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Hlavní faktory ovlivňující intenzitu biodegradace ropných látek při sanaci kontaminovaného horninového prostředí *in situ*

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Seznam příloh

Seznam zkratek

AS	air sparging
HPV	hladina podzemní vody
NEL	nepolární extrahovatelné látky
RU	ropné látky
RT	respirační test
OPV	ochranné pásmo vod
PVC	polyvinylchlorid
TOC, C org	celkový organický uhlík
VE	venting

1 ÚVOD

Biodegradace ropných uhlovodíků, zejména lehčích palivových frakcí, se v posledních patnácti letech stala široce využívanou technologií pro sanaci kontaminovaných hornin a podzemních vod. V první polovině devadesátých let byly odzkoušeny metody pro biodegradaci ropného znečištění nesaturované zóny (Anderson 1995, Leeson a Hinchee 1997), koncem devadesátých let pak byly publikovány zkušenosti s aplikací air spargingu pro biodegradaci ropných uhlovodíků v saturované zóně (Marley a Bruell, 1995; Hinchee, Miller, Johnsson 1995; Leeson et al. 1999). Sanačním principem *in situ* biodegradace je aerobní oxidace ropných látek pomocí metabolické aktivity půdních mikroorganismů, které kontaminant využívají jako primární zdroj uhlíku a energie. Určujícími parametry efektivity biodegradace jsou faktory klíčové pro aktivitu aerobních půdních mikroorganismů. Vliv řady přírodních faktorů na biodegradační aktivitu v nesaturované zóně byl hodnocen prostřednictvím programu amerických armádních vzdušných sil „Bioventing Initiative" (Leeson, Hinchee, 1997), byla uveřejněna i řada prací týkající se designu air spargingových systémů s cílem dosáhnout optimální provzdušnění kontaminovaných vrstev (Leeson et al. 1999; Johnson et al., 2001).

K dispozici je však velmi málo publikací, které by hodnotily vztah mezi efektivitou sanace (tzn. množstvím odstraněného kontaminantu) a hlavními přírodními a technologickými faktory při dlouhodobé provozní sanaci silně kontaminovaných ploch. Výše zmíněný výzkumný program americké armády hodnotil data získaná na 125 kontaminovaných lokalitách, kde průměrná vstupní koncentrace NEL (nepolární extrahovatelné látky, angl. TPH – total petroleum hydrocarbons) byla 2300 mg/kg a pouze 16% vzorků z těchto lokalit mělo koncentraci vyšší než 5 000 mg/kg NEL. Obsah kontaminace na studovaných lokalitách byl výrazně nižší, než je v zájmovém území bývalého vojenského letiště Hradčany, hodnoceném v rámci této práce (viz kap. 2.2). Úroveň vstupní kontaminace má zásadní vliv na projektování výkonu instalované sanační technologie, potřebné při biodegradaci ropných látek *in situ* pro provzdušnění kontaminovaných vrstev a odhad doby sanace. Tato práce se zabývá hodnocením pozorované biodegradační aktivity ve vztahu k aeraci sanovaných vrstev (tj. objemu vzduchu vtláčenému air sparingem do sanované plochy), teplotě podzemní vody a obsahu ropných uhlovodíků v zájmovém území, což jsou hlavní faktory ovlivňující metabolickou aktivitu půdních mikroorganismů (Leeson, Hinchee 1997). Kyslík je nezbytný jako terminální akceptor elektronu při metabolických pochodech a ropné uhlovodíky slouží jako zdroj uhlíku a energie pro půdní bakterie. V teplotním rozmezí 0 - 40 °C dochází při nárůstu teploty o 10°C ke zdvojnásobení rychlosti odbourávání polutantu (Anderson, 1995a; Leeson, Hinchee 1997).

Odborná literatura uvádí další faktory, důležité pro biodegradační aktivitu půdních mikroorganismů – pH, vlhkost, dostupnost nutrientů a biodostupnost kontaminantů (Leeson, Hinchee 1997). Vliv pH a vlhkosti není tak zásadní – tyto faktory mají negativní vliv, pokud překročí optimální rozmezí. Pro pH je to 5 – 9 s optimem okolo 7 (Dragun, 1988) a tento rozsah je na lokalitě dle dlouhodobých výsledků monitoringu splněn (Prokšová et al., 2006). Limitace biodegradace nízkým obsahem půdní vlhkosti je diskutována zejména v oblastech s aridním klimatem (Leeson, Hinchee 1997), v zájmovém území je kontaminace vázána v hlubších vrstvách v okolí hladiny podzemní vody (HPV, kap. 2.2) a limitace vlhkostí se nepředpokládá. Výsledky laboratorních testů a provozního sledování biologické sanace ukázaly (Herčík et al., 1999; Herčík et al., 2000), že v zájmovém území je pro optimální biodegradaci RU vedle dostatečného přísunu O_2 nutno zajistit obohacení horninového prostředí biogenními prvky – zejména N a P. Součástí technologie sanace je aplikace nutrietů a limitace nedostatkem nutrietů se v rámci této práce nehodnotí a nepředpokládá, protože v hodnocených plochách probíhá aplikace živin již několik let (Prokšová et al., 2006). Biodegradovatelnost a

biodostupnost RU se testovala kolonovými testy se vzorky zemin odebraných v různých částech lokality. Po 7 měsících kultivace, která simulovala optimální podmínky sanace, bylo v kolonách biodegradováno 80 – 100 % vstupní koncentrace RU (viz příloha 1). Testy prokázaly, že kontaminanty lze za optimálních podmínek téměř plně degradovat a v sanačních plochách se nepředpokládá limitace biodegradovatelností či biodostupností substrátu (viz příloha 1).

Předkládaná rigorózní práce vychází částečně z výsledků, které byly publikovány v rámci řady odborných konferencí a v několika odborných časopisech, nejdůležitější publikace pro tuto práci jsou uvedeny v přílohách 1 – 4 předkládané rigorózní práce.

2 METODIKA

2.1 Charakteristika lokality

Bývalé letiště sovětské armády Hradčany u Mimoně (okres Česká Lípa), situace viz obr. 1, patří v České republice mezi lokality, které jsou nejvíce kontaminovány ropnými látkami. Lokalita byla vojensky užívána v letech 1940–1991 (od roku 1968 sovětskou armádou) a výsledkem armádních aktivit byla masivní kontaminace zemin a podzemních vod. Kontaminaci tvoří ze 70% letecký petrolej, nad sanační limity byla kontaminována plocha 28,3 ha, viz obr. 1 v příloze 2.

Zájmové území je součástí České křídové pánve. Kvartér je zastoupen deluviálními a fluviálními sedimenty říční terasy, tvořené písky o mocnosti 0,5 – 6,0 m s vloženými nesouvislými vrstvami jílu a štěrku o mocnosti do 10 cm. V podloží terasy se nacházejí třetihorní mořské křídové sedimenty zastoupené střednozrnnými pískovci středního turonu o mocnosti cca 50 m. Na sedimenty je vázán vodohospodářsky velmi významný kolektor podzemní vody s volnou hladinou. Propustnost kolektoru je průlinově-puklinová, koeficient filtrace má v průměru hodnotu 7 m/den. Hladina podzemní vody v areálu letiště nachází v hloubce 3 až 12 m pod terénem. Proudění podzemní vody v oblasti letiště směřuje k SZ k drenážní bázi tvořené řekou Ploučnicí.

Okolí letiště je vodárensky významným územím, které je součástí Chráněné oblasti akumulace podzemních vod Severočeská křídová pánev. V širokém okolí lokality se podzemní voda využívá jako zdroj kvalitní a relativně levné pitné a užitkové vody pro zásobování veřejných vodovodů a průmyslových podniků. V území nejsou jiné významné zdroje vody, které by mohly zásobování podzemní vodou nahradit.

2.2 Charakteristika kontaminace

Zájmové území bylo místem častých havarijních úniků pohonných hmot. Vznikla kontaminace s proměnlivými parametry, skládající se z různých paliv s převahou leteckého petroleje. Na lokalitě před zahájením sanace existovaly dva typy znečištění. První typ znečištění vznikl v místech skladovacích nádrží paliva a manipulačních ploch. Jsou to zdrojové oblasti znečištění a je zde kontaminován celý profil zemin od povrchu až do 1,5 m pod hladinu podzemní vody. Jedná se plochu tzv. východního stáčiště (na obr. 1 a 2 v příloze 2 pole G, BV a E), plochu západního stáčiště (pole F a B) a místo tankování letadel (pole I, profil kontaminace viz obr. 8 v příloze 4).

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Obr. 1 Situace lokality ve výřezu leteckého snímku

Druhým typem znečištění jsou oblasti, kam se šířila kontaminace po hladině podzemní vody ve směru jejího proudění. Kontaminované zeminy mají mocnost 0,5 – 1,5 m, větší část znečištění je pod HPV (obr. 3 v příloze 4) a představují ostatní sanační pole (obr. 2 v příloze 2).

Kontaminace v oblasti východního stáčiště je vázána zejména na kvartérní terasu, která zde má mocnost 4 – 6 m a kontaminace se zde pravděpodobně šířila říčním paleokorytem. K první detekci kontaminace lokality došlo v roce 1986, kdy se kontaminační mrak na východním stáčišti (pole O) začal ve formě fáze RU drénovat do říční nivy. V oblasti západního stáčiště je mocnost vrstvy kvartérních sedimentů menší (max. 2 m) a kontaminace je vázána především na vrstvy středoturonských pískovců.

Podrobné postupy vzorkování, analýz a bilančních výpočtů RU jsou popsány v příloze 3, stručný výtah metodik viz kap. 2.4.1 Mechanismus průniku RU pod HPV viz obr. 2 v příloze 4.

V roce 1997 byla pro lokalitu zpracována analýza rizik (Němeček, 1997), která stanovila cílové sanační limity. Sanační limit pro zeminu byl stanoven na 5 000 mg/kg NEL pro sušinu zeminy, pro podzemní vodu 1 mg/l sumy BTEX a 5 mg/l NEL s absencí ropné fáze na hladině podzemní vody. Celkem bylo před zahájením finální sanace lokality v roce 1997 nad úroveň sanačních limitů kontaminováno 28,3 ha. Celkové množství ropných uhlovodíků v horninovém prostředí na lokalitě před zahájením sanace v roce 1997 bylo odhadnuto na 7057 tun s chybou +-30% (α=0,1). (Prokšová et al., 2007)

Maximum znečištění bylo před zahájením sanace přítomno v hloubce 3 – 8 m pod terénem, ve vrstvě s mocností cca 2 m v oblasti kolísání hladiny podzemní vody. Před zahájením sanace byly na sanačních polích průměrné koncentrace v této hloubce 6 000 – 14 850 mg/kg, maximální koncentrace NEL dosahovaly 30 000 – 84 000 mg/kg a na ploše 13,8 ha byla přítomna volná fáze RU v mocnosti 1 cm až 90 cm s průměrem 15 cm. (Herčík et al., 2002)

2.3 Metodika sanace

Pro sanaci lokality se používají metody čištění *in situ*, tzv. kombinovaná sanace, která využívá fyzikální a biologické postupy. V prvním kroku se provozuje venting a vakuové odsávání volné fáze. Venting spočívá v odsávání půdního vzduchu podtlakovými ventilátory z relativně husté sítě (15x15 m) maloprůměrových vrtů (výstroj 63 mm). Odsávaný vzduch odnáší těkavější složky přítomných RU, které jsou zachycovány na filtrech s aktivním uhlím. Další efekt je přísun atmosférického kyslíku do nesaturované zóny k podpoře biodegradace.

Ventingové vrty jsou vystrojeny cca 2 m pod HPV, což umožňuje jejich další využití k čerpání volné fáze RU. Vrty jsou osazeny vnitřní výstrojí o průměru 2 cm a jsou po 15 - 25 připojeny na vakuovou pumpu, která z HPV odsává směs vody, vzduchu a ropné fáze. Ropná fáze a kontaminovaná voda se separují v gravitačních odlučovačích. Schéma sanace viz obr. 4 v příloze 4.

Po odstranění ropné fáze z HPV začíná druhý krok sanace – řízená biodegradace. Cílem řízené biodegradace *in situ* je vytvořit optimální podmínky pro rozvoj autochtonních aerobních půdních mikroorganismů, schopných využívat ropné znečištění jako zdroj uhlíku a energie, metabolizovat jej na oxid uhličitý a vodu a tak snižovat znečištění horninového prostředí na přijatelnou úroveň.

V druhém kroku je sanační systém rozšířen o air sparging . Při této sanační metodě se do sítě vrtů, ukončených ve zvolené hloubce pod hladinou podzemní vody (na lokalitě 6 – 7 pod HPV), vtláčí kompresorem vzduch. Vzduch se rozptyluje v pórovém a puklinovém prostředí kolektoru a obohacuje podzemní vodu kyslíkem a současně na sebe váže těkavé polutanty. Tentýž proces probíhá i při průchodu vzduchu na rozhraní nasycené a nenasycené zóny, v místech nejsilnější kontaminace. Ve svrchní části nenasycené zóny je vzduch zachycován ventingovými vrty. Základní podmínkou pro průběh aerobních pochodů je dostupnost O_2 jako terminálního akceptoru elektronů. Protože maximum kontaminace je na lokalitě vázáno ve vrstvách těsně nad a pod HPV, air sparging je hlavním aeračním systémem pro biodegradaci RU. Schéma sanace viz obr. 5 v příloze 4. V době projektování sanace v roce 1997 byl AS inovativní sanační technologií a v průběhu sanace se zjistilo, že projektovaná aerační kapacita není dostatečná pro optimální provzdušnění. Proto byl výkon AS technologie v letech 2003 – 2004 zásadně posílen, objem vtláčeného vzduchu byl zvýšen 2 – 3 x a síť vrtů byla zahuštěna na 7x7 m v místech zvlášť významných deficitů.

Výsledky laboratorních testů a provozního sledování biologické sanace potvrdily, že v zájmovém území je pro optimální biodegradaci RU vedle dostatečného přísunu O_2 nutno zajistit obohacení horninového prostředí biogenními prvky – zejména N a P. Součástí technologie sanace je aplikace těchto látek. Přísun nutrientů se zajišťuje periodickým dávkováním roztoku zemědělských hnojiv do ventingových rozvodů.

Pro potřeby provozu sanace bylo kontaminované území rozděleno na jednotlivá sanační pole o plochách 0,5 – 4 ha, viz obr. 2 v příloze 2. Pole byla postupně pokryta vrtnou sítí a byla instalována sanační technologie. V období 1997 – 2005 bylo kombinovanou sanací (podle sanační bilance) z lokality odstraněno 3 182 tun RU, z toho 93 % biodegradací, 5% vakuovou extrakcí volné ropné fáze a 2 % fyzikálním ventingem a air spargingem. (Prokšová et al., 2006)

2.4 Metodika hodnocení účinnosti sanace

Součástí procesu sanace horninového prostředí je hodnocení efektivity sanačního zásahu – tj. hodnocení dynamiky odstraňování a změn obsahu celkového množství kontaminantů a jejich koncentrací v horninovém prostředí. K hodnocení změn v obsahu ropných látek kontaminujících horninové prostředí byly vybrány dva základní postupy. V prvním případě se úbytek RU posuzuje podle změn koncentrace RU v zemině, druhý přístup je založen na sledování jednotlivých ukazatelů sanační technologie, kdy se množství sanovaných RU bilancuje podle výsledků monitoringu sanačního procesu. Podrobné metodiky hodnotících postupů jsou uvedeny v příloze 3, níže se uvádí stručný popis postupů. Průběh sanace se hodnotí samostatně v jednotlivých sanačních plochách.

2.4.1 Metodika vzorkování zemin a bilance množství ropných látek podle výsledků stanovení obsahů NEL v zeminách (zeminová bilance)

Na lokalitě pro bilanci obsahu RU v zeminách byla zavedena metoda, která je založena na odběru bodových vzorků vrtného jádra z diskrétních hloubkových intervalů 0,5 m. Vzorkovací vrty jsou rozmístěny v přibližně pravidelné síti v hustotě 20 vrtů na 1 ha. Při opakovaném vzorkování (s intervalem 2 – 4 let) se nové vrty na odběr vzorků realizují v těsné blízkosti předešlých vrtů. Při vzorkování je nezbytné ověřit celou mocnost kontaminovaného profilu, tzn. ukončit vzorkování až v hloubce, kde již není přítomna kontaminace. Bodový odběr je volen proto, že kontaminant je tvořen těkavými a polotěkavými ropnými látkami a při použití standardních postupů pro homogenizaci vzorků (kvartace) by docházelo ke ztrátě

analytu a zkreslení výsledku. (Boulding, 1995) Ve vzorcích zeminy je analyzován obsah nepolárních extrahovaných látek NEL pomocí IR detekce (metoda ISO TR 11046).

Získaný soubor dat se sestaví do matice výsledků, hladina podzemních vod se používá jako rozhraní pro sestavení, podle které se kontaminovaný horninový profil dělí na nenasycenou a nasycenou zónu. K nasycené zóně se přiřazuje kapilární lem, jehož výška se standardně zavádí hodnotou 0,5 m.

Výběrová data získaná z lokality byla podrobena statistické analýze a jako nejvhodnější způsob určení střední hodnoty byl v roce 2001 navržen useknutý průměr při hodnotě $\alpha = 0,15$. Z výběru dat zvoleného sanačního pole se vypočte useknutý průměr a jeho konfidenční interval obsahu NEL v nesaturované a saturované zóně. Získaný průměr se násobí plochou sanačního pole a vzorkovanou mocností a výsledkem je bilance obsahu RU v sanačním poli v tunách. Podrobný popis postupu viz kap. 2.2 v příloze 3.

Při statistickém zpracování je zanedbáván aspekt prostorového rozložení dat, proto dalším způsobem interpretace obsahů NEL v zeminách je konstrukce dvojrozměrných map, které znázorňují distribuci kontaminantů v ploše. Pro konstrukci map jsou vzorkovací body zaměřeny v geodetických souřadnicích. K vrtům jsou přiřazeny údaje o koncentraci NEL, vypočtené jako jednostranně uřezaný průměr hodnot vyšších než 1000 mg/kg NEL z vrstev saturované zóny. (viz kap. 2.2. v příloze 3) Základní grafická interpretace je provedena v software Surfer 6 s použitím krigingu jako interpolační metody. Takto získaný výstup je korigován geologem do finální podoby mapy.

2.4.2 Bilance odstraněných ropných látek podle monitoringu sanace (sanační bilance)

Monitoring sanace vychází ze sledování dynamických parametrů technologie, kdy se množství sanovaných RU hodnotí podle odnosu těkavých organických látek (TOL) ventingem, bilance biodegradace podle monitoringu respiračních plynů (O_2, CO_2) a bilance RU získaných vakuovým odsáváním volné fáze.

Množství TOL odstraněných fyzikálním ventingem a air spargingem se kvantifikuje podle koncentrací těkavých RU v odsávaném objemu půdního vzduchu. Množství biodegradovaných RU se odvozuje obdobně. Monitorují se koncentrace respiračních plynů v odsávaném půdním vzduchu a rozložené RU se kvantifikují stechiometricky z objemu kyslíku spotřebovaného v sanační ploše, kontrolně se sleduje produkce CO_2. Měření pro bilanci odnosu TOL a biodegradace se provádějí minimálně 1 x měsíčně a pro výpočet celkového množství odstraněných RU se mezi daty měření výsledky extrapolují. Respirační bilance se koriguje tzv. pozaďovou respirací, která byla kvantifikována podle provozu sanačního pole v nekontaminovaném území po dobu dvou let a je 2,3 t org. látek/ha/rok. (Herčík et al., 2000)

Bilance RU odstraněných vakuovým odsáváním volné fáze vychází z přímého měření objemu RU fáze po gravitační separaci a koncentrace NEL v odsazené kontaminované vodě. Podrobný popis metodiky viz kap. 2.3 v příloze 3.

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2.5 Metodika sledování faktorů ovlivňujících intenzitu biodegradace

2.5.1 Monitoring teploty podzemní vody a HPV

Teplota podzemní vody se měří *in situ*, 0,5 m pod HPV v síti ventingových vrtů (70 – 100 vrtů/ha sanační plochy) terénním přístrojem Oxi Set, WTW. Z měřených dat je vypočten aritmetický průměr pro dané sanační pole a jeho konfidenční interval (α=0.05). Teplota se sledovala 4 – 5 x za rok v prvních letech sanace, v pozdějším období 2 x ročně. Data o teplotě podzemní vodě se také graficky interpretují do map, jako interpolační metoda se používá kriging s použitím software Surfer 6. Jedním z faktorů, který ovlivňuje pozorovanou teplotu podzemní vody je hloubka HPV pod terénem. HPV se v sanačních plochách sleduje při odběrech podzemní vody ve ventingových vrtech elektrickými hladinoměry 2x ročně. Režimní kolísání HPV se sleduje v síti vybraných 10 hydrogeologických vrtů na celé lokalitě s intervalem 1x měsíčně.

2.5.2 Objem vzduchu vtláčeného air spargingem

Objem vzduchu vtláčený AS do sanační plochy je dán výkonem kompresoru a měří se 1x měsíčně průtokoměrem s přesností +-5 m³.

2.6 Metodika hodnocení vlivu jednotlivých faktorů na intenzitu biodegradace

Pro hodnocení vlivu teploty podzemní vody a množství vtláčeného vzduchu na intenzitu biodegradace jsou použita data ze sanačních polí I, J, a L. Naměřená data byla vynesena do grafů s časovými osami a jsou diskutovány možné souvislosti.

Následně byla hodnocena vzájemná korelace jednotlivých faktorů. Hodnocené faktory – objem vtláčeného vzduchu, obsah kontaminace a intenzita biodegradace byly přepočteny na jednotkovou plochu a vyhodnocena jejich možná závislost použitím lineární regrese. Dále je hodnocena korelace mezi teplotou podzemní vody, biodegradační aktivitou a hladinou podzemní vody v jednotlivých plochách.

3 VÝSLEDKY A DISKUZE

3.1 Intenzita biodegradace v plochách I, J a L

Podrobný postup sanace pole I je uveden v kap. 3.1 v příloze 3. Obr. 2 zobrazuje biodegradační aktivitu, měřenou v sanačním poli v průběhu osmi let sanace, přepočtenou na jednotkovou plochu, objem vzduchu vtláčený AS do jednotkové plochy a průměrnou teplotu podzemní vody v poli. Z grafu je zřejmé, že v ploše bylo pozorováno cyklické kolísání biologické aktivity v průběhu jednotlivých let sanace, které lze dát do souvislosti s pozorovaným kolísáním průměrné teploty podzemní vody (viz obr. 2). Rozdíl mezi minimální teplotou podzemní vody v zimním a maximální teplotou v letním období činil 5 – 6 °C. Biodegradační aktivita, pozorovaná v letním období byla v průběhu sanace 2x až 4x vyšší, než biodegradační aktivita naměřená v zimním období.

