Canadian Environmental Protection Act, there are no standards for PAHs in diesel. About 60 of Canada's contaminated sites involve petroleum hydrocarbons. The factors affecting the cost of clean up include: the accessibility to the site, weather conditions, quantity of spilled fuel, the extent of environmental damage and the time required for the clean up. The Canada-wide standards for petroleum hydrocarbons in soil separate soil into four categories based on land usage: agricultural, residential, commercial and industrial. It

also specifies the methods and outcome for the assessment and management of contaminated sites but timelines are left for individual jurisdictions to decide.

The remediation methods included soil washing, landfilling, incineration, thermal desorption, radio frequency heating, chemical addition, landfarming, biopiling, composting, bioventing, liquid delivery and bioreactors. The advantages and disadvantages of several remediation methods were determined. Five criteria were used for the evaluation of these methods: efficiency, applicability, cost, time and cleanliness. The results showed that the biological methods were more effective than nonbiological ones and the bioreactors scored the highest among the biological methods. Further evaluation was performed on several solid, liquid and gas bioreactors which included static bed, continuous mix, horizontal drum, fungal compost, slurry-phase, DITS, biofilters and packed bed bioreactors. Eight criteria were used for their evaluation : efficiency, time, cost, maintenance, simplicity, release of VOCs to the atmosphere, containment of contaminants and control of operating parameters. The results showed that the continuous mix bioreactor was the most effective system.

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