Obr. 2 Biodegradační aktivita pozorovaná v poli I (plocha 1,4 ha)
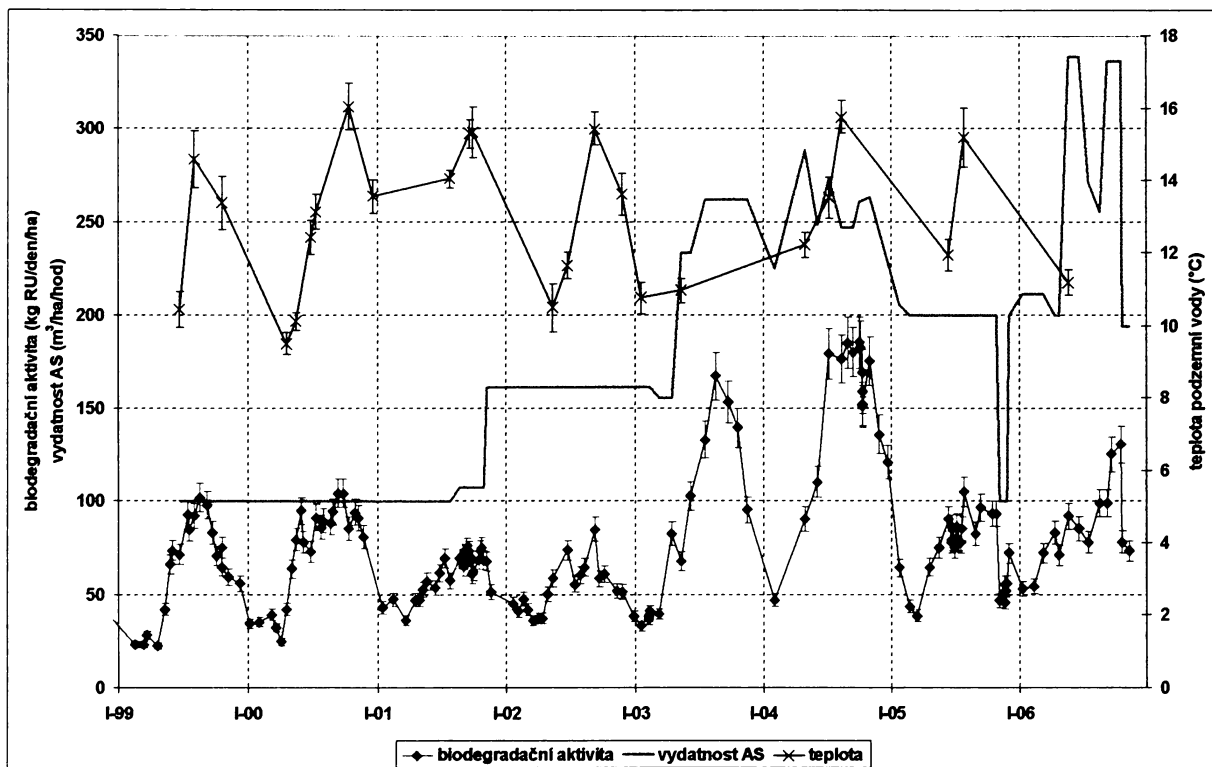
Po dvou letech sanace byl v ploše pozorován pokles biodegradační aktivity a předpokládalo se vyčerpání substrátu. Vzorkování zemin v letech 2001 a 2003 potvrdilo odstranění části znečištění, zejména v nesaturované zóně (obr. 4 v příloze 3) ale účinnost sanace v saturované zóně byla nízká. Proto byla v roce 2003 učiněna opatření ke zvýšení efektivity biologické sanace – byla zahuštěna síť AS vrtů (z 60 AS vrtů na 80) a zejména byl zvýšen objem vzduchu vtláčený do plochy. Výsledkem intenzifikace bylo výrazné zvýšení biodegradační aktivity pozorované v letech 2003 – 2004 – po 4 letech sanace byla v ploše zvýšena biodegradační aktivita na 2,5 násobek hodnoty pozorované v letech 2001 – 2002. Lze předpokládat, že zvýšením objemu vláčeného vzduchu a zahuštěním sítě došlo k rozšíření efektivního dosahu AS vrtů (tzv. radius of influence), jak je popsáno v (Johnsson, 2001) a byla podpořena biodegradace v dosud nedostatečně aerovaných částech horninového profilu. Vzorkování zemin v roce 2005 potvrdilo snížení celkového obsahu kontaminace v poli I (obr. 4 v příloze 3), snížení kontaminace jednotlivých sond a plošný rozsah nadlimitně kontaminované plochy v poli (obr. 5 v příloze 3). Část pole s dosaženými sanačními limity byla ze sanace v roce 2005 vyřazena. Průměrná biodegradační aktivita, pozorovaná v roce 2006 byla však o 43 % nižší, než průměrná biodegradační aktivita v roce 2004, přestože že průměrný objem vzduchu vtláčený do plochy byl stejný. Lze předpokládat, že v letech 2005 – 2006 se v sanačním poli začala výrazněji projevovat limitace substrátem.

Vstupní bilance kontaminace pole I podle vzorkování zemin v roce 1998 byla 317 tun NEL/ha, bilance v roce 2003 110 tun NEL/ha. Konfidenční interval zeminové bilance ($\alpha=0,1$) je 25 – 30 % (podrobněji viz příloha 3), obr. 4 a 10. V roce 2005 bylo v poli celkově bilancováno 89 tun NEL/ha, pole bylo dále rozděleno na plochu nadlimitní a podlimitní (obr. 5 v příloze 3) a tyto dvě plochy byly bilancovány samostatně. V podlimitní ploše (0,8 ha) bylo zjištěno 19 tun NEL/ha, v nadlimitní ploše (0,6 ha) bylo bilancováno 181 tun NEL/ha.

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Uzavření části pole s velmi nízkým obsahem kontaminace vedlo ke zvýšení biodegradační aktivity v poli I v roce 2006, ale již se nepodařilo dosáhnout výsledku z roku 2004. Vzhledem k tomu, že ostatní faktory (teplota, objem vtláčeného vzduchu, sanace v ploše s vysokým obsahem zbytkové kontaminace) byly s rokem 2004 srovnatelné, lze předpokládat, že s postupujícím časem sanace došlo ke zhoršení biodostupnosti substrátu anebo v nadlimitní části pole zůstaly biologicky pomaleji rozložitelné látky.

Podle výsledků laboratorních kolonových testů se zeminou z pole I byla ověřena téměř úplná biodegradovatelnost přítomného ropného znečištění – viz příloha 1. V testované zemině byla koncentrace NEL snížena po 6 měsících biodegradace z 8 100 mg/kg na 11 mg/kg. Vstupní kontaminace pole I však byla velmi heterogenní (viz obr. 5 v příloze 3) a vstupní koncentrace byly místy značně vyšší (až 41 000 mg/kg), než testovaná koncentrace. Z porovnání vstupních koncentrací a koncentrací v roce 2005 je zřejmé, že v částech pole I bylo dosaženo po 6 letech sanace výsledků srovnatelných i výrazně lepších, než při laboratorním testu – např. sondy IZ-6/IZ-104 (pokles obsahu NEL z 17 000 mg/kg na 260 mg/kg) nebo sondy IZ-4/JZ-126 (pokles obsahu NEL z 22 000 mg/kg na 21 mg/kg). V silně kontaminovaných částech je však pokles pomalejší – v části pole se vstupní kontaminací zemin 20 000 – 39 000 mg/kg NEL (sondy IR-4, IZ-42 a IZ-20) byl po 6 letech zaznamenán pokles na 14 300 – 15 525 mg/kg NEL (sondy IZ-116, IZ-123). Vzhledem k pozorovanému snížení biodegradační aktivity v poli je tato zbytková kontaminace pravděpodobně tvořena látkami, které jsou hůře biodostupné a pomaleji rozložitelné. Pro predikci dalšího vývoje sanace a ověření, zda je biologická metoda schopná dosáhnout sanačních limitů, by bylo vhodné laboratorní kolonové testy zopakovat.
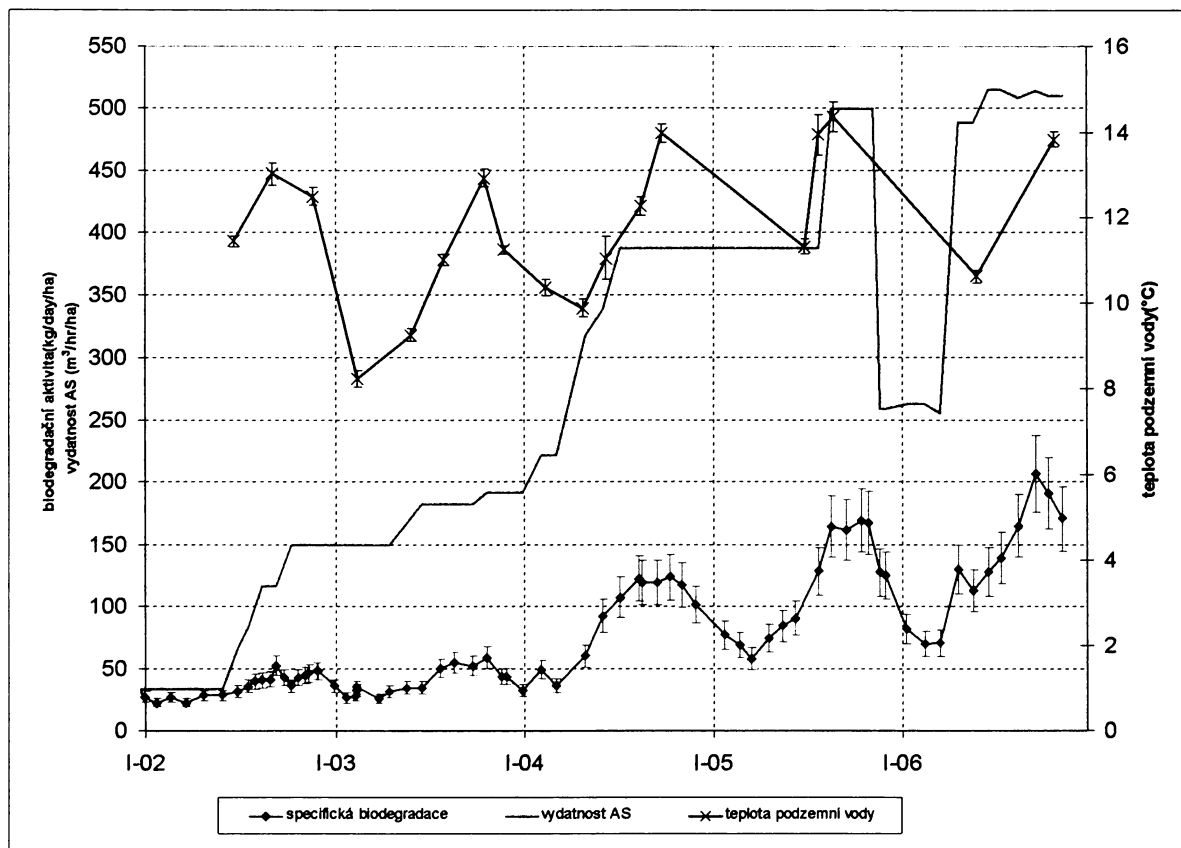
Obr. 3 uvádí biodegradační aktivitu pozorovanou v poli J, přepočtenou na jednotkovou plochu, objem vzduch vtláčený do jednotkové plochy a průměrnou teplotu podzemní vody v poli. Také v tomto poli bylo zaznamenáno periodické kolísání biodegradační aktivity, které lze spojit s pozorovanými změnami teploty podzemní vody v průběhu roku. Pozorovaný rozdíl letních teplotních maxim a zimních minim je 5 – 6 °C a v průběhu sanace lze spolu se zvyšováním biodegradační aktivity pozorovat i zvýšení průměrné teploty podzemní vody o 1 – 2 °C.

V poli J byl pozorován velmi výrazný vliv objemu vtláčeného vzduchu na biodegradační aktivitu. Sanace probíhá v poli J pět let, od roku 2002. V letech 2004 – 2006 byl objem vzduchu vtláčený AS do pole dvoj- až trojnásobný v porovnání s roky 2002 – 2003 a byla zaznamenána biodegradační aktivita troj-až čtyřnásobně větší. Biodegradační aktivita pozorovaná v zimních měsících v období 2004 – 2006 byla vyšší, než biodegradační aktivita v letním období 2002 – 2003. Výsledky z pole J potvrzují významný vliv vydatnosti AS na intenzitu biodegradačních procesů při sanaci *in situ*.

Vstupní bilance obsahu kontaminatu v poli J byla 328 tun NEL/ha, v roce 2005 proběhlo vzorkování zemin, které ověřilo v části plochy (2,7 ha) dosažení sanačních limitů. Celková bilance NEL v poli J v roce 2005 byla 82 tun/ha, v nadlimitní části byla bilance 139 tun NEL /ha, v podlimitní části byla bilance 36 tun NEL/ha. Po vyřazení podlimitních částí pole v létě 2005 z aktivní sanace bylo v poli pozorováno zvýšení specifické biodegradace, které bylo pozorováno i v následujícím roce 2006. Tento výsledek ukazuje, že biodegradační proces v poli J zatím není limitován biodostupností či biodegradovatelností substrátu.

Porovnání výsledků v období 2004/2005 a 2005/2006 také ukazují na možnost zvýšení efektivity a ekonomičnosti provozu AS systému – v období 2005/2006 se snížením vydatnosti AS v zimním období, kdy je biodegradační aktivita nižší a zvýšení výkonu v letním období podařilo dosáhnout lepších výsledků biodegradace než v předchozím období, kdy byl výkon AS po celou dobu konstantní.

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Obr. 3 Biodegradační aktivita pozorovaná v poli J (plocha 4,9 ha)

Obr. 4 uvádí biodegradační aktivitu pozorovanou v poli L přepočtenou na jednotkovou plochu, objem vzduch vtláčený do jednotkové plochy a průměrnou teplotu podzemní vody v poli. I v poli L bylo zaznamenáno periodické kolísání biodegradační aktivity, které lze spojit s pozorovanými změnami teploty podzemní vody v průběhu roku. Pozorovaný rozdíl letních teplotních maxim a zimních minim je 2 – 4 °C a v prvních čtyřech letech sanace bylo pozorováno zvýšení průměrné teploty podzemní vody o 2 °C, spolu se zvyšováním biodegradační aktivity. V následujících dvou letech pak došlo k poklesu průměrné teploty o 1 °C a byl pozorován i pokles biodegradační aktivity.

Také v poli L byl pozorován výrazný vliv objemu vtláčeného vzduchu na biodegradační aktivitu. Sanace probíhá v poli L šest let, od roku 2001. V roce 2004 byl objem vzduchu vtláčený AS do pole zdvojnásoben v porovnání s roky 2001–2003 a následně bylo zaznamenáno zdvojnásobení pozorované biodegradační aktivity. Pokles biodegradační aktivity, pozorovaný v roce 2005, byl projevem limitace substrátem. Vstupní bilance plochy L byla 297 tun NEL/ha, podle vzorkování zemin v roce 2006 byla celková bilance zemin 61 tun NEL/ha. V části pole byly splněny sanační limity (1,8 ha s bilancí 20,5 tun NEL/ha), bilance NEL v části s dosud překročenými sanačními limity (0,7 ha) byla 170 tun NEL/ha. Po uzavření podlimitní části pole v červnu 2006 však byla pozorována poměrně nízká biodegradační aktivita, zvýšení bylo dosaženo až po intenzifikaci AS. Přestože vtláčené množství o 30% vyšší než v roce 2005 roce a sanace se soustředila do míst s vysokou zbytkovou kontaminací, pozorovaná biodegradace byla jen nepatrně vyšší než pozorování z roku 2005. Lze proto předpokládat, že

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v poli L je zbytková kontaminace v nadlimitní ploše tvořena látkami, které jsou biodegradovatelné pomaleji popř. hůře biodostupné.

Obr. 4 Biodegradační aktivita pozorovaná v poli L (plocha 2,5 ha)
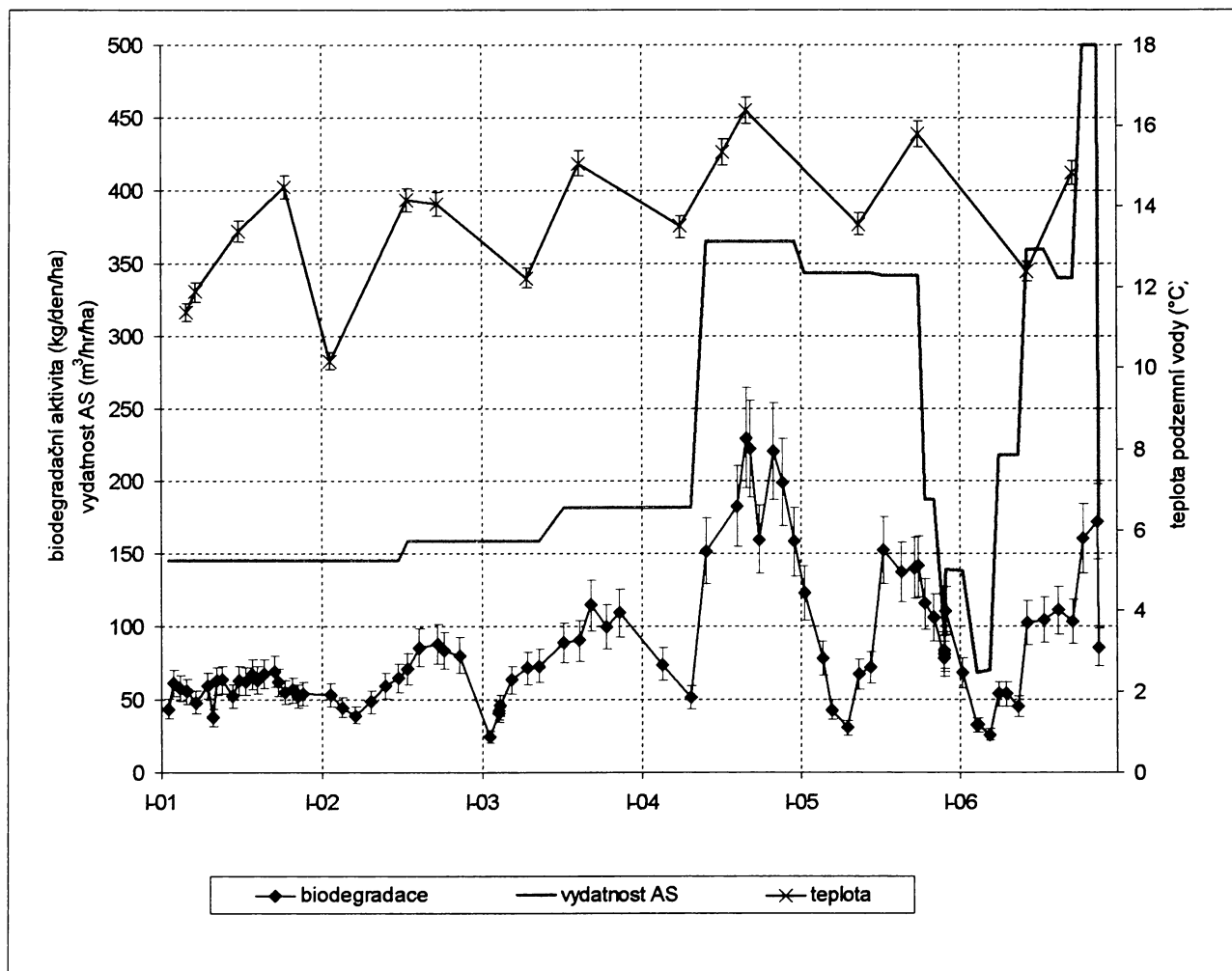
3.2 Korelace mezi vydatností AS, obsahem RU v poli a intenzitou biodegradace

Tabulka 1 uvádí data použitá pro korelaci jednotlivých faktorů. Uvádí objem vzduchu, vtláčený specificky do jednotlivých sanačních polí a pozorovanou specifickou biodegradaci. Pro hodnocení závislosti mezi pozorovanou biodegradační aktivitou a objemem vtláčeného vzduchu jsou použita data získaná ve všech sanačních plochách v srpnu – září 2004 a v srpnu – září 2006 (vždy průměr dvou měřených hodnot). Na jaře 2004 proběhla rozsáhlá intenzifikace a objem vtláčeného vzduchu byl před měřením 3 měsíce stabilní, měření probíhala v období maximální biodegradační aktivity. Sanace v hodnocených plochách před intenzifikací probíhala 2 – 6 let. Data z roku 2006 reprezentují intenzitu biodegradace po 4 – 8 letech.

Pro hodnocení závislosti mezi obsahem RU a intenzitou biodegradace jsou použity dvě sady dat – je korelována vstupní bilance kontaminantů s naměřenou intenzitou biodegradace

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v roce 2004 po intenzifikaci a bilance kontaminantů v roce 2006 s maximální biodegradační aktivitou pozorovanou v roce 2006. V roce 2004 bylo k dispozici více údajů o specifické biodegradaci z pole J, protože v poli byly testovány dílčí plochy s odlišným zapojením sanační technologie (rozdílný objem vzduchu vháněného AS).

Tabulka 1 uvádí specifickou bilanci NEL v jednotlivých polích před zahájením sanace a bilanci NEL k 31.12. 2006 v polích. Bilance v roce 2006 je rozdělena na nadlimitní části (plochy, kde ještě nebyl dosažen sanační limit a sanace pokračuje) a podlimitní části (plochy, kde bylo sanačních limitů již dosaženo a sanace je ukončena). Dále tabulka uvádí dobu sanace pro jednotlivá pole a celkovou plochu kontaminace lokality a plochu s dosaženými sanačními limity.
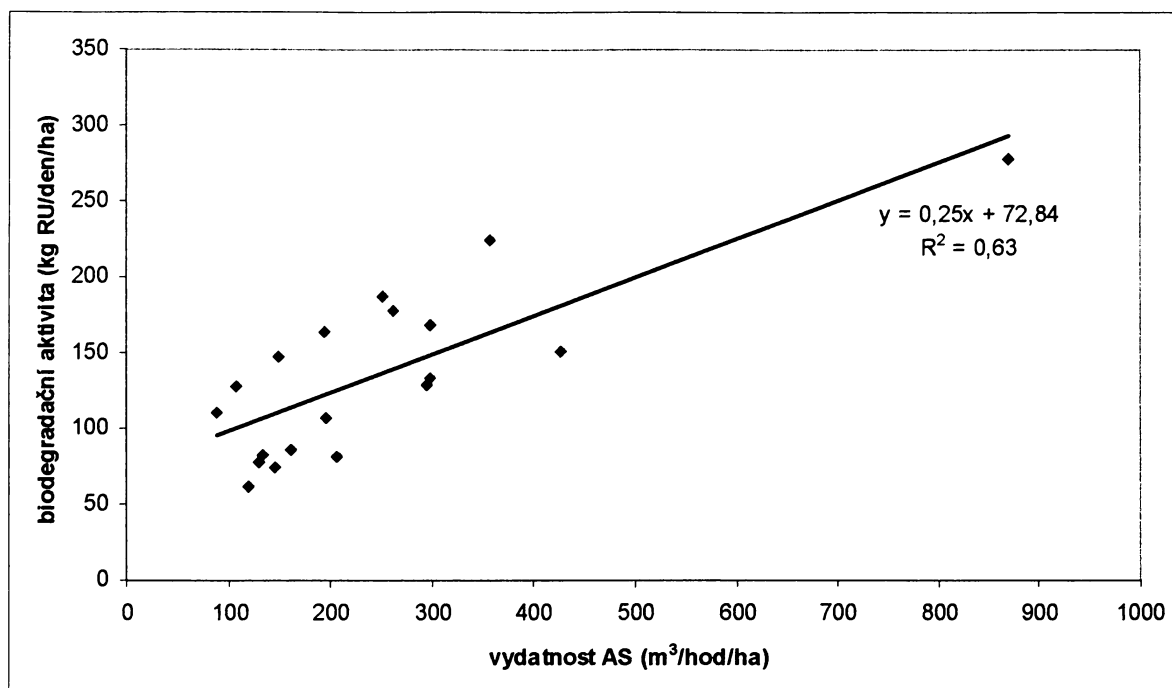
Tabulka 1: Biodegradační aktivita, vydatnost AS a bilance NEL v jednotlivých sanačních plochách

| Pole | srpen-září 2004 | | srpen-září 2006 | | NEL vstup** | NEL 2006 | | doba sanace |
	vydatnost AS (m³/hod/ha)	specifická biodegradace (kg/den/ha)	vydatnost AS (m³/hod/ha)	specifická biodegradace (kg/den/ha)	(tuny/ha)	(tuny/ha)		roky
						nadlimitní	podlimitní	
B	120	62	153	61	212	170	38	8
BV	299	169	474	231	279	149	35	8
E	262	178	365	113	339	144	42	8
F	134	82	279	72	126	167	31	8
G	295	130	408	124	470	191	75	8
I	252	187	337	128	317	148	19	8
J1*	427	152	512	186	328	73	36	6
J4	870	278			328			
J5	206	81			328			
K	197	107	180	83	209	121	6	6
L	358	224	425	139	297	134	21	6
N	195	164	421	216	270	53	31	5
O	162	86	517	118	160	57	23	5
P3	145	75	451	285	190	91	34	3
S	108	128	267	142	112	80	41	3
V1	89	110	466	148	188	121	78	6
V2	298	134	510	151	163	113	36	5
V3	150	148	712	354	108	153	30	5
Plocha (ha)					28,3	9,7	18,6	

* v roce 2006 pole J celkem

** konfidenční interval bilance je +- 25 – 30 % (Prokšová et al., 2007)

Obr. 5 Korelace mezi biodegradační aktivitou a vydatností AS v srpnu – září 2004

Obr. 6 Korelace mezi biodegradační aktivitou a vydatností AS v srpnu – září 2006
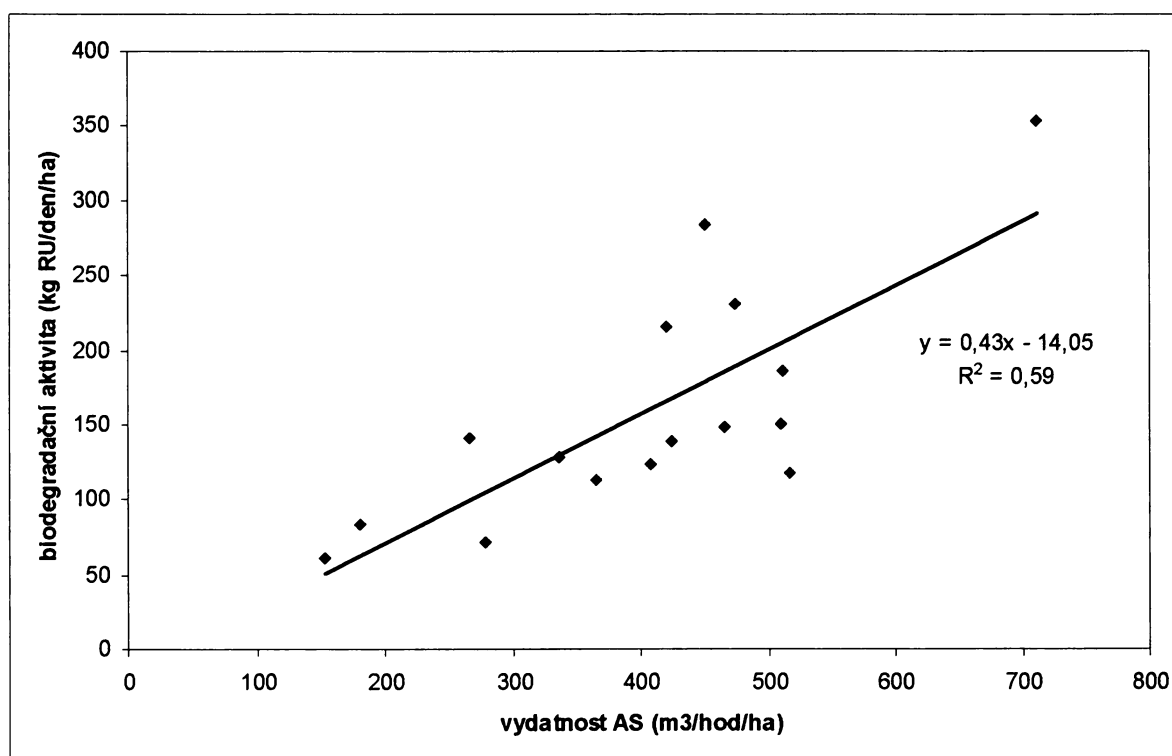
Z obr. 5 a 6 je zřejmé, že mezi objemem vzduchu a pozorovanou biodegradační aktivitou pravděpodobně existuje závislost. V roce 2004 byl dostatek dat pro oddělené hodnocení polí na jednotlivých stáčištích, výsledky uvádí obr. 5 v příloze 2. Při odděleném

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hodnocení západního a východního stáčiště byla zjištěna korelace mezi vydatností AS a biodegradační aktivitou podstatně významnější (R^2 =0,73 resp. 0,98).

Bylo také zjištěno, že v plochách západního stáčiště je k dosažení stejné biodegradační aktivity potřeba o 40% vyšší objem vzduchu, nejpravděpodobnější příčinou jsou rozdíly v geologické stavbě jednotlivých ploch (podrobněji příloha 2 kap. 3.2), ale pro ověření této hypotézy by bylo nutné provést podrobnější průzkum.

Rešerší odborných publikací na téma air spargingu nebyly nalezeny srovnatelné výsledky, týkající se vztahu mezi objemem vtláčeného vzduchu a pozorovanou biodegradační aktivitou. Vztahem mezi objemem vtláčeného vzduchu a distribucí vzduchu v horninové matrici se zabývají publikace (Johnson P.C. et al, 2001) a (Johnson R.C. et al. 2001), kdy podle výsledků pokusů se doporučuje pro AS větší objem vtláčeného vzduchu, protože výsledkem je rovnoměrnější distribuce vzduchu v horninové matrici a větší objem ovlivněného kontaminovaného prostoru

Obr. 7 Korelace mezi biodegradační aktivitou v srpnu – září 2004 a vstupní bilancí NEL
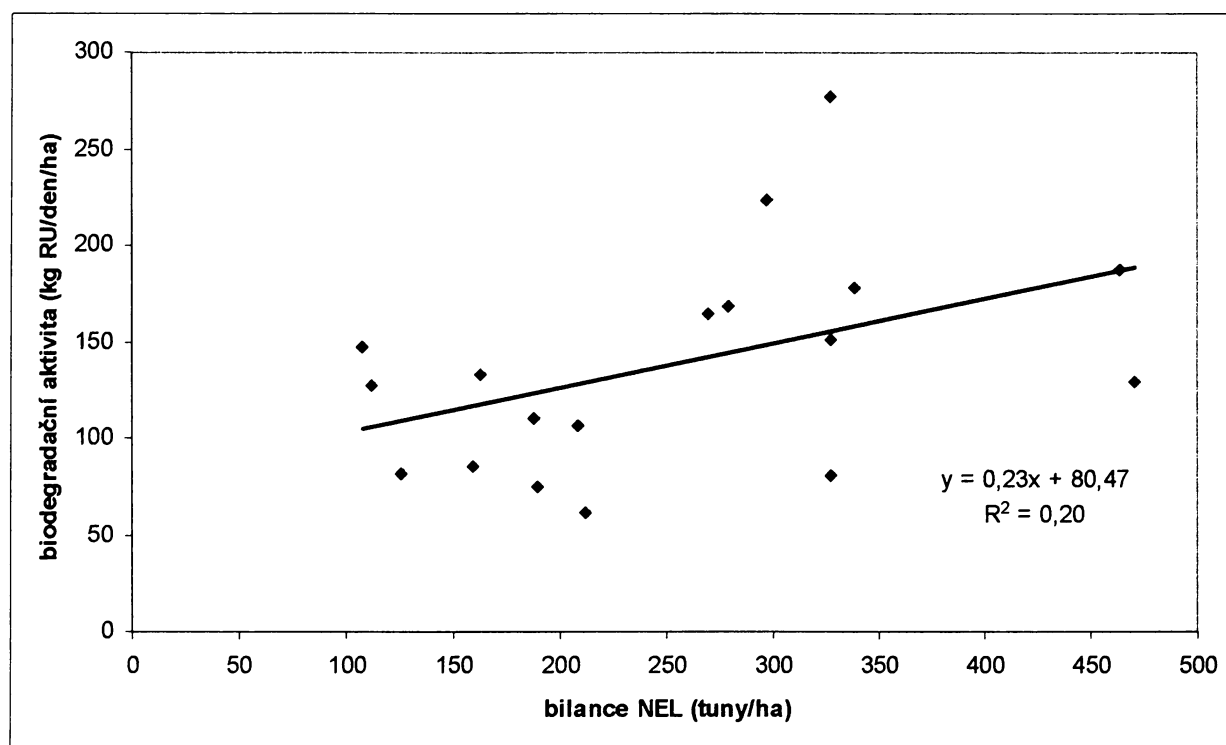
Korelace mezi vstupním obsahem NEL a pozorovanou biodegradační aktivitou v roce 2004 byla velmi slabá (viz obr. 7). Silnější závislost byla zjištěna při odděleném hodnocení jednotlivých stáčišť (obr. 6 v příloze 2, R^2 =0,56 resp. 0,37), ale stále je tato korelace podstatně méně významná než korelace mezi biodegradační aktivitou a vtláčeným objemem vzduchu.

Mezi obsahem NEL bilancovaným v roce 2006 a biodegradační aktivitou v sanačních plochách nebyla nalezena vzájemná závislost (viz obr. 8). Z grafu je zřejmá skupina polí se stále vysokou zbytkovou kontaminací, ale relativně nízkou biodegradací – G, B, F, E a I. Jedná se o nejdéle sanovaná pole ve zdrojové oblasti, kde byly části s extrémně vysokými obsahy RU, pole G, I a E jsou nejkontaminovanější části lokality (viz tab. 1). Je

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pravděpodobné, že v dílčích částech těchto polí dochází k limitaci biologické sanace biodostupností a biodegradovatelností substrátu, viz diskuze k výsledkům sanace v poli I v kap. 3.1. Výsledky sanace v těchto polích nejsou v souladu s výsledky kolonových testů, které indikovaly téměř úplnou biodegradovatelnost substrátu (tab. 1 v příloze 1), ale tyto testy byly prováděny se zeminou, která představovala průměrnou, ne maximální kontaminaci na lokalitě.

Obr. 8 Korelace mezi biodegradační aktivitou v srpnu – září 2006 a bilancí NEL v nadlimitních plochách v roce 2006
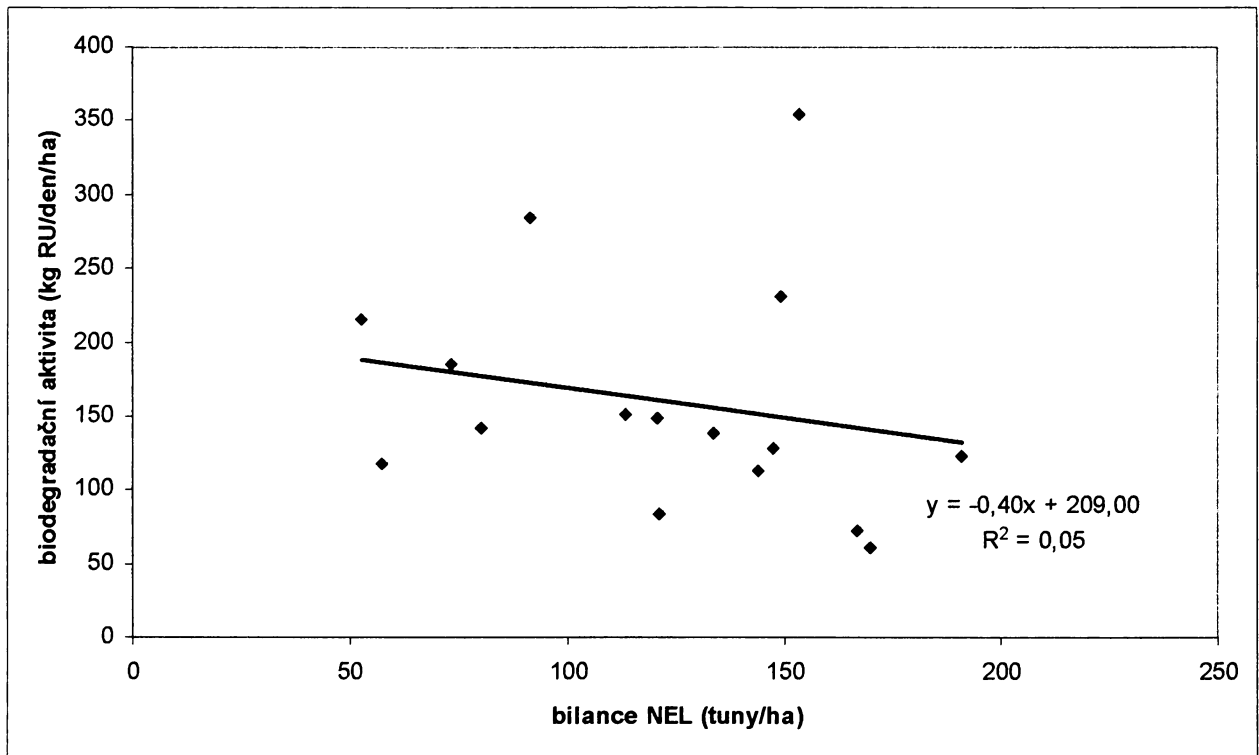
3.3 Korelace mezi teplotou podzemní vody, intenzitou biodegradace a hladinou podzemní vody

Pro hodnocení korelace mezi teplotou, biodegradační aktivitou a HPV je použita průměrná teplota podzemní vody v polích, měřená v srpna-září roku 2004, specifická biodegradační aktivita měřená v těchto plochách v srpnu – září 2004 (průměr dvou maxim) a průměrná HPV, měřená v lednu-březnu 2004. Data uvádí tabulka 2.

Tabulka 2: Biodegradační aktivita, teplota podzemní vody a hladina podzemní vody v roce 2004

|	HPV (m pod trénem)	teplota podzemní vody 2004 (°C)	specifická biodegradace srpen - září 2004 (kg/ha/den)
B	5,4	11,8	62
BV	4,2	13,9	169
E	5,0	14,3	178
F	6,3	11,9	82
G	3,3	15,9	130
I	4,0	15,7	187
J	4,8	14,1	152
K	5,5	11,5	107
L	6,5	16,4	224
N	6,2	14,7	164
O	6,0	14,8	86
P1	5,3	10,4	77
P3	5,5	11,9	75
S	3,0	14,4	128
V1	5,9	13,5	110
V2	3,8	13,9	134
V3	3,8	13,4	148

Korelaci mezi teplotou podzemní vody a pozorovanou biodegradační aktivitou uvádí obr. 9. Mezi teplotou a biodegradační aktivitou pravděpodobně existuje vzájemná závislost, koeficient korelace je obdobný jako mezi objemem vtláčeného vzduchu a biodegradační aktivitou. Na teplotu podzemní vody však nelze při biodegradaci *in situ* pohlížet jako na zcela nezávislý parametr – v sanačních plochách bylo pozorováno zvyšování průměrné teploty v průběhu sanace (viz obr. 3 a 4) a plošná interpretace měření ukazuje značnou variabilitu teploty podzemní vody v sanačním poli (viz obr. 7 v příloze 4). Byly pozorovány při měření *in situ* teploty až 25 °C, což je teplota výrazně vyšší, než pozorovaná v pozaďovém poli R (viz obr. 6 v příloze 4), kde se teplota pohybovala mezi 10 – 12 °C. Tyto výsledky indikují, že sanační proces, zvláště v plochách s vyšší intenzitou biodegraradace, má vliv na zvýšení teploty podzemní vody. Tuto hypotézu podporuje i fakt, že závislost mezi teplotou podzemní vody a hloubkou HPV pod terénem v sanačních polích na lokalitě je téměř nulová, viz obr. 10 a tab. 2, přestože vzhledem k pozorovanému ovlivnění teploty podzemní vody změnami teploty v průběhu roku by měla být teplota vody pozorovaná v určité hloubce pod terénem stejná.

V teplotě jednotlivých polí se stejnou hloubkou HPV jsou pozorovány významné rozdíly – např. mezi plochami F a L s obdobnou hloubkou HPV je rozdíl v průměrné teplotě 4° C a rozdíl v biodegradaci téměř trojnásobný (viz tab. 2).

16

Obr. 9 Korelace mezi biodegradační aktivitou v srpnu – září 2004 a průměrnou teplotou podzemní vody v srpnu – září 2004
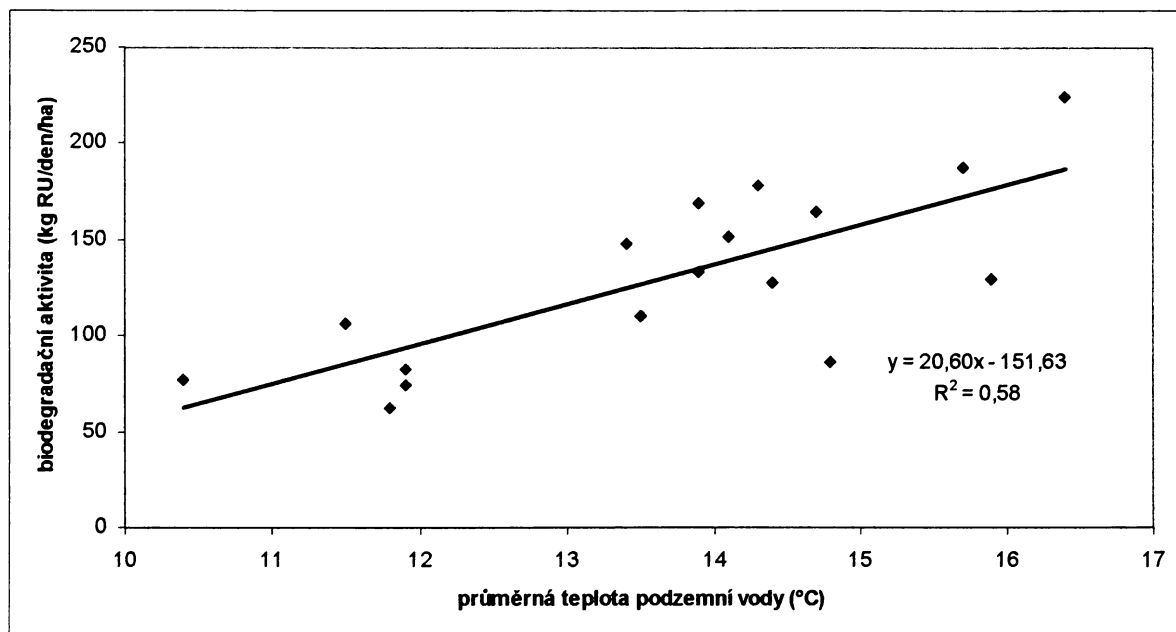
Obr. 10 Korelace mezi průměrnou teplotou podzemní vody v srpnu – září 2004 a hladinou podzemní vody
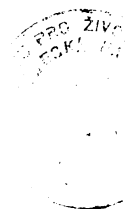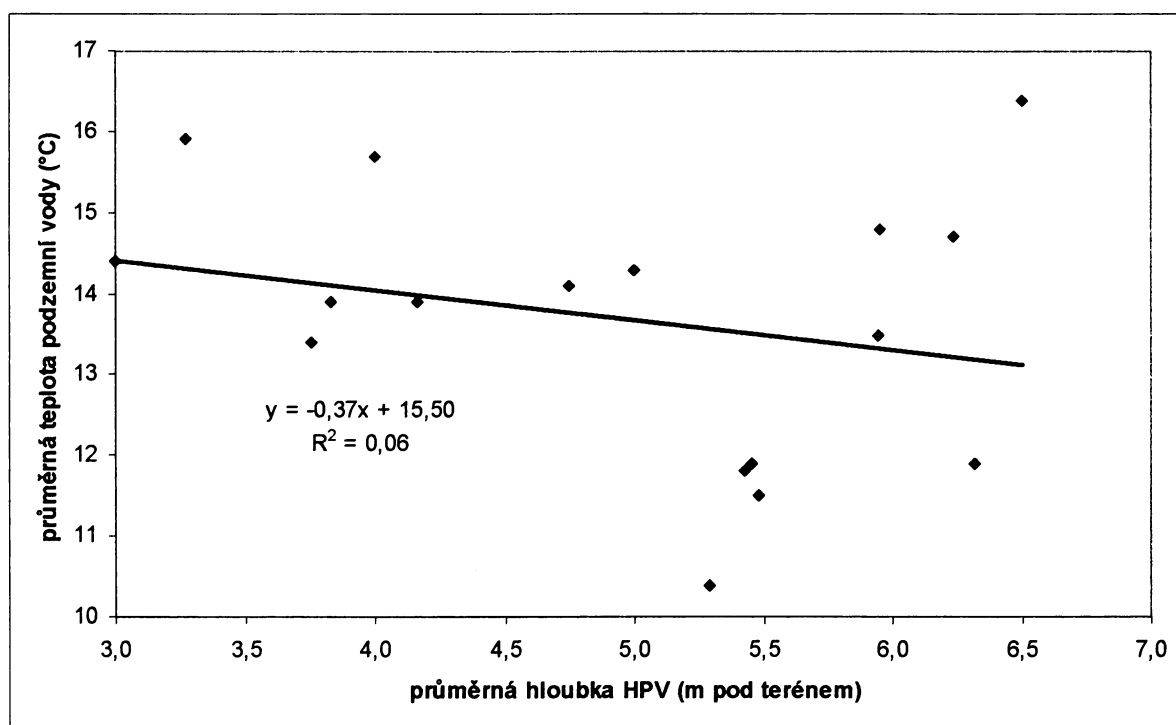
4 ZÁVĚR

Tato rigorózní práce předkládá výsledky dlouhodobého pozorování faktorů, ovlivňujících biodegradační aktivitu autochtonní půdní mikroflóry při biologické sanaci znečištění zemin a podzemní vody ropnými látkami na bázi leteckého paliva v sedimentárních horninách.

Na základě vyhodnocení několikaletého monitoringu lze učinit tyto závěry:

- Hlavním přírodním faktorem, který ovlivňuje dosaženou biodegradační aktivitu je teplota podzemní vody. V plochách s hloubkou HPV 3 – 6,5 metrů pod terénem bylo pozorováno výrazné cyklické kolísání biodegradační aktivity, které lze dát do jednoznačné souvislosti s pozorovaným kolísáním teploty podzemní vody v průběhu roku. Byla také nalezena korelace (R^2 = 0,58) mezi teplotou podzemní vody a biodegradační aktivitou. Výsledky dlouhodobých pozorování dále indikují, že intenzivní biodegradační proces má vliv na zvýšení průměrné teploty podzemní vody o 1 – 2 °C.

- Mimo přírodních faktorů byl pozorován výrazný vliv zapojení sanační technologie na intenzitu biodegradace. Po výrazném zvýšení objemu vzduchu vháněného do sanačních ploch air spargingem došlo k několikanásobnému nárůstu pozorované biodegradační aktivity v polích, kde sanace probíhala 2 – 4 roky. Dále byla zjištěna střední až silná korelace mezi objemem vháněného vzduchu a biodegradační aktivitou v jednotlivých sanačních plochách.

- Podle výsledků této práce vliv není obsahu kontaminace v silně kontaminovaných sanačních plochách na pozorovanou biodegradační aktivitu příliš významný. U ploch s vstupní kontaminací 100 – 450 tun NEL/ha, vázaných na mocnost 2 – 4 m byla po 2 – 6 letech sanace zjištěna slabá až střední korelace mezi obsahem kontaminace a pozorovanou biodegradační aktivitou. Po 4 – 8 letech sanace byl vztah mezi bilancí kontaminace (rozmezí 50 – 200 tun NEL/ha, vázané na mocnost 2 m) a dosaženou biodegradaci téměř nulový.

- V částech kontaminovaných ploch byla ověřena téměř úplná odbouratelnost ropného znečištění zvolenou sanační technologií, indikovaná laboratorními kolonovými testy. V plochách s velmi vysokou vstupní kontaminací (212 – 470 tun NEL/ha) se však po 6 – 8 letech sanace začala pravděpodobně projevovat limitace sanačního procesu biodostupností a biodegradovatelností substrátu, která nebyla indikována kolonovými laboratorními testy. Pro ověření této hypotézy by bylo nezbytné laboratorní testy zopakovat.

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Prokšová S. et al.(2007): Etapová zpráva o sanaci ekologické zátěže na lokalitě Hradčany X. etapa, Earth Tech CZ Praha

Příloha 1

Capacity of the Bioremediation Technology for Clean-Up of Soil and Groundwater Contaminated with Petroleum Hydrocarbons

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ENVIRONMENTAL REMEDIATION

Capacity of the Bioremediation Technology for Clean-Up of Soil and Groundwater Contaminated with Petroleum Hydrocarbons

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ABSTRACT

A column reactor was designed and used to simulate conditions affecting the bioremediations of petroleum hydrocarbons. The work illustratively describes the aerobic (model) clean-up of soil samples enabling to predict the efficiency of a technology installed in parallel on contaminated former airport. The data showing the performance of thus precharacterized technology are presented.

Key Words: Bioremediation; In situ; Laboratory simulation; Petroleum hydrocarbons.

INTRODUCTION

The clean-up of the former army air base Hradcany (Czech Republic) is the most important long term project covered from the budget of Czech Ministry of

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Environment. A huge environmental liability in the form of soil and groundwater pollution with petroleum hydrocarbons (mainly jet fuel, diesel oil, gasoline and fuel oil) is present at the site. Microbial screening had shown that microorganisms (in the first place *Comamonas acidovorans*) naturally present in the soils were actively mineralizing petroleum hydrocarbons as above.[1] A combination of several clean-up technologies is used for the site decontamination.[2] The main remediation method after the soil vapor extraction (SVE) and recovery of free product by vacuum pumping is enhancing the conditions for in situ aerobic biodegradation. The remedial system is widened by nutrient amendment (N, P) for full support of indigenous aerobic microorganisms.[3] A crucial condition for the aerobic biodegradation is a sufficient supply of oxygen. Two systems are used for oxygen delivery—SVE and air sparging (AS). Ambient air is used as an oxygen carrier. SVE is effective only in the upper layers of the unsaturated zone, for aeration of deeper layers and groundwater AS is used.

The most important question is whether the biological methods are able to decrease concentration of pollutants below the remedial limit (petroleum hydrocarbons in groundwater $5\,\mathrm{mg\,L^{-1}}$, petroleum hydrocarbons in soil $5000\,\mathrm{mg\,kg^{-1}}$).

MATERIALS AND METHODS

Reactor System

A modular tool enabling to simulate a performance of real bioremediation technology in vitro was designed. This system is based on the aerated glass column reactor ($400 \times \varnothing 80\,\mathrm{mm}$), fitted with cooling jacket, regulated valves for input, resp. output gases (sterile air, CO_2) and sampling equipment making possible to take up soil and water samples. Water and nutrient solutions (N, P) were added by the tubing pump (Masterflex L/S). Sterilized air for column aeration was free of CO_2. Carbon dioxide produced by microorganisms in soil was adsorbed in 1 M KOH solution (Fig. 1).

Soil Samples

Sample EZ—soil from the field where the biological treatment was initiated 3 years ago; fine-grained sand with clay. Sample JZ—soil from the field where the biological treatment was initiated a year ago; medium-grained sand without clay. Sample IZ—soil from the field where the biological treatment have not ever been initiated; medium-grained sand without clay.

Analytical Methods

The determination of biodegradation activity in soil samples proceed from methods by Anderson.[4] Concentration of biodegraded hydrocarbons in columns was calculated from production of CO_2 contained in outlet air (acidimetric method). The determination of petroleum hydrocarbons in soil were analyzed using
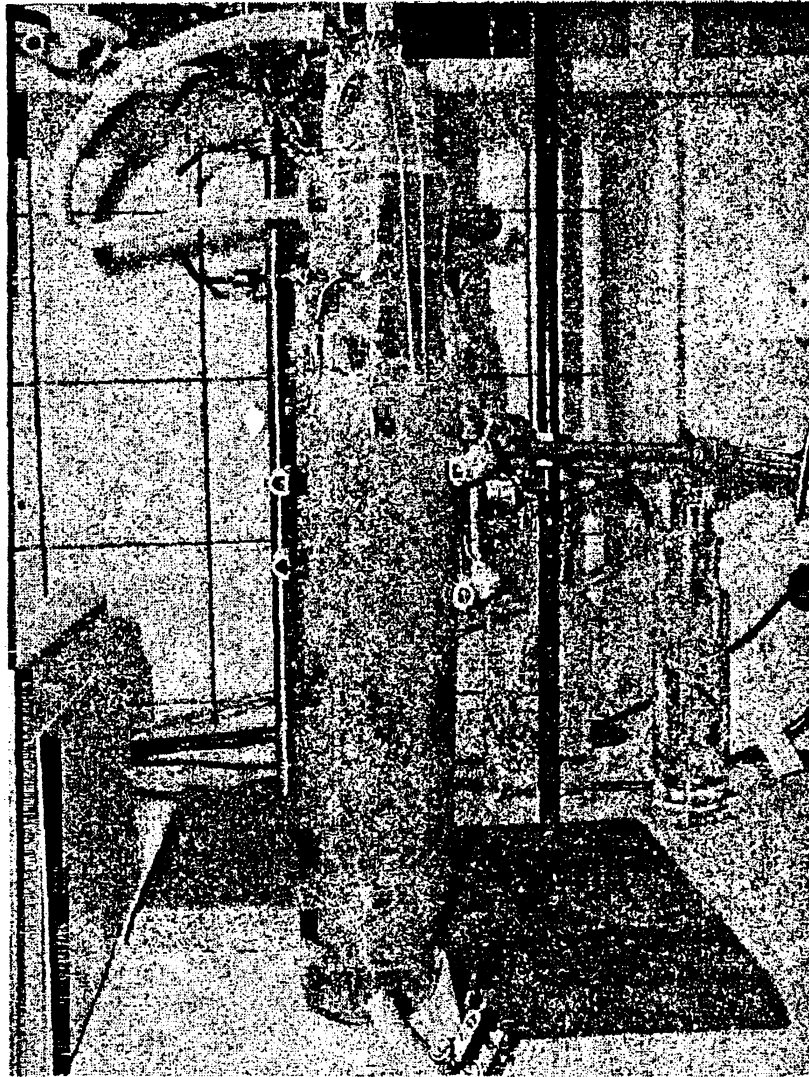
Figure 1. Down-flow reactor vessel.

EPA 418.1 method (modified for soils).[5] Total count of aerobic degrading bacteria (as CFU) was determined according to DECHEMA.[6]

RESULTS AND DISCUSSION

Any development of experimental approach to screen for conditions affecting the bioremediation of contaminated material as well as enabling to predict the bioremediation efficiency is wanted by these technologies research and development. In this context, a conceptual framework and a reactor system (see Material and methods) were designed to simulate different variations of given bioremediation task, providing a tool to scale up and verify conditions assessed as optimizing, i.e., oxygen accessibility, water activity, nutrient profile, temperature effect, among others. Estimates of key characteristics needed for evaluation of technological efficiency can be made in much shorter time and the monitoring of the remedial activity of samples of contaminated soils makes possible to estimate real (technological) time necessary to meet final requirements.
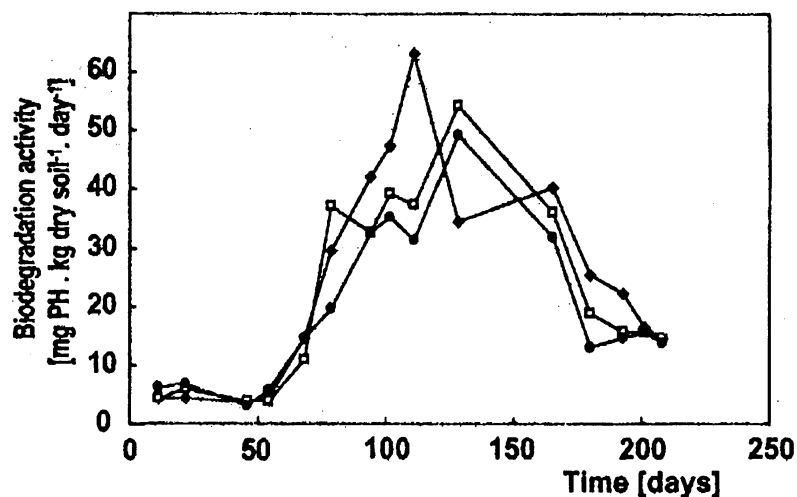
Figure 2. Time course of biodegradation activity under conditions simulating the optimum (technology) conditions. Soil samples: ■—EZ; □—JZ; ●—IZ. Experimental conditions: temperature—15°C; water activity—90%; concentration of O_2 in output—18% vol.; a growth nonlimiting concentration of N and P nutritions. PH = Petroleum hydrocarbons.
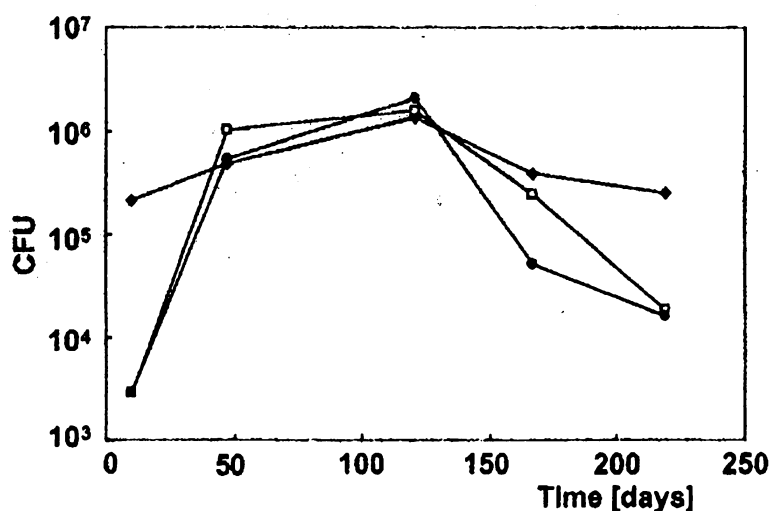
Figure 3. Time course of degrading microflora accumulation under conditions simulating the optimum (technology) conditions. Soil samples: ■— EZ; □—JZ; ●—IZ. Experimental conditions: see legend Fig. 2.

Table 1. Changes in the concentration of pH determined under conditions simulating real technology performance.

| Sample | pH Concentration [mg pH · kg dry weight^{-1}] | | Decrease [%] |
	Start: 7th August 2001	End: 4th March 2002	
EZ	6,650	1,300	80
JZ	16,500	480	97
IZ	8,100	11	100
Remedial limit		5,000	

Figure 4. Balance of petroleum hydrocarbons remedied from the underground water and soil in Hradcany Airport during 1997–2001.

Table 2. Installed clean-up technology on Hradcany airport (2001).

Technology	No. of wells	No. of engines	Unit output
Venting	1,240	28 blowers	$180\,m^3\,h^{-1}$
Air sparging	1,350	44 compressors	$100\,m^3\,h^{-1}$
Dual phase extraction	180	8 vacuum pumps	$80\,m^3\,h^{-1}$
Ground water pumping	12	12 submersible pumps	$0.5\,l\,s^{-1}$
Nutrient solution amendment	1,100		$6000\,m^3\,year^{-1}$

Table 3. The treatment costs of Hradcany airport soil and groundwater clean-up in the year 1999.

Clean-up method	Pollutants	Cost per kg of removed pollutants in US $ — Range[3]	Cost per kg of removed pollutants in US $ — Average
Controlled bioremediation[1]	petroleum hydrocarbons	0.52–1.6	1.45
Dual phase extraction	petroleum hydrocarbons	1.25–20.5	1.75
Venting[2]	petroleum hydrocarbons	2.50–12.6	4.20
Water pumping and treating	petroleum hydrocarbons	3.40–8.6	5.20

Annotations: [1]price included air sparging and fertilizer addition; [2]price included "physical" venting output only; [3]range of unit prices is calculated according to the clean-up results on the various remediation fields.

For instance, as shown by the time course of hydrocarbon consumption and degrading microflora development (Figs. 2 and 3), observed in 3 samples of contaminated soil (Hradcany Airport), the wanted clean-up efficiency, i.e., $5000\,mg\,kg^{-1}$, was significantly exceeded. In parallel, additional data show final values of petroleum hydrocarbons concentration (Table 1), proving sufficient biodegradation capacity of present microflora.

' Moreover, a decrease in the concentration of hydrocarbons is accompanied with a deterioration of present microflora. Data obtained using above reactor system can be easily compared with the results of in situ technology performance (Fig. 4). In this connection, the installed technologies and operating costs are summarized in Tables 2 and 3.

CONCLUSION

The balance of petroleum hydrocarbons removal from underground water and soil of a particular locality shows optimum efficiency of a technology designed and predicted through laboratory (reactor) simulation of actual bioremediation task.

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Capacity of the bioremediation technology for clean-up of soil and groundwater contaminated with petroleum

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INTRODUCTION

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MATERIAL AND METHODS

Reactor system:A modular tool enabling to simulate a performance of real remediation technology in vitro was designed.This system is based on a jacketed glass column reactor (400 x 80 mm), fitted with cooling system, regulated valves for input, resp. output gases (sterile air, CO₂) and dosing equipment making possible to take up soil and water samples. Air and nutrient solutions (N, P) were added by the tubing pump (airflex L/S). Sterilized air for column aeration was free of CO₂. Carbon dioxide produced by microorganisms in soil was adsorbed in 1 M KOH solution.

Samples: Sample EZ - soil from the field where the biological treatment was initiated 3 years ago; fine-grained sand with clay. Sample JZ - from the field where the biological treatment was initiated a year ago; fine-grained sand without clay. Sample IZ - soil from the field where biological treatment have not ever been initiated; medium-grained sand without clay.

Analytical methods: The determination of biodegradation activity in soil samples proceed from methods by Anderson (1989). Concentration of degraded hydrocarbons in columns was calculated from production of CO₂ contained in outlet air (acidimetric method). The determination of petroleum hydrocarbons in soil were analyzed using EPA 418.1 method (modified for soils) (US EPA, 1983). Total count of aerobic degrading bacteria (as CFU) was determinated according to DECHEMA (1992).

RESULTS AND DISCUSSION

A development of experimental approach to screen for conditions affecting the bioremediation of contaminated material as well as enabling to predict the bioremediation efficiency is wanted by these technologies R & D. In this context, a conceptual framework and a reactor system (see material and methods) were designed to simulate different conditions of given bioremediation task, providing a tool to set up and verify conditions assessed as optimizing, i.e. oxygen accessibility, water activity, nutrient profile, temperature effect, among others. Estimates of key characteristics needed for evaluation of technological efficiency can be made in much shorter time and the monitoring of the remedial activity of samples of contaminated soils makes possible to estimate real (technological) time necessary to meet final requirements. For instance, as shown by the time course of hydrocarbon consumption and degrading microflora development (Figs. 3 and 4), observed in 3 samples of contaminated soil (Hradcany Airport), the wanted clean-up efficiency, i.e. 500 mg kg⁻¹, was significantly exceeded. In parallel, additional data show final values of petroleum hydrocarbons concentration (Tab. 1), proving sufficient biodegradation capacity of present microflora. Moreover, a decrease in the concentration of hydrocarbons is accompanied with a deterioration of present microflora. Data obtained using above reactor system can be easily compared with the results of in situ technology performance (Fig. 5). In this connection, the installed technologies and operating costs are summarized in Tables 2 and 3.

CONCLUSION

The above experimental approach was found to be useful in a wide range of applications (PAHs, NO₃⁻ remediations).

Fig. 1 The site layout with petroleum hydrocarbons contamination extent in 1998

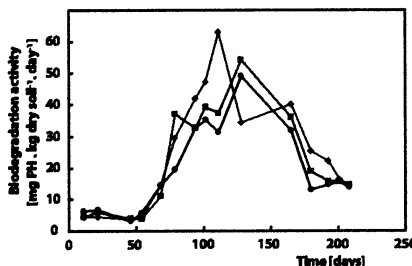1000 - 5000 mg/kg   5000 - 10000 mg/kg   > 10000 mg/kg

Fig. 2 Clean-up field

Fig. 3 Time course of biodegradation activity under conditions simulating the optimum (technology) conditions.
(Soil samples: ◆ - EZ; ■ - JZ; ● - IZ. Experimental conditions: temp. - 15 °C; water activity - 90 %; O₂ conc. in output - 18 % vol.; a growth non-limiting concentration of N and P nutritions. PH = Petroleum hydrocarbons.)
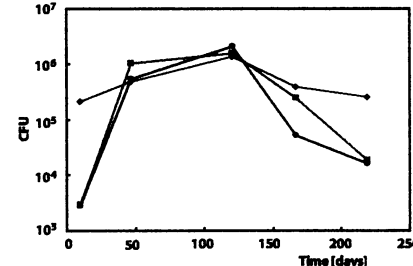
Fig. 4 Time course of degrading microflora accumulation under conditions simulating the optimum (technology) conditions.
(Soil samples: ◆ - EZ; ■ - JZ; ● - IZ. Experimental conditions: see legend Fig. 3.)

Tab. 1 Changes in the concentration of PH determined under conditions simulating real technology performance.

Sample	PH concentration [mg PH . kg dry weight⁻¹]		Decrease
	Start: 7th August 2001	End: 4th March 2002	[%]
EZ	6650	1300	80
JZ	16500	480	97
IZ	8100	11	100
Remedial limit	5000		

Tab. 2 Installed Clean-up Technology on Hradcany Airport (2001)

Technology	No. of wells	No. of engines	Unit output
venting	1240	28 blowers	180 m³ h⁻¹
air sparging	1350	44 compressors	100 m³ h⁻¹
dual phase extraction	180	8 vacuum pumps	80 m³ h⁻¹
ground water pumping	12	12 submersible pumps	0,5 l sec⁻¹
nutrient solution amendment	1100		6 000 m³ year⁻¹

Tab. 3 The treatment costs of Hradcany Airport soil and groundwater clean-up in the year 1999.

Clean-up method	Pollutants	Cost per kg of removed pollutants in US $	
		Range	Average
controlled bioremediation (1)	oil hydrocarbons	0,52 - 1,6	1,45
dual phase extraction	oil hydrocarbons	1,25 - 20,5	1,75
venting (2)	oil hydrocarbons	2,5 - 12,6	4,20
water pumping and treating	oil hydrocarbons	3,4 - 8,6	5,20
water pumping and treating	chlorinated solvents		513,30

(1) price included air sparging and fertilizer addition; (2) price included "physical" venting output only; Range of unit prices is calculated according to the clean-up results on the various remediation fields
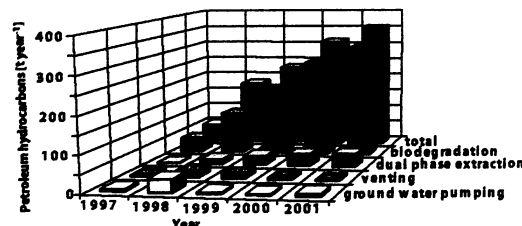

Fig. 5 Balance of petroleum hydrocarbons remedied from the underground water and soil in Hradcany Airport during 1997 - 2001.

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Příloha 2

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MAJOR FACTORS AFFECTING IN SITU BIODEGRADATION RATES OF JET-FUEL DURING ACTIVE CLEAN-UP IN SEDIMENTARY BEDROCK

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1 INTRODUCTION

Biodegradation of petroleum hydrocarbons (TPH), mostly lighter fractions, became a widely used clean-up technology for contaminated soil and groundwater during last twenty years. Methods for remediation of unsaturated zone were tested in the first half of nineties (Anderson 1995, Leeson and Hinchee 1997), experiences with air sparging (AS) for biodegradation of TPH in saturated zone were published several years later. (Marley a Bruell, 1995; Hinchee, Miller, Johnson 1995; Leeson et al. 1999) The clean-up principle of *in situ* biodegradation is aerobic oxidation of TPH by bacterial metabolism of soil microflora, which use contaminant as a primary source of carbon and energy. Factors, which affect efficiency of clean-up, are driving factors of aerobic soil bacteria activity. Importance of a variety of factors for bacterial activity in unsaturated zone during bioventing of TPH was evaluated by The Bioventing Initiative of U.S. Air Force (Leeson and Hinchee, 1997) and also a number of papers about air sparging implementation and design were published. (Leeson et al. 1999; Johnson et al., 2001) But only limited information on evaluating influence of natural and technological factors on clean-up efficiency (i.e. amount of removed contaminant) during a long-term clean-up of heavily contaminated areas is available. The above mentioned Air Force Initiative evaluated data from 125 sites with average soil TPH content 2300 mg/kg and only 16% of soil samples exceeded 5 000 mg/kg TPH. Contamination content on studied sites was significantly lower in comparison to the site, studied in this paper (chapter 2.1). Initial contamination content is crucial for design and especially output of air supply for aeration of contaminated strata; an underestimation of required aeration technology can negatively influence the technology performance and clean-up time. This article evaluates influence of groundwater temperature, volume of air injected by AS and contamination content on biodegradation activity rates observed during the clean-up of the Hradčany site.

2 METHODICS

2.1 SITE CHARACTERISTICS

The site was used for military purposes from 1940–1991 and military activities resulted in extensive contamination of the soil and groundwater by petroleum products (70% is represented by jet fuel) in an area of 28 hectares (Figure 1). Average thickness of the contaminated soil layer was 1.75 m and its depth varied between 3 - 10 m below the surface; TPH average content was 11 000 mg/kg in this layer and contamination was detected up to 2 m under groundwater table level (Machackova et al 2005). The total amount of TPH, which was released into soil and groundwater, was estimated on 7 150 tons in 1997. (Hercik et al, 2002)

The site's subsoil is Quaternary sandy-gravel river terrace deposits (thickness 4 m), underlain by Cretaceous marine sediment, consisting of weathered medium-grain sandstone approximately 50 m thick. The site is a part of the Bohemian Cretaceous Basin, the most important resource of high quality groundwater in the Czech Republic. The endangered aquifer is the only source of drinking water in the region and the presence of extensive contamination limits future use and revitalization of the site.
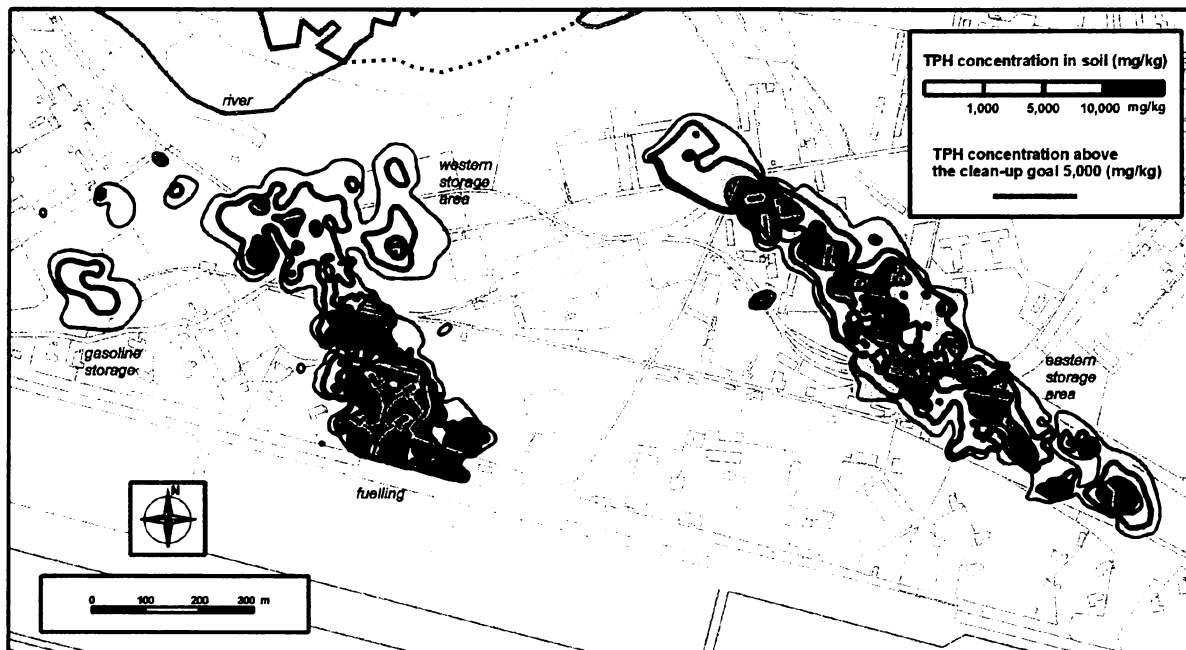
Figure 1: Site layout with areas contaminated above the clean-up goal - 2000 Conditions

Until 1997, the site was remediated using pump-and-treat and soil venting techniques. The complex remediation of the site based on a combination of several remediation technologies started in 1997, when *in situ* technologies were gradually applied on the site. Removal of volatile organic compounds (VOCs) via soil vapor extraction (SVE) and air sparging (AS), light non-aqueous phase liquid (LNAPL) vacuum extraction, and aerobic TPH biodegradation supported by oxygenation via air sparging and application of nutrient solutions have been applied on the site. (Masak et al. 2003) The clean-up had two phases – first phase was focused on maximum removal of LNAPL (vacuum extraction), second phase was aimed on optimization of favorable conditions for aerobic biodegradation in the entire contaminated profile (air sparging + nutrients). The contaminated area was divided into individual remediation fields with areas of 0.5 – 4 hectares for the purpose of remedial operations (Figure 2) and the clean-up technology was consequently installed in each of these fields. From 1997 – 2005, 3 182 tons of TPH were removed from the site, biodegradation removed 93% of the total amount, vacuum extraction of LNAPL removed 5 % and SVE/AS removed 2% of the total amount. (Hercik et al., 2006)

2.2 BIODEGRADATION ACTIVITY MONITORING

The core method for observing *in situ* biodegradation activity in contaminated strata is based on monitoring of respiration gases in clean-up fields. The mass of biodegraded petroleum contamination is calculated using respiratory gas (O_2, CO_2) monitoring data from venting system. The metabolized hydrocarbons are stoichiometrically quantified from the volume of oxygen consumed in the remediation zone using equation [1] (Anderson, 1995; Leeson and Hinchee, 1997). The production of CO_2 is monitored as well, for control purposes. (Leeson and Hinchee, 1997) In 2005, the ratio of the mass estimation based on the oxygen consumption to the estimation based on carbon dioxide production was 91 – 100 %. (Herčík et al, 2006) Measurements used for biodegradation quantification were conducted at month intervals and the calculation of the total mass of removed contamination was based on results extrapolated between measurement dates.
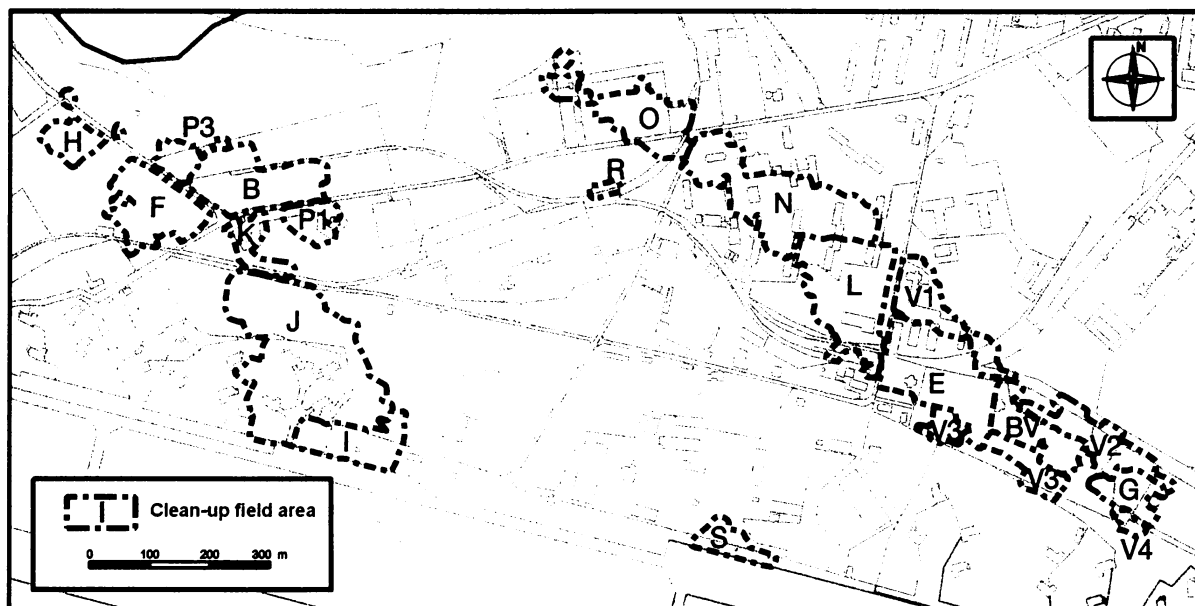
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Figure 2:. Remediation Field Locations

[1] $B_c = ((Q \times (20.9 - c_{RP})/100) \times \rho_{RP} \times C$

B_c Total balance of biodegraded hydrocarbons in kg/day for a given remediation field

Q Ventilator flow rate in m^3/day

c_{RP} Respiratory gas concentration (O_2) in volume %

ρ_{RP} Respiratory gas specific weight (O_2 1.429 kg/m^3, regular conditions)

C Stoichiometric ratio C_xH_y/O_2, 0.29, C_xH_y/CO_2, 0.31

The accuracy and representativeness of the mass balance was estimated by the measurement error. Calculations were based on the measured volume of extracted air and the concentrations of VOCs and respiratory gases. The extracted air volume is obtained by multiplying the streamline flow velocity in the SVE system, measured with a hot-wire anemometer (TA4/5, Airflow), by a known cross-sectional area of the SVE piping. The air volume measurement error was determined from the anemometer relative error, which was 5%. Concentrations of respiratory gases are measured in the venting piping with a portable multi-gas analyzer (Anagas 95, GI). The relative error of respiratory gas concentration measurements is 2.5%. When calculating biodegradation mass balance, the measured values were multiplied and the mass balance error was obtained as a summation of the relative measurement errors. The confidence interval ($\alpha=0.05$) was determined as double the measurement error; i.e.15% in the case of the biodegradation mass balance.

The respiratory balance was further adjusted using background respiration levels, which were quantified on the basis of the remediation field R operation in a non-contaminated area for a period of two years. The background respiration was 2.3 t of organic substances/ha/year and this amount aliquot to the clean-up field area was subtracted from the biodegradation mass balance calculation. (Hercik et al., 2001)

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2.3 GROUNDWATER TEMPERATURE MONITORING

Temperature is one of the main factors affecting biodegradation activity. (Leeson, Hinchee 1997) Monitoring of groundwater temperature is held together with groundwater dissolved oxygen concentrations. It is measured *in situ*, 0.5 m under the groundwater table by a field measuring device (Oxi Set, WTW) in venting wells. Measured data are averaged for the field, well density is 70 – 100 wells for a hectare of a clean-up field and confidence intervals (α=0.05) of averages are given in figures. Groundwater temperature was monitored 4 – 5 times per year in the clean-up beginning; during last years monitoring was held two times per year.

2.4 AIR SPARGING INPUT

As maximum of contamination is bounded to strata under GWL, air injection through AS is the principal aeration system in clean-up of the Hradcany site. AS was an innovative strategy during the preparation of the project in 1997 and was not well described in full-scale operation. It led to an underestimation of a necessary air (resp. oxygen) input into clean-up fields and resulted into an inadequate aeration of groundwater, observed in first years of clean-up. The air input had to be increased during the clean-up up two to three folds in 2003 - 2004, based on recommendations in literature. (Johnson et al., 2001) Relation between observed biodegradation rates and AS injection rates was chosen for evaluation of AS clean-up efficiency. For correlation data from autumn 2004 were chosen, when clean-up operation had stabilized after AS intensification in spring 2004 (AS injection rates were steady at least for three months prior measurements). AS air volume input is given by the operation parameters of compressors used, which is monthly controlled by an air-flow meter with the accuracy +- 5 m^3.

2.5 SOIL TPH CONTENT

A method based on soil sampling from discrete depth intervals (0.5 m) was used to calculate the mass of TPH in soil. A spiral auger was used for sample collection with discrete samples obtained from the tip of the auger immediately after drilling. Samples were collected at defined depths with an accuracy of -/+ 15 cm. The sampling points were arranged in a regular network 20 x 20 m; twenty boreholes per hectare were made. During sampling, it is necessary to evaluate the thickness of the contaminated layer to assess the entire contaminated profile, i.e. sampling must extend to a contamination-free depth. During the investigation of the Hradcany site, it was found that 80% of the contamination being bounded to layers under GWL and contamination was detected in depth up to 2 m under GWL; despite the natural fluctuation of GWL observed at the site is 0.5 m. (Machackova et al., 2005; Hercik et al., 2006)

Point soil sampling was selected because the contaminant is dominantly volatile and semi-volatile petroleum substances, and the standard procedures used for the compositing of samples (quartering) would result in a loss of the VOCs. (Boulding, 1995) Soil samples were subject to analysis of TPH through IR detection (ISO TR 11046 method). The confidence interval of laboratory determination of TPH-IR, with α=0.05 expressed as twice the relative standard deviation, is 30%.

TPH detection using IR can be affected by the presence of non-polar substances of natural origin, but this method was selected as main monitoring tool because the more precise analytic methodology (gas chromatography) is very expensive and naturally-occurring organic substances are minimal in site soils (background values TOC 0.019% dry weight, TPH < 21

mg/kg dry weight). For mass quantification of TPH in soil of each individual remediation field, the TPH-IR soil data set was converted into a results matrix; After statistical data analyze (Herčík et al, 2002), the trimmed mean showed the best correlation in all the samples of the entire Hradcany site. The selection of the trimmed mean represented a compromise between the sensitivity of the sample average and the robustness of the sample median. (Hercik et al., 2002) The calculation of mean values was based on the trimmed average for $\alpha = 0.15$, which disregards 15% of the smallest and largest sample values. (Havranek, 1993)

During the statistical analysis, the spatial distribution of data is neglected and data are transformed to a one-dimension data file. Further interpretation of the TPH content in the soil was based on two-dimensional maps showing the spatial layout of contaminants. Data on TPH concentrations were used to calculate a one-side trimmed mean of values greater than 1 000 mg/kg of TPH, the basic graphic interpretation was produced with Surfer 6 software with Kriging selected as the interpolation method. The computer output was optimized by hand to produce a final map, which enables to evaluate spatial changes of TPH distribution in clean-up fields during the clean-up.

3 RESULTS AND DISSCUSSION

3.1 BIODEGRADATION RATES IN CLEAN-UP FIELDS

Figure 3 shows biodegradation activity, groundwater temperature and air sparging air input in the L field (2.4 ha) in the period 2001 – July 2006. Figure 3 shows changes of biodegradation activity influenced by the seasonal groundwater temperature fluctuation and the clean-up process intensity. The average groundwater temperature in the L field seasonally changes in a range 4 -5 °C, which results in an observable fluctuation of the biodegradation activity. On the contrary, a rise of the average groundwater temperature about 1.5 – 2 °C is observable during the clean-up, together with the rise of the biodegradation activity. The most probable cause of increasing temperature is a low efficiency of bacterial metabolism, when a portion of metabolic energy is released in a form of waste heat.

Another factor, significantly influencing observed biodegradation rates, is the oxygen delivery to the contaminated strata, which is driven by AS air input into the field. As fig. 3 documents, even after 3 years of the clean-up operation a significant rise (2.5 fold) of biodegradation activity was reached in the L field after intensification of AS operation in 2004. Relationship between AS input and observed biodegradation rate is further discussed in chapter 3.2. Decrease of biodegradation, observed in 2005 - 2006 was most probably caused by a substrate limitation in the part of the L field. Total initial balance of TPH in the L field, based on soil sampling, was 728 tons and 401 tons of contaminant was removed till the end of 2005, based on respiration balance. Soil sampling was held in June 2006 and verified decrease of the area contaminated above the soil clean-up goal. The contaminated area was 2.4 ha in 2001 and it decreased to 1.1 ha in 2006. TPH mass balance changes based on soil sampling were not available at the time of the paper preparation.
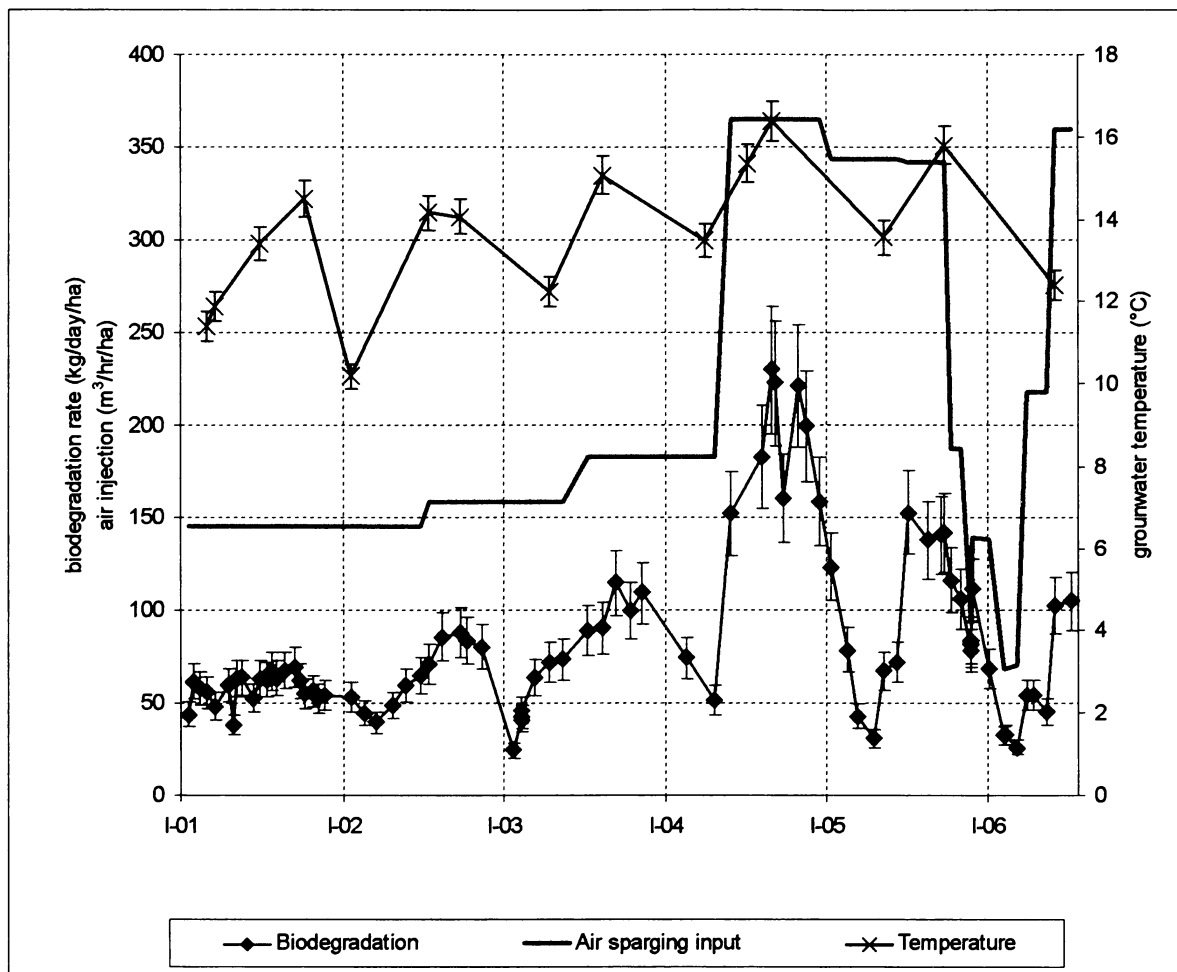
Figure 3: Specific biodegradation rate and GW temperature in clean-up field L (2.4 ha)

Figure 4 shows changes of specific biodegradation rates in the J field in the period 1999 – July 2006. Because of huge contamination, LNAPL removal was under operation in period 1999-2001 and biodegradation was stimulated only by venting. Implementation of AS and nutrients on the whole J field took place in 2001-2002 and a slight increase of biodegradation activity was observed in 2003, but it was inadequate to the field contamination content; the initial field soil TPH mass balance was 1613 tons in J field. AS input was increased to the field and a significant rise in the biodegradation rate was observed in the period 2004 – 2005. But in comparison to the field L, notable higher AS input was necessary for reaching the same biodegradation activity, this fact is further discussed in chapter 3.2. Groundwater temperature changes and following biodegradation activity fluctuation observed in the J field are similar to results from the L field.

Decrease of biodegradation activity rate, observed in 2006, has been probably caused by partial substrate depletion; soil sampling is planned for autumn 2006. Based on respiration balance, 678 tons of TPH was removed from the field since the clean-up start.
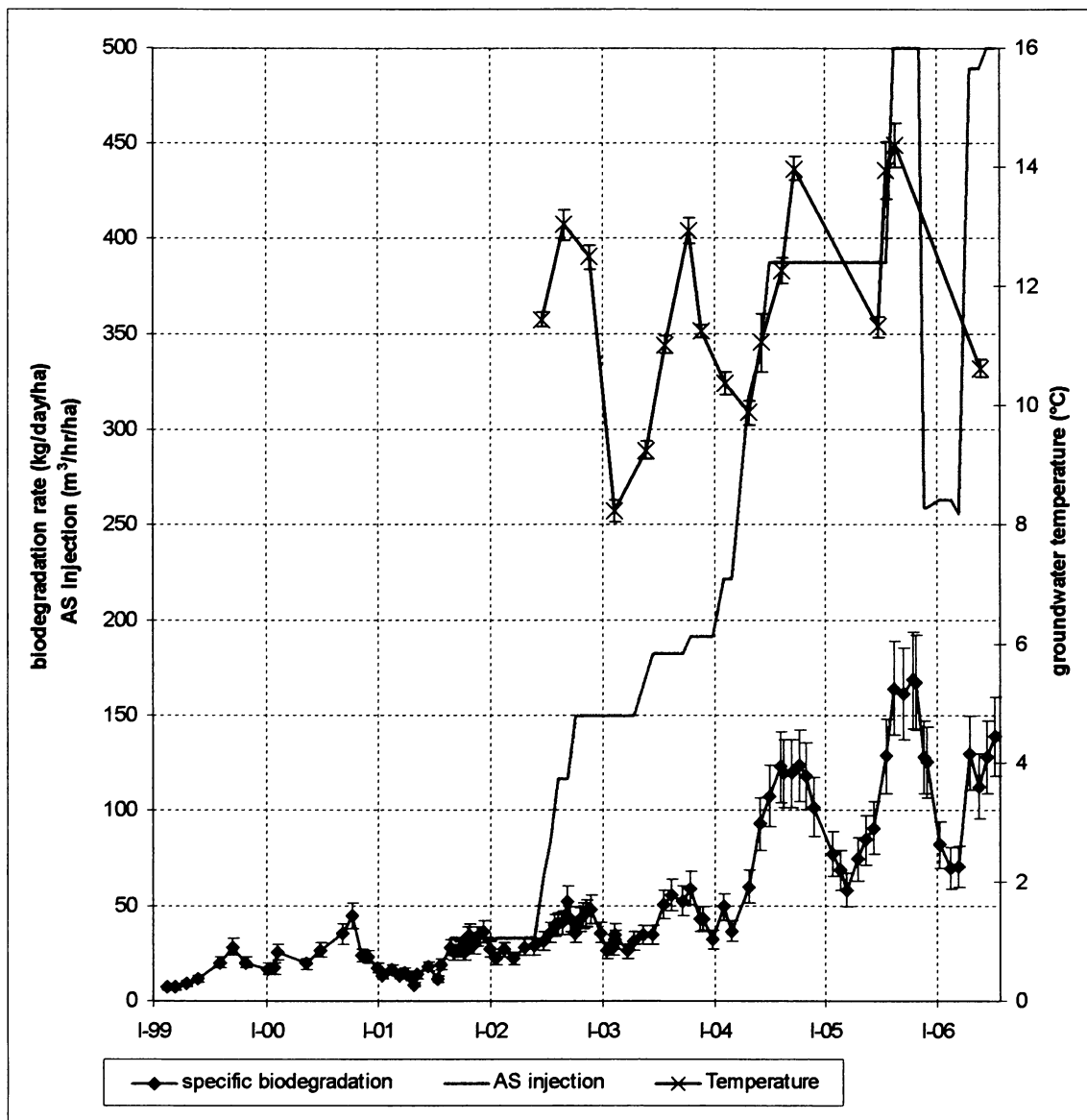
Figure4: Specific biodegradation rates and GW temperature in clean-up field J (4.9 ha)

3.2 RELATIONSHIP BETWEEN AS INPUT, TPH CONTENT AND BIODEGRADATION RATE

Figure 5 documents relationship between specific air injection rates and biodegradation rates in clean-up fields at the Hradčany site (total evaluated area 18 ha). Strong linear correlation (R^2 = 0.98) was observed in fields in the western part of the site, slightly weaker correlation (R^2 = 0.73) was documented in the eastern part, but a narrower range of AS air input rates was applied there. This result demonstrates that sufficient oxygenation is the crucial technological factor which influences biodegradation activity rates during active bioremediation, based on stimulation of aerobic activity of soil microflora.

The significant difference appeared in AS efficiency between the eastern and the western part – for the same biodegradation activity AS input about 40% higher is necessary in the western part. Possible reasons were preliminary evaluated. Fields in the western part has slightly lower average soil specific contamination content (220 t TPH /ha in comparison to 260 t TPH /ha), but the difference is not too significant if considering the importance of soil contamination

content for observed biodegradation rate discussed below. The most probable reason is variation in geological conditions; contamination is bounded to deeper and less permeable layers in the western part, formed by Cretaceous sandstone in comparison to the eastern part, which is formed of Quaternary river terrace.
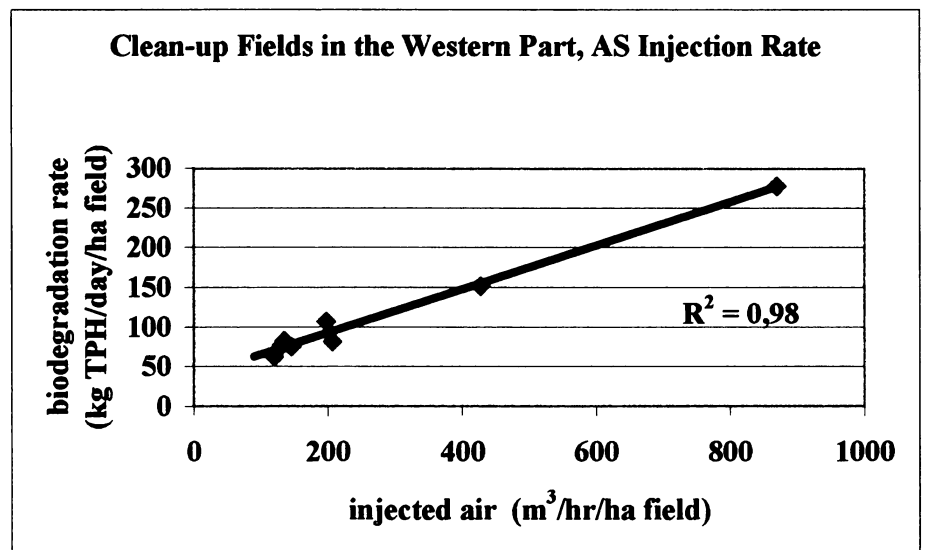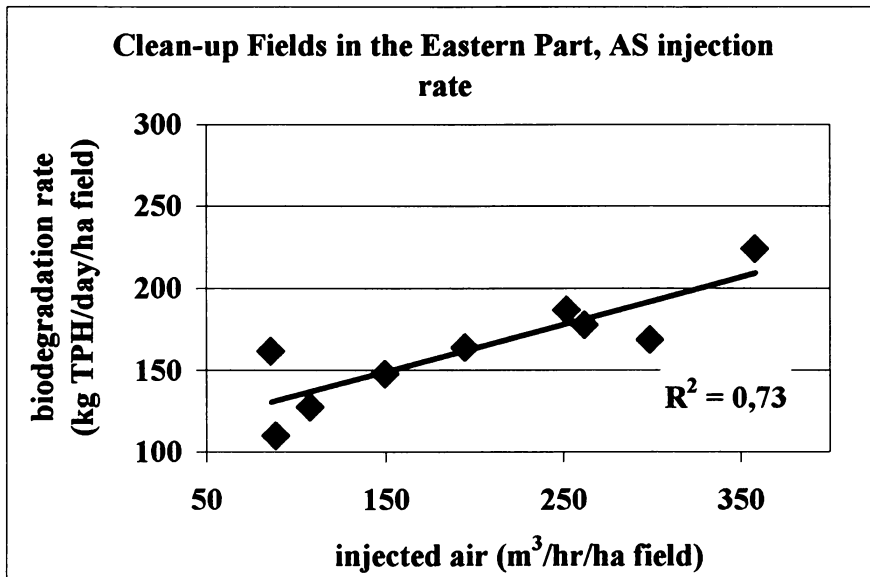

Figure 5: Correlation between the AS air output and observed biodegradation rates, data measured in September 2004

Influence of the initial soil contamination content on biodegradation activity was also evaluated. Initial soil mass balance of TPH in evaluated clean-up fields was in range 111 – 450

tons TPH/ha field with average value 243 tons/hectare and it was correlated with biodegradation activity rates observed in September 2004 (Figure 6). Considerably weaker correlation was found (R^2 = 0.38 for western part and R^2 = 0.56 for eastern part) between observed biodegradation rates and contamination content. These observations show contamination content not being the main factor for *in situ* biodegradation rates in heavily contaminated areas (above 100 tons TPH per ha) during bioremediation. A decrease of biodegradation activity rates was observed after removal of 42% respectively 55 % (based on stoichiometric respiration balance) of the initial soil contamination content in fields J resp. L. Further evaluation between soil contamination content will be held in next year, after complete re-sampling of soil TPH content in clean-up fields.
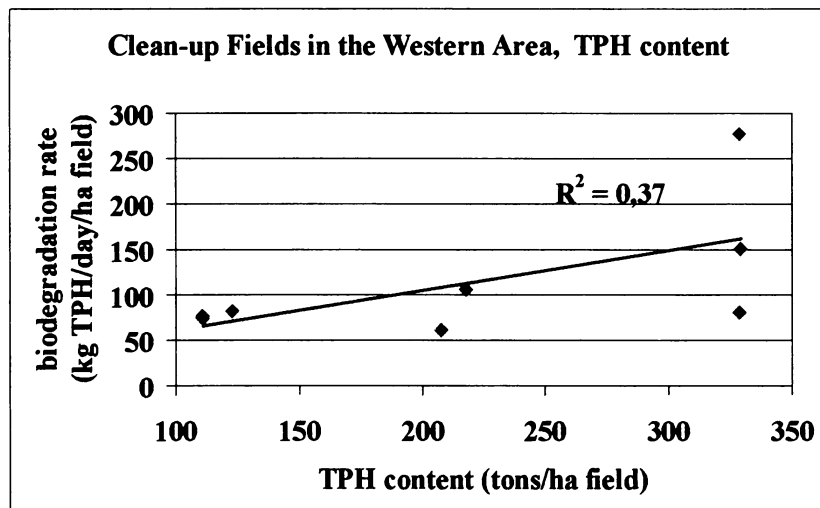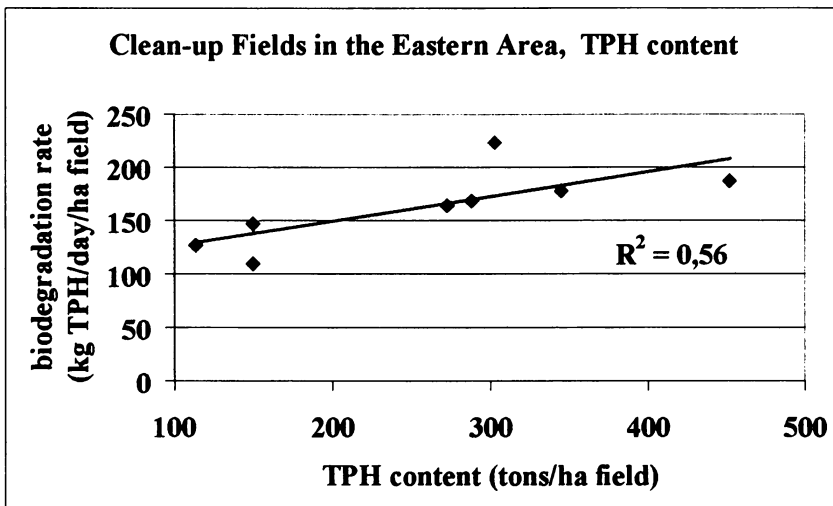
Figure 6: Correlation between initial TPH content and observed biodegradation rates, biodegradation data measured in September 2004

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4 CONCLUSIONS

Observations of influence of three major factors on *in situ* biodegradation rates of jet-fuel during several years of active clean-up were evaluated. Long-term monitoring of groundwater temperature showed seasonal rise and fall of temperature and it consequently caused fluctuation of biodegradation activity during clean-up. On the contrary, rise of average groundwater temperature was observed in the clean-up fields, most probably as a result of clean-up process.

The significant rise of biodegradation rates, observed after air sparging intensification, and strong linear correlation between air injection rates and biodegradation activities showed that the air injection rate is the principal factor for biodegradation efficiency in heavily contaminated areas. It has far more important role for reached biodegradation activity than contamination content, which influence slightly appeared after removal of about 50% of initial contamination.

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Příloha 3

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Methods Used for Assessment of *In Situ* Jet-Fuel Remediation Efficiency – Evaluation of Two Different Approaches

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Abstract: In 1997, total petroleum hydrocarbon (TPH) remediation started at a former Air Force Base, which operated from 1940 to 1991. TPH had been released to soil and groundwater at the site by military activities. The TPH was 70% jet fuel and the affected area was 28 hectares. Remediation involved a combination of technologies, including removal of volatile organic compounds using soil vapor extraction and air sparging, free product vacuum recovery and aerobic biodegradation of organics with oxygen supplied by the air sparging system, along with nutrient addition. The primary remedial method was found to be biodegradation, which has removed 93% of the contaminants from the site to date. A significant aspect of the remedial action was performance monitoring, including documentation of remediation efficiency. The goal of our research was to assess the relative accuracy of methods commonly used for monitoring *in situ* TPH removal. Two such methods were selected for our research: monitoring changes in soil TPH concentration (specified as non-polar extractable substances) and monitoring respiration activity in soil with a subsequent stoichiometric mass balance to estimate the mass of TPH destroyed. The study demonstrated that both of the methods provided comparable results regarding the effectiveness of *in situ* TPH remediation, despite the fact that their methodologies are very different.

Key words: jet fuel, petroleum hydrocarbons, biodegradation activity, soil sampling, TPH, *in situ* clean-up efficiency

1. Introduction

A critical element of subsurface remediation is assessment of remediation efficiency; especially assessment of the dynamics of contaminant removal and changes in the total mass of contamination in the subsurface. These parameters are key indicators of remediation efficiency, demonstrate appropriateness of the selected remediation technology and are essential for estimating the duration of remedial activity and comparison with the proposed remedial period.

The research was focused on assessment of the efficiency of the remedial activity during *in situ* clean-up of groundwater (Wittlingerova and Landa, 2003) and soil contaminated with jet fuel at the former Soviet Hradcany Air Force Base in the Czech Republic. Two basic methodologies were selected for assessment of changes in mass of petroleum hydrocarbons contaminating the subsurface environment. The first methodology assesses the petroleum content decrease based on changes in total petroleum hydrocarbons (TPH) concentrations in soil samples. The other methodology is based on monitoring individual remedial technology indicators, where the mass of petroleum contamination removed is stoichiometrically balanced using the results of remedial process monitoring.

2. Methods

2.1. Site Characteristics

The site was used for military purposes from 1940–1991. These military activities resulted in extensive contamination of the soil and groundwater by petroleum products (70% is represented by jet fuel) in an area of 28 hectares (Figure 1). The site's subsoil is Quaternary sandy-gravel river terrace deposits (thickness 4 m), underlain by Cretaceous marine sediment, consisting of weathered medium-grain sandstone approximately 50 m thick.

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Fig.1. Site layout with areas contaminated above the clean-up goal - 2000 Conditions

Until 1997, the site was remediated using pump and treat and soil venting techniques. The complex remediation of the site based on a combination of several remediation technologies started in 1997, when *in situ* technologies were gradually applied on the site. Removal of volatile organic compounds (VOCs) via soil vapor extraction (SVE) and air sparging (AS), light non-aqueous phase liquid (LNAPL) vacuum extraction, and aerobic TPH biodegradation supported by oxygenation via air sparging and application of nutrient solutions have been applied on the site. (Masak et al. 2003) The clean-up had two phases – first phase was focused on maximum removal of LNAPL (vacuum extraction), second phase was aimed on optimization of favorable conditions for aerobic biodegradation in the entire contaminated profile (air sparging + nutrients). The contaminated area was divided into individual remediation fields with areas of 0.5 – 4.0 hectares for the purpose of remedial operations (Figure 2) and the clean-up technology was consequently installed in each of these contaminated areas. From 1997 – 2005, 3,182 tons of TPH were removed from the site, biodegradation removed 93% of the total amount, vacuum extraction of LNAPL removed 5 %, and SVE/AS removed 2% of the total amount. (Hercik et al., 2006)

Fig.2. Remediation Field Locations
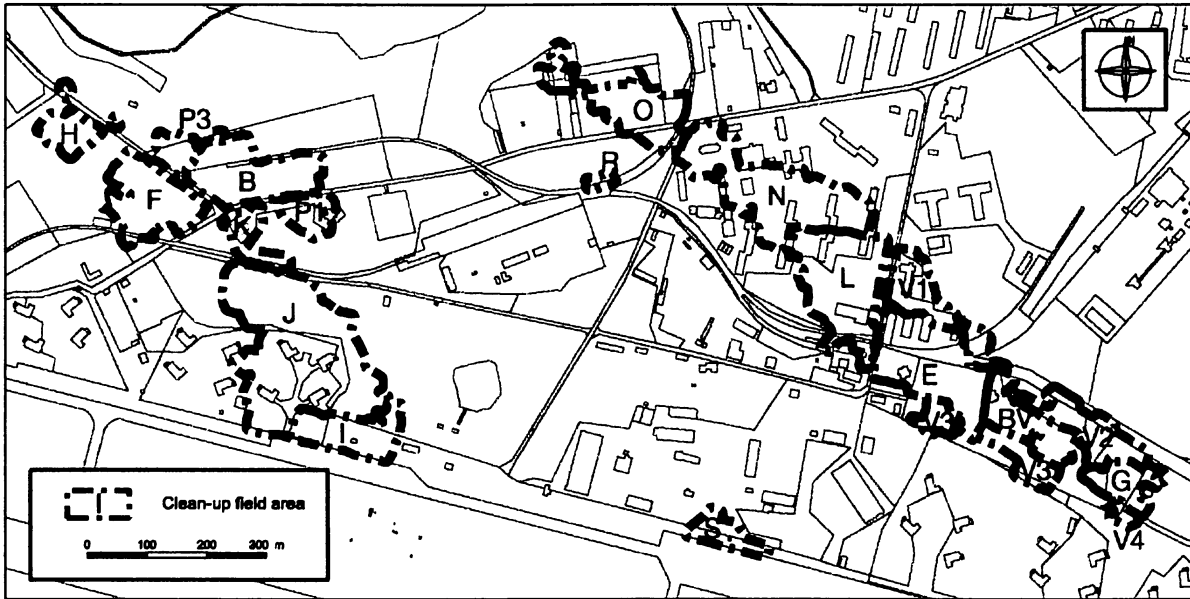
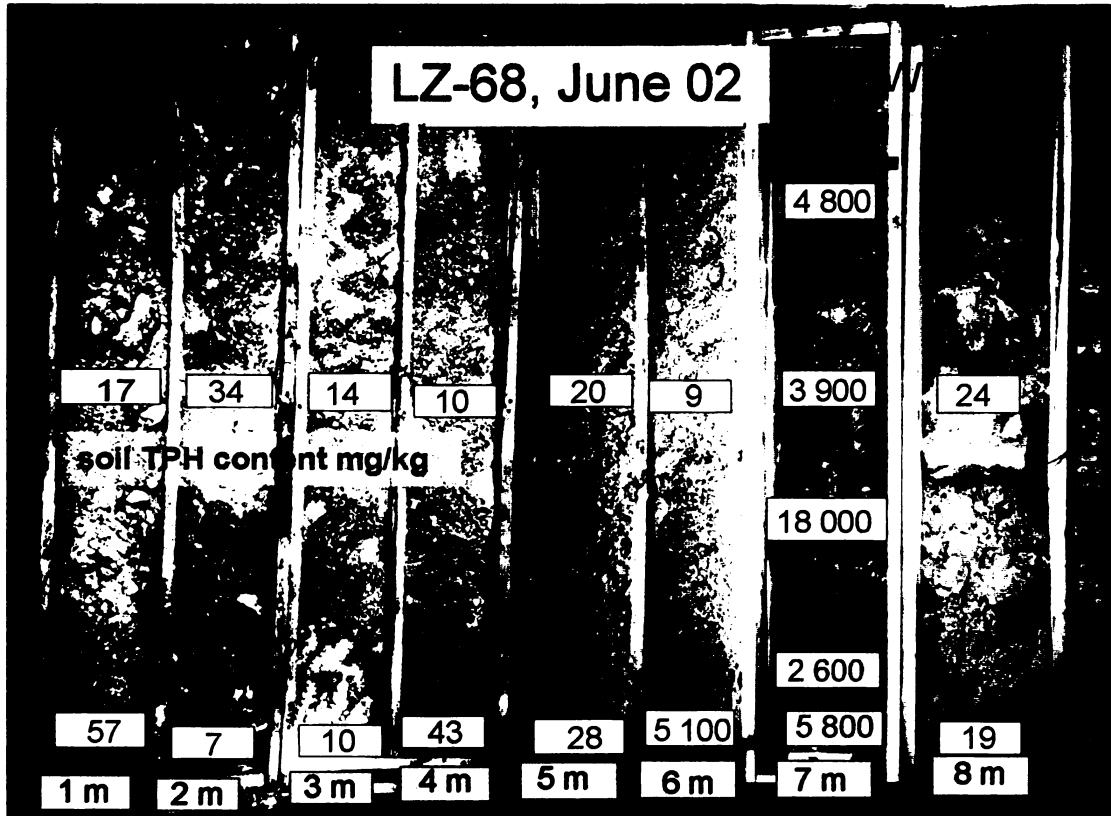## 2.2. Mass Balance of Petroleum Hydrocarbons Remediated Using Soil Samples (Soil mass balance)

A method based on soil sampling from discrete depth intervals (0.5 m) was used to calculate the mass of TPH in soil. A spiral auger was used for sample collection with discrete samples obtained from the tip of the auger immediately after drilling. This method ensured that no contamination was carried down into deeper layers (cross contamination). Samples were collected at defined depths with an accuracy of -/+ 15 cm. The sampling points were arranged in a regular network 20 x 20 m; twenty boreholes per hectare were made. For repeated sampling (with an interval of 2 – 4 years) the new boreholes were made in close proximity to previous sampling points.

The fuels are LNAPL, i.e. substances that are lighter than water and immiscible with water. It was recommended (Downey et al., 1999) that samples for LNAPL characterization be collected only down to the groundwater table. When subsurface releases of LNAPL exceed the soil retention capacity in an unsaturated zone, petroleum substances affected by gravity can reach the groundwater level (GWL), where they form a layer floating on the GWL. They typically do not migrate into deeper layers of the aquifer; however, their movement over time follows natural groundwater fluctuations. But in the event of massive petroleum leakage, a floating LNAPL lens is created on the GWL and as a result of fluid pressure and density differences, this lens may depress the GWL farther than natural fluctuation would cause. After this, as the LNAPL migrates in the direction of groundwater flow, the thickness dissipates, the fluid pressure decreases and the GWL reaches its original depth. However, a significant part of the petroleum remains trapped in soil pores below the GWL even after its level equilibrates (residual saturation). (Machackova et al., 2005)

Because of this process, it is necessary to evaluate the thickness of the contaminated layer to assess the entire contaminated profile, i.e. sampling must extend to a contamination-free depth. If soil sampling does not address the entire depth of petroleum contamination under the GWL, the contamination assessment is incomplete. During the investigation of the Hradcany site, it was found that 80% of the contamination being bounded to layers under GWL and contamination was detected in depth up to 2 m under GWL, despite the natural

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fluctuation of GWL observed at the site is 0.5 m. (Machackova et al., 2005; Hercik et al., 2006) An example of a soil core, documenting migration of LNAPL under GWL, is given on figure 3.

Fig. 3. Photo of soil core from L field with point TPH soil concentrations Note the change of color of contaminated soil layers under GWL, caused by attenuation processes (precipitates of reduced iron and manganese with sulfide)

LZ-68, June 02

4 800

17 34 14 10 20 9 3 900 24

soil TPH content mg/kg

18 000

2 600

57 7 10 43 28 5 100 5 800 19

1 m 2 m 3 m 4 m 5 m 6 m 7 m 8 m

Point soil sampling was selected because the contaminant is dominantly volatile and semi-volatile petroleum substances, and the standard procedures used for the compositing of samples (quartering) would result in a loss of the VOCs. (Boulding, 1995) Similarly, drilling was performed in a controlled manner to prevent excessive heat prior to sampling. The samples were stored in air-tight glass bottles, placed on ice and transported to laboratories in coolers. Soil samples were subject to analysis of TPH through IR detection (ISO TR 11046 method). The confidence interval of laboratory determination of TPH-IR, with $\alpha=0.05$ expressed as twice the relative standard deviation, is 30%.

TPH detection using IR can be affected by the presence of non-polar substances of natural origin, but this method was selected as main monitoring tool because the more precise analytic methodology (gas chromatography) is very expensive and naturally-occurring organic substances are minimal in site soils (background values TOC 0.019% dry weight, TPH < 21 mg/kg dry weight). Analyses of TPH by gas chromatography with flame ionization detector (GC-FID) were used for 5% of samples to verify the LNAPL type. Based on GC-FID results, 90% of hydrocarbons at the site consisted of C_9 - C_{13} fraction at the clean-up beginning and the shift towards heavier fractions was observable during the clean-up. (Hercik et al, 2001)

For mass quantification of TPH in soil of each individual remediation field, the TPH-IR soil data set was converted into a results matrix; the groundwater level was used as a primary dividing line for creation of the matrices. Based on this, the contaminated profile was separated into unsaturated and saturated zones. A capillary fringe with a standard height of 0.5

m was added to the saturated zone. This division is based on contamination distribution, where the contamination is concentrated mostly in the top layer of the saturated zone; therefore the saturated zone was defined as being from 0.5 m above the GWL to 1.0-1.5 m under the GWL. The remedial progress in individual zones is considered as well. (Machackova el al. 2005)

The data obtained at the site were subject to an initial data assessment. This evaluation indicated that it is very difficult to determine the probability distribution of TPH concentrations in the soil at the Hradcany site. The use of a log-normal distribution was not appropriate for the site. Some groups of data did not allow credible estimates of this model parameter due to low numbers of observations and some groups of data showed a wide dispersion. (Hercik et al., 2002) Base don this assessment, the trimmed mean was selected for obtaining the estimated concentration. In comparison with the arithmetic average and the median, the trimmed mean showed the best correlation in all the samples of the entire Hradcany site. The selection of the trimmed mean represented a compromise between the sensitivity of the sample average and the robustness of the sample median (Hercik et al., 2002)

The calculation of mean values was based on the trimmed average for $\alpha = 0.15$, which disregards 15% of the smallest and largest sample values. (Havranek, 1993) The sample data (Table 1) are used for the calculation of the trimmed average (via formula [1]) and the confidence interval ($\alpha=0.1$) of the TPH content in unsaturated and saturated zones of an individual clean-up field. The obtained average is then multiplied by the remediation field area and the sampled thickness of unsaturated and saturated zones. The result is an estimate of the mass of petroleum contamination (in tons) in the remediation field.

$$\bar{x}_\alpha = \frac{px_{(\alpha n+1)} + x_{(\alpha n+2)} + \cdots + x_{(n-[\alpha n]-1)} + px_{(n-[\alpha n])}}{n(1-2\alpha)}$$

[1]

where $[\alpha n]$ represents the integral part of number αn, $p = 1 + [\alpha n] - \alpha n$ and $x_{(i)}$ means the ith order statistics.

During the statistical analysis, the spatial distribution of data is neglected and data are transformed to a one-dimension data file. Further interpretation of the TPH content in the soil was based on two-dimensional maps showing the spatial layout of contaminants. These maps were based on sampling points with geodetic coordinates obtained with an accuracy of 1 cm (in S-JTSK and Balt systems). Data on TPH concentrations were used to calculate a one-side trimmed mean of values greater than 1,000 mg/kg of TPH from layers of the saturated zone (zone II, see Table 1). (Landa, 2000) The basic graphic interpretation was produced with Surfer 6 software with Kriging selected as the interpolation method. The computer output was optimized by hand to produce a final map, which enables to evaluate spatial changes of TPH distribution in clean-up fields during the clean-up.

2.3. Mass Balance of Petroleum Hydrocarbons Removed Based on Monitoring (Remediation mass balance)

Remediation monitoring uses monitoring specific to the technology applied. The mass of removed petroleum contamination is assessed by evaluating VOCs removed through SVE, the mass balance of biodegradation calculated using respiratory gas (O_2, CO_2) monitoring data and free product mass removed via vacuum extraction.

The mass of VOCs removed through SVE/AS is quantified using the concentrations of VOCs in the extracted air volume (Anderson, 1995), and the mass of biodegraded petroleum hydrocarbons is calculated using concentrations of respiratory gases in the extracted soil air

The metabolized hydrocarbons are stoichiometricaly quantified from the volume of oxygen consumed in the remediation zone using equation [2] (Anderson, 1995; Leeson and Hinchee, 1997). The production of CO_2 is monitored as well, for control purposes. (Leeson and Hinchee, 1997) Measurements used for the mass of removed VOCs and biodegradation were conducted at month intervals and the calculation of the total mass of removed contamination was based on results extrapolated between the measurement dates.

[2]
$$B_c = ((Q \times (20.9 - c_{RP})/100) \times \rho_{RP} \times C$$

B_c Total balance of biodegraded hydrocarbons in kg/day for a given remediation field
Q Ventilator flow rate in m³/day
c_{RP} Respiratory gas concentration (O_2) in volume %
ρ_{RP} Respiratory gas specific weight (O_2 1.429 kg/m³, regular conditions)
C Stoichiometric ratio C_xH_y/O_2, 0.29, C_xH_y/CO_2, 0.31

The accuracy and representativeness of the mass balance was estimated by the measurement error. Calculations were based on the measured volume of extracted air and the concentrations of VOCs and respiratory gases. The extracted air volume is obtained by multiplying the streamline flow velocity in the SVE system, measured with a hot-wire anemometer (TA4/5, Airflow), by a known cross-sectional area of the SVE piping. The air volume measurement error was determined from the anemometer relative error, which was 5%. VOC contents are monitored through TPH-GC laboratory analyses utilizing air sorption on an active carbon filter (NIOSH –1501 methodology). The confidence interval for the VOC analysis with α=0.05 is 15%. Concentrations of respiratory gases are measured in the venting piping with a portable multi-gas analyzer (Anagas 95, GI). The relative error of respiratory gas concentration measurements is 2.5%. When calculating the VOC and biodegradation mass balance, the measured values were multiplied and the mass balance error was obtained as a summation of the relative measurement errors. The confidence interval (α=0.05) was determined as double the measurement error; which was 25% in the case of the mass of removed VOCs and 15% in the case of the biodegradation mass balance.

The representativeness of mass removal calculations in the SVE/AS system is affected by another factor – the efficiency of capturing the air flowing through a saturated zone in the venting system. In order to verify the capturing efficiency (Leeson et al., 1999) helium tracer tests were performed in 2002 in three discrete areas (total area 1.5 ha). The observed re-extraction reached 60–90% and its average was 68% (±9%). Based on these results (Leeson et al., 1999), the SVE system capture efficiency was deemed acceptable. The result indicates that the VOC removal mass and the respiratory mass balance were underestimated, but it could also mean that part of the extracted air was not drawn from the contaminated layers and was therefore not involved in the remediation process (Johnson et al., 2000). Based on this assessment, the helium tracer test results were not used for modification of the remediation mass balance results but were only used for evaluation of SVE/AS system effectiveness.

The respiratory balance was further adjusted using background respiration levels, which were quantified on the basis of the remediation field R operation in a non-contaminated area for a period of two years. The background respiration was 2.3 t of organic substances/ha/year and this amount to the clean-up field area was subtracted from the biodegradation mass balance calculation.(Hercik et al., 2001)

The mass of TPH removed through free phase vacuum extraction was derived from direct measurement of the volume of the oil removed using calibrated containers, as well as TPH contamination levels in water after gravimetric separation. The estimated error of this mass estimate is 20%.

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3. Results

The evaluation of remediation efficiency through the two tested methods was performed at two selected remediation fields with areas of 1.2 ha (Field E) and 1.4 ha (Field I) at the Hradcany site. (Figure 2)

3. 1. Field I – Results of Soil and Remediation Mass Balance Estimates

Remediation of Field I started in 1998. SVE/AS and vacuum extraction of LNAPL from the GWL were used for the first 18 months of remediation. Air sparging and application of nutrient solutions through venting piping was initiated after removal of the most mobile portion of LNAPL. Due to the rapid decrease of VOCs in the extracted air, SVE operations ended in 2000, venting in air injection mode was used afterwards with short operating periods in extraction mode for monitoring purposes. (Leeson and Hinchee, 1997) Remediation of the unsaturated zone ended in 2001, when the remediation goals were reached. Since 2002, SVE has been used periodically for monitoring of respiratory gases, AS was used to stimulate in situ biological activity. Remedial progress was monitored during four soil sampling events, which took place in 1998, 2001, 2003, and 2005.

Table 1 shows a sample calculation matrix for the TPH mass estimate in Field I with sampling results from 2001. Figure 4 shows the changes of the TPH mass in Field I evaluated on the basis of soil sampling results. Figure 5 describes the interpretation of contamination spatial distribution changes in the saturated zone (Layer II) between years 1998 and 2005.

Tab. 1. Calculation matrix for petroleum mass in soil based on TPH sampling results (in mg/kg dry soil, June 2001)

Zone	Unsaturated zone – Layer I						Saturated zone – Layer II				
Bore mark / depth under the terrain (m)	0.5 m	1 m	1.5 m	2 m	1.5 m	3 m	3.5 m	4 m	4.5 m	5 m	5.5 m
IZ-046	11	5	7	5	6	7	22,000*	13,000	3,700	30	30
IZ-047	4,000	13	10	7	5	42	8700	12,000	1,800	230	30
IZ-048	91	9	9	6	72	18	6,300	18,000	18,000	9,500	3,000
IZ-049	33	75	10	18	92	72	1500	6,900	2,100	110	30
IZ-050	30	7	8	7	7	970	6,100	15,000	3,700	1,600	970
IZ-051	13	4	8	4	5	360	11,000	6,700		760	280
IZ-052	120	36	15	25	79	14	130	1,400	4,500	4,800	1,900
IZ-053	5,300	780	24	740	800	740	7,800	18,000	14,000	8,100	2,700
IZ-054	170	28	11	12	4	140	8,300	12,000	400	23	45
IZ-055			59	46	260	440	4,800	480	940	20	30
IZ-056	64	1,600	1,600	260	8	32	5,000	8,100	610	43	94
IZ-057	220	7	21	9	27	33	1,500	820	30	59	30
IZ-058		50	21	9	21	2,900	12,000	3,700	2,700	740	170
IZ-059	7	17	9	4	940	1,500	6,300	4,700	950	39	30
IZ-060	8	8	7	9	12	59	2,600	22	260	91	30
IZ-061	42	22	6	4	4	9	3,200	320	180	310	93
IZ-062	73	18	1,500	2900	1,300	3,400	6,100	480	850	880	73
IZ-063	43	13	34	7	4	6	6,700	16,000	1,700	650	30
IZ-064	170	17	5	4	6	240	4,500	8,900	1,400	110	87
IZ-065	3,100	1,400	76	110	94	52	4,200	170	320	36	30
IZ-066	8,900	7,900	6,300	4,200	2,400	470	7,000	4,600	2,900	1,500	830
IZ-067	7,200	5,500	64	570	1,300	590	13,000	3,500	840	1,600	370

*Clean-up goal is 5,000 mg/kg TPH, above-limit values are marked in bold

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Fig. 4. Changes of TPH mass balance in Field I (1.4 ha) based on soil samples
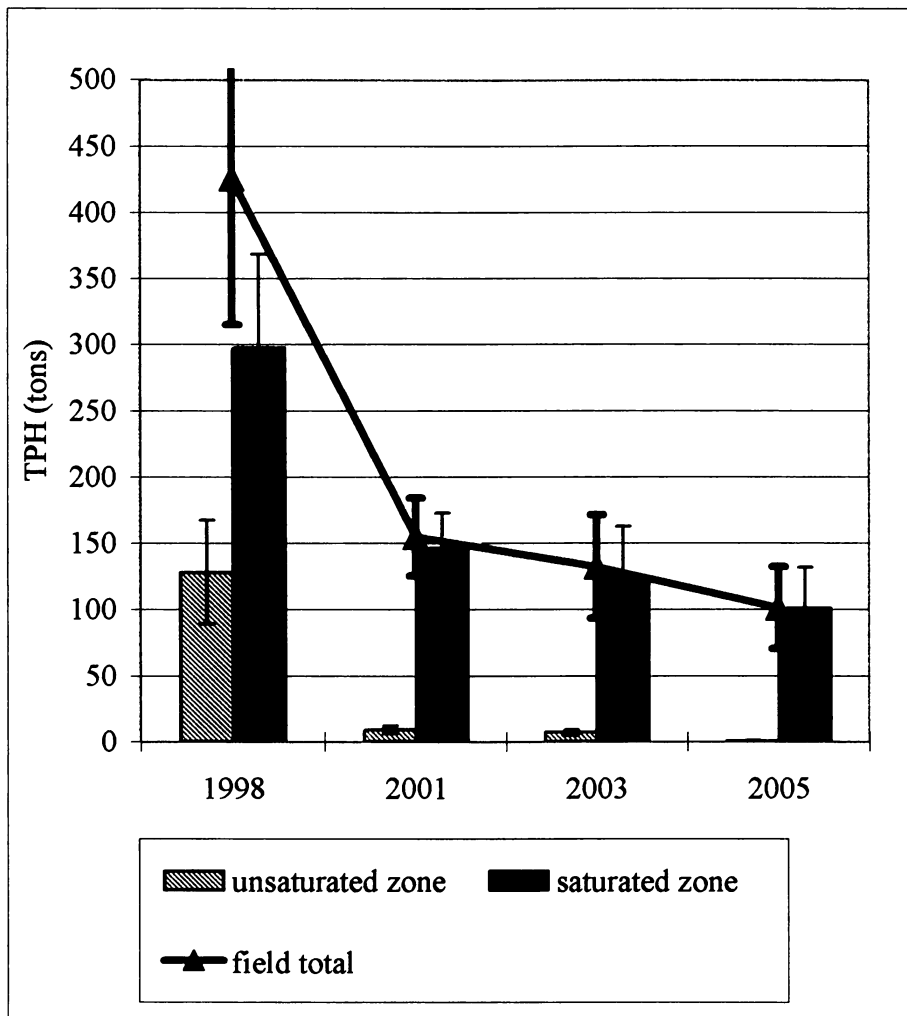

Figure 6 shows the removed amounts of petroleum hydrocarbons based on remediation monitoring results (remediation mass balance). A rapid decrease in the efficiency of physical remediation of the unsaturated zone is apparent on Figure 6. During the period April 1998 – September 2005, free phase vacuum extraction removed 11.9 tons of LNAPL from the I field, SVE removed 11.5 tons of VOCs and biodegradation removed 250.5 tons of petroleum hydrocarbons. Thus biodegradation was responsible for 91% of the contamination that was removed from the I field. The impact of seasonal fluctuation of temperatures on biodegradation intensity is also observable on Figure 6. In 2001 and 2002, a decrease of intensity of biodegradation activity was observed, indicating a substrate depletion. However, soil sampling in 2003 did not show a corresponding decrease in petroleum contamination levels. (Figure 4) As a result of this decline, remedial efforts were intensified in 2003. The volume of air injected into the field by air sparging was increased from 100 m^3/hour/ha to 250 m^3/hour/ha. This increase caused the radius of influence of the AS boreholes to increase (Johnson 2001) and conditions in previously insufficiently aerated parts of the field were optimized. Optimization resulted in higher biodegradation activity rates observed in 2003 and 2004. (Figure 6) The biodegradation activity decrease in 2005 indicated substrate depletion in the remediation field. Soil sampling demonstrated that remediation goals in an area of 0.5 ha were achieved. Remediation ended in that sector and only 0.9 ha of the field remained in operation. The spatial change of contamination distribution in the field presents Figure 5.

Fig. 5. Changes of contaminant spatial distribution in Field I during remediation (saturated zone)
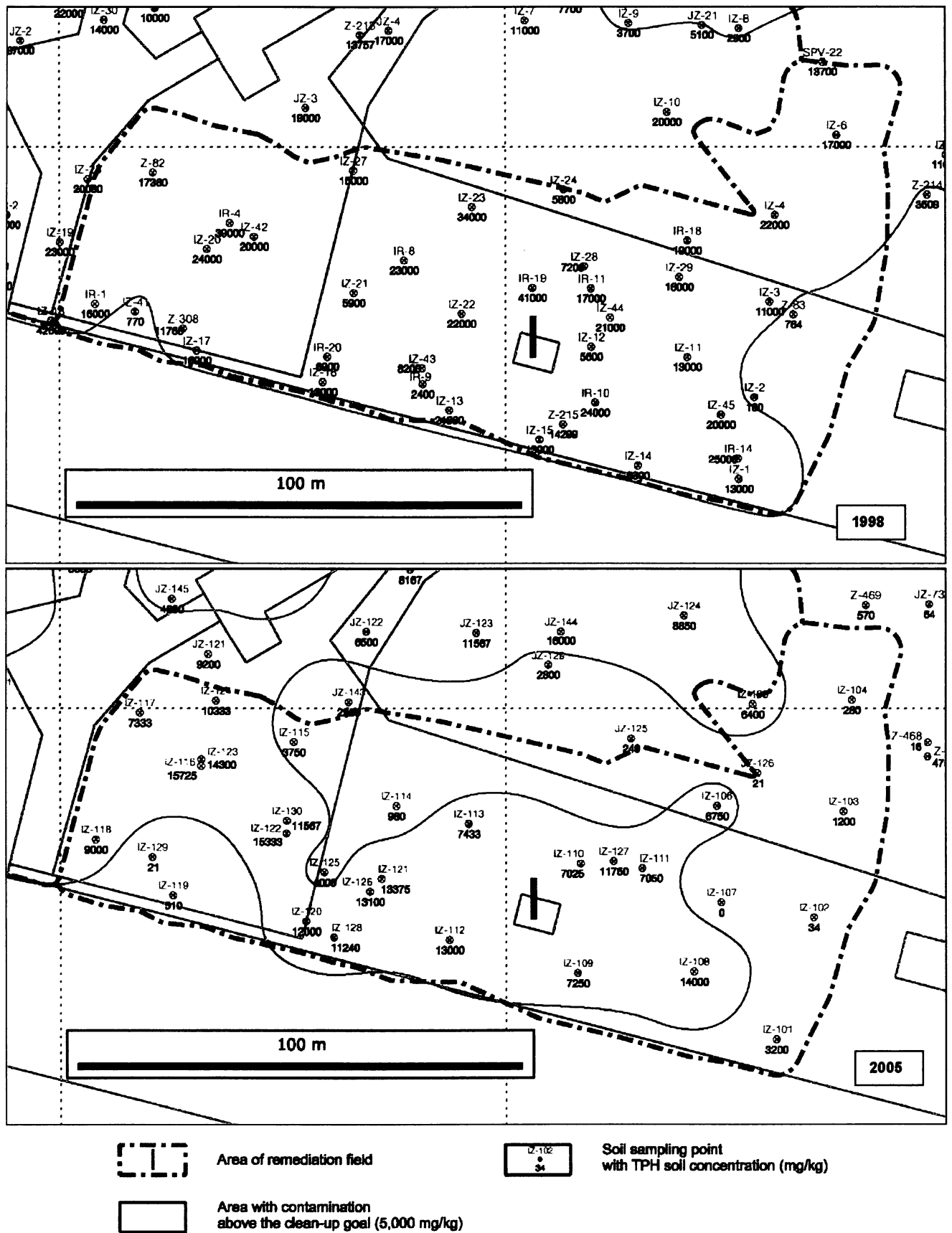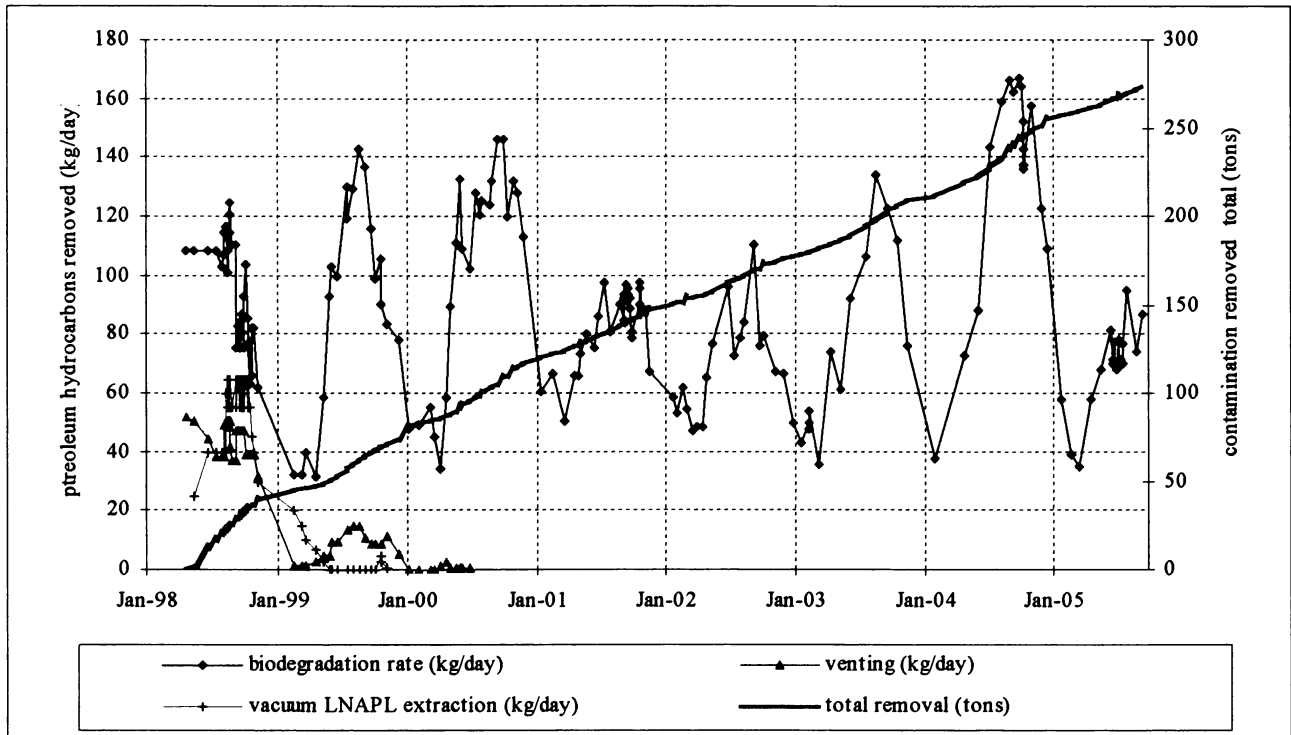

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Figure 6 Petroleum hydrocarbons removed from Field I based on the remediation mass balance

3.2. Field E – Results of Soil and Remediation Mass Balance Estimates

Remediation of the E field started in 1995. Experimental remediation (SVE, LNAPL extraction) of the unsaturated zone took place between 1995 and 1998. In 1998, remediation of the saturated zone (air sparging, nutrient solution application) started. The evaluation was based on the remediation monitoring results and soil sampling results obtained between 1998 and 2002. During the first phase of remediation, different methodologies were used for the mass balance estimates of contamination and therefore results are not comparable. During the assessed period between 1998 and 2002, petroleum contamination was removed from the remediation area through biodegradation only. Figure 7 shows the petroleum contamination mass changes based on soil sampling in Field E. Figure 8 shows changes in spatial contamination distribution and Figure 9 shows the results of biodegradation activity measurement and respiration mass balance.

In 1998, the saturated zone of the E field was more contaminated than the unsaturated zone because contamination in the unsaturated zone was dominantly removed during the earlier remedial period. During the following four years of remediation, the total petroleum mass decreased to 22% of the initial mass in 1998. Removal of some of the TPH contamination was also indicated by the biodegradation activity changes (see Figure 9), where levels dropped significantly in 2001. Based on the results of soil sampling in Field E in 2002, remediation goals were reached over 0.7 ha. The remediation of only 0.5 ha remained in progress. Figure 7 shows changes in the spatial distribution of TPH in the saturated zone. Portions with residual contamination did not form a continuous area, so individual recalcitrant areas were connected to other fields still in operation and further respiratory mass balance calculations were no longer possible. Additional soil sampling will be conducted in 2006.

Fig. 7. Changes of the petroleum contamination mass in Field E (1.2 ha) based on soil sampling
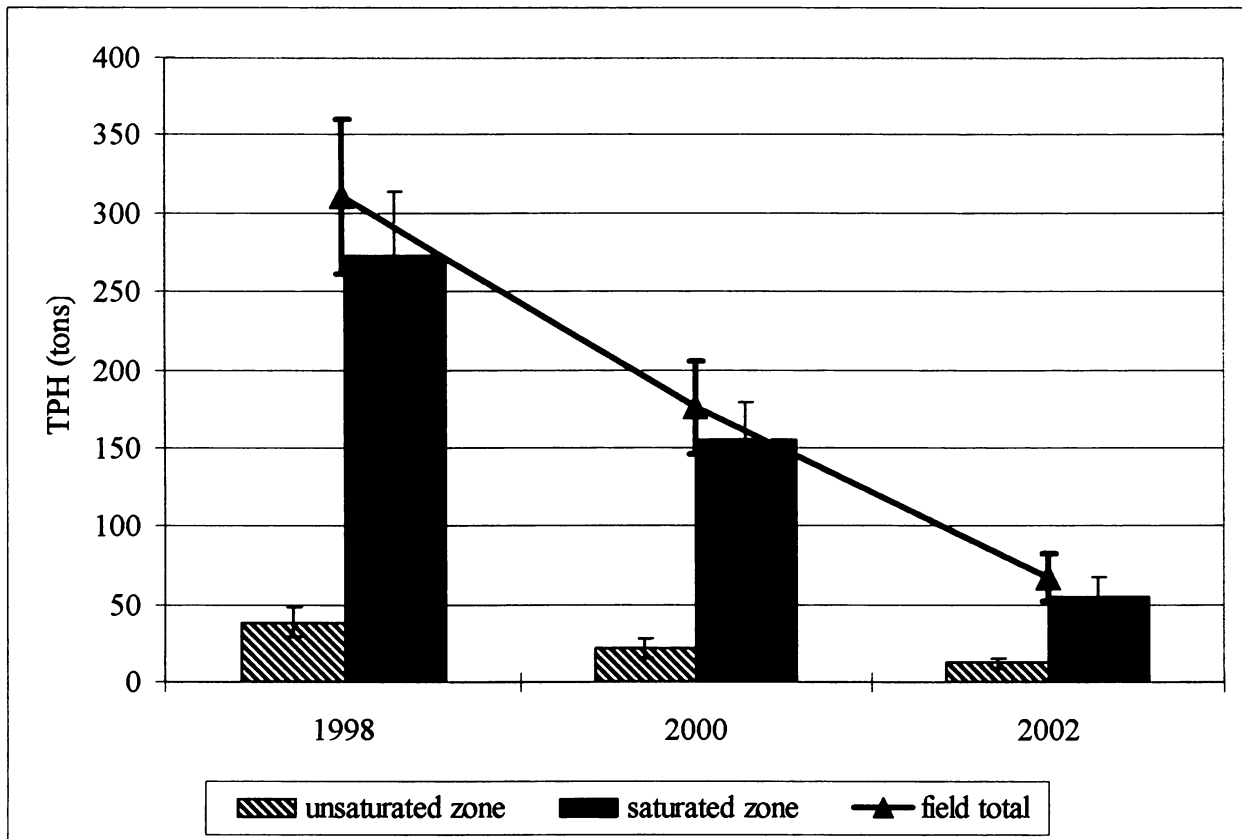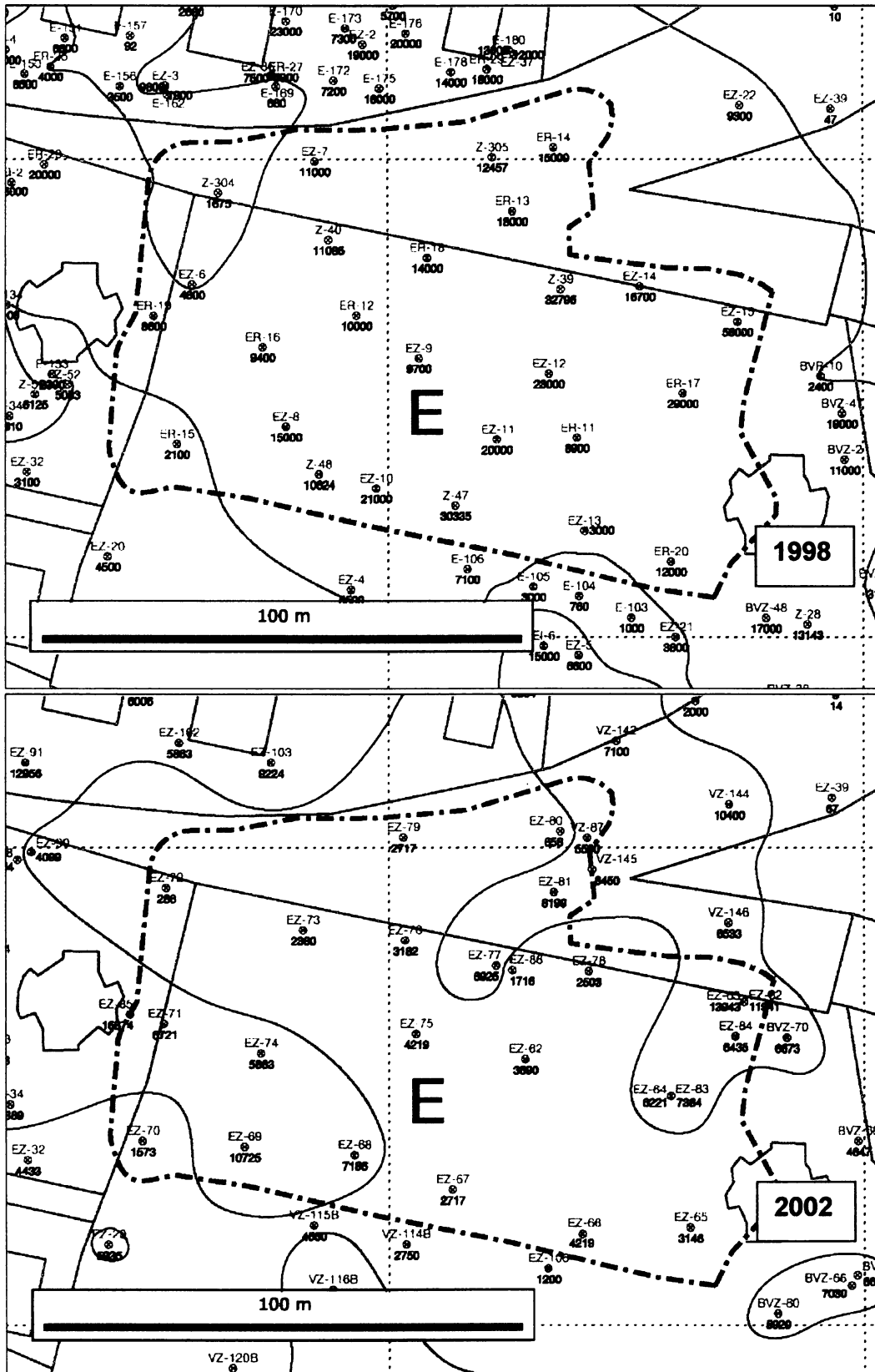
Figure 8 Changes in contaminant distribution in Field E during remediation (saturated zone)
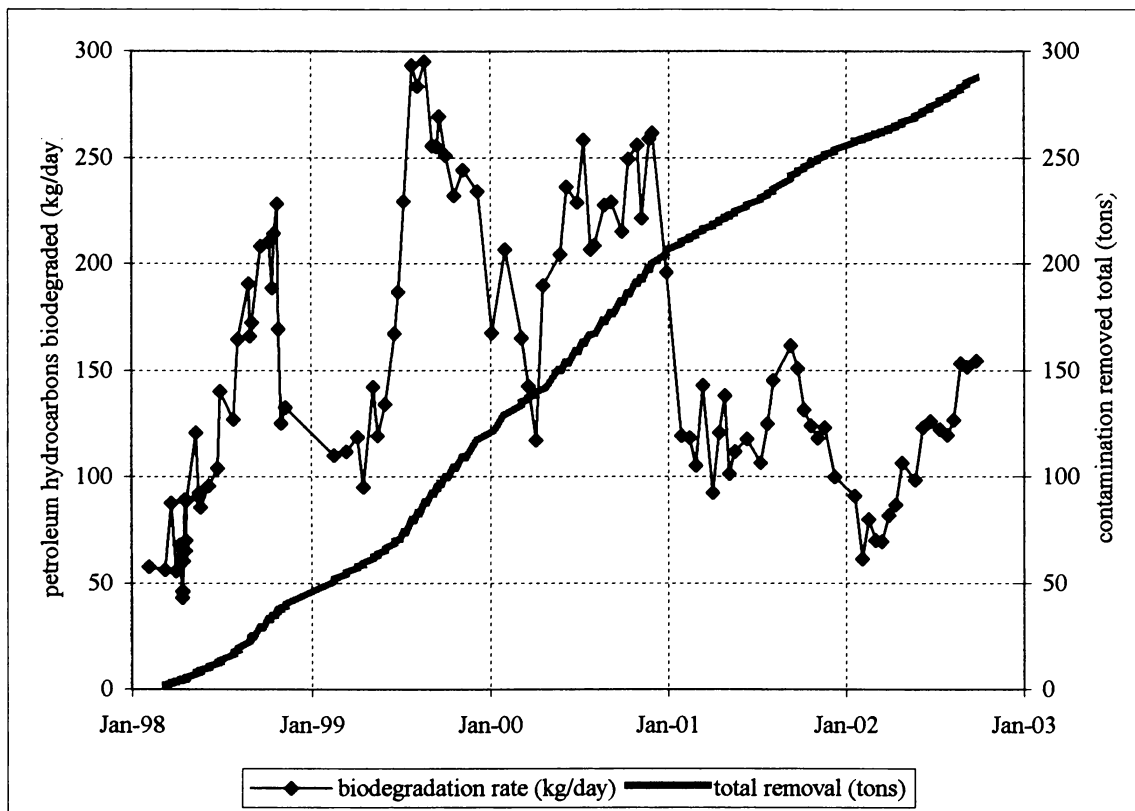

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Fig. 9. Mass of petroleum contamination removed from Field E based on remediation mass balance

4. Discussion

Results of the assessment of soil contaminant mass (Fig. 4 and 7) in both study fields show that the TPH content is continuously decreasing in the treated area. The TPH mass in the unsaturated zone is decreasing much more rapidly than in the saturated zone. Between 1998 and 2001, the TPH mass in the unsaturated zone of I field decreased by an order of magnitude, while the TPH mass in the saturated zone decreased only 40%. One explanation is that remediation was started later in the saturated zone (2000); however, soil contamination results obtained in subsequent years also show a slower decrease of the TPH content in the saturated zone. Faster remedial progress in unsaturated soils is likely the result of easier oxygen saturation than in the saturated zone. Soil vapor used as an oxygen carrier has a maximum oxygen saturation capacity of 21%, while the groundwater maximum saturation reaches only 0.001% under similar technological conditions. This makes reaching optimum aerobic conditions in the saturated zone much more technologically demanding and results in slower bioremediation of highly contaminated horizons below the GWL in comparison to the unsaturated zone.

Comparison of results of the soil and remediation mass estimates in Fields I and E during the study period is provided in Figures 10 and 11. The full lines of soil mass show the TPH levels decreasing during distinct sampling events, compared to the initial TPH mass estimation based on mean values. The dotted lines define the upper and lower confidence intervals (maximum and minimum decrease with $\alpha=0.1$). The remediation mass balance is shown with a confidence interval of respiratory balance $\alpha=0.05$, which was chosen to be the error estimation of remediation mass balance as the biodegradation represents 91% of the contaminant removed from Field I and 100 % of the contaminant removed from Field E.

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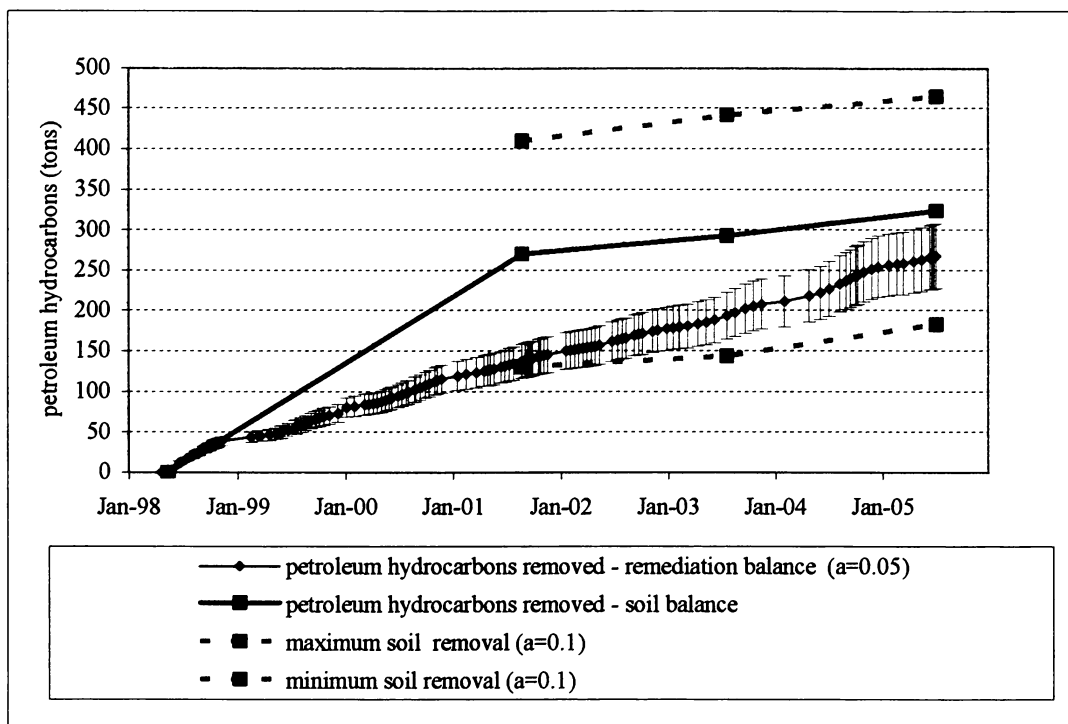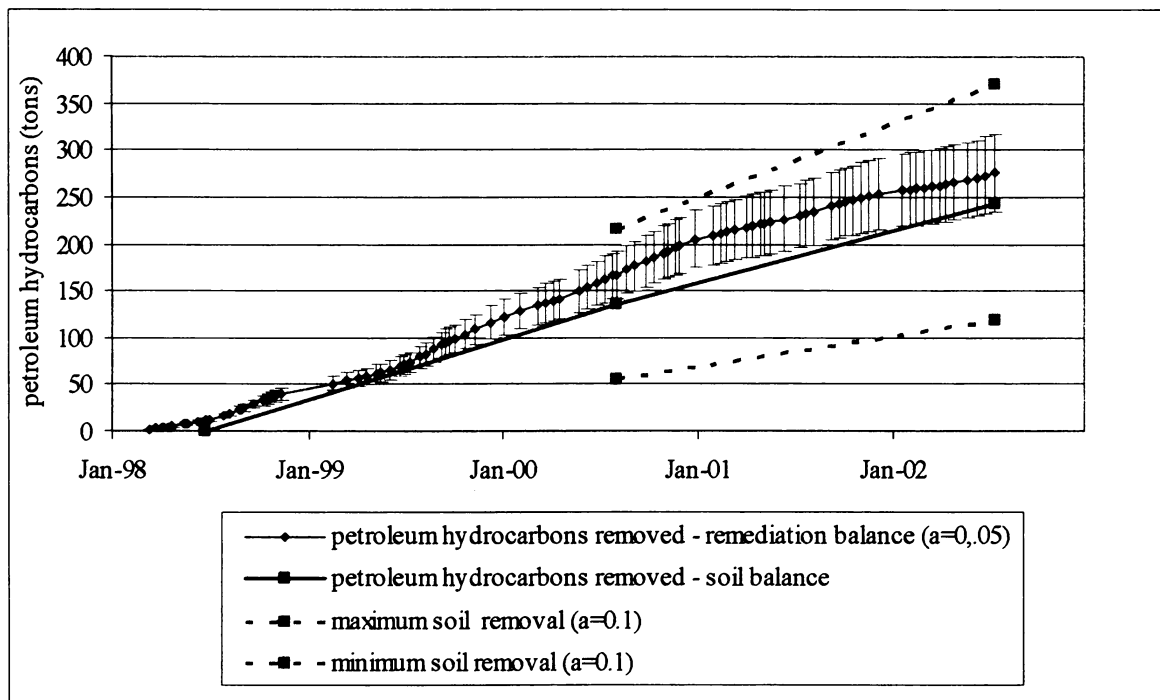Fig. 10. Comparison of soil and remediation mass estimates, Field I

Fig. 11. Comparison of soil and remediation mass estimates, Field E

Figures 10 and 11 document confidence intervals of soil and remediation mass estimates overlap. This shows very good correlation of both of these methods used for quantification of contaminant removed. The graphs further show that contamination mass

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decreases estimated using soil sampling results are less accurate compared to estimates based on remediation mass balance estimates based mainly on respiratory gas data. This is caused by data dispersion (Table 1), which was used to estimate the soil TPH mean and its confidence interval. A larger number of soil samples would have increased the accuracy of the soil mass estimate; however, it would mean higher costs of sampling. Since it is possible to compare the results via remediation mass balance methods (which use data routinely collected and available at significantly lower cost), it is not necessary to increase cost to improve the accuracy of the TPH mass removal estimate. Nevertheless, the lower accuracy of soil sampling results must be taken into consideration when planning sampling strategies. The average rate of TPH removal at the site is 25 tons of TPH/ha/year. (Hercik et al. 2006) The TPH soil mass balance confidence interval is 20 - 30%, yielding approximately 20 to 40 tons. Remediation results may not be demonstrable at a particular level of statistical significance in a period of time of less than 3 years (Figure 5, interval 2003–2005), since the removed amount of contaminant is lower than the confidence interval.

The remediation mass balance method shoved to be more accurate and more operational than the soil sampling estimate – data on remediation process efficiency are routinely obtained at monthly intervals. However, it is an indirect mass balance, which does not directly evaluate the decrease of contaminating substances in the environment – it is derived mostly from the metabolic activity of soil microflora. In addition, since the remediation mass balance is an estimate of removal rates, it can not be used to estimate the mass of remaining TPH in soil, or to determine if remediation goals have been reached. During monitoring of respiratory activity, it is necessary to consider potential sources of errors (background respiration, which does not have to be negligible at localities with a higher organic content, possible air leaks and short-circuiting outside the remediation area, which should be evaluated via helium tests). It is also very important to pay attention to the accuracy of measurement procedures. The remediation mass balance estimate is also unable to cover spatial changes in a contaminated body – i.e. reaching the remediation limits in a part of the remediation area, which will not need further remediation. But biodegradation activity changes may be used as an indicator of a time period suitable for soil sampling – contaminant depletion is often signaled by decreased biodegradation rates in the field (Field E in 2001 and Field I in 2005). Nevertheless, decreased biodegradation activity may also mean an insufficient function of remediation technology, which was detected in Field I in 2003.

5. Conclusions

The foregoing assessment has demonstrated that results obtained by each of the two methods used for monitoring the efficiency of *in situ* remediation of jet-fuel subsurface contamination at the Hradcany site, are comparable despite being based on different principles. Although the remediation mass balance approach is an indirect method, based mainly on monitoring of microbial aerobic respiration activity, it may be used for assessing contaminant removal with the same reliability as the results of TPH analyses in soil samples. A combination of both methods may be used as a convenient tool for monitoring of remediation process efficiency and for the identification of potential errors of individual estimates or insufficient function of biodegradation technology.

6. Acknowledgements

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Příloha 4

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In Situ Bioremediation of Petroleum Hydrocarbons at the Former Soviet AFB Hradcany, Czech Republic

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ABSTRACT: The remediation of large-scale petroleum contamination at the former Soviet army air base Hradcany belongs to the most important clean-up projects in the Czech Republic. The presence of petroleum hydrocarbons (PH, mainly jet fuel) in groundwater endangers groundwater resources and limits future use and revitalization of the site. The total balance of PH released to the environment was 7.150 tons. For the remediation a complex approach including physical and biological methods is used. The remediation principle is biological oxidation of petroleum hydrocarbons by the indigenous bacterial strains. To the end of 2004, the remediation technology was implemented on the area of 27 ha and **3467** tons of PH was removed to that date.

SITE CHARACTERISTIC

From World War Two the site was used as a military airport.. The German Army founded it, afterwards the Czechoslovak Army operated it and from 1968 to 1990 the Soviet Army used it. The first investigative and emergency remedial works commenced in 1989 and full-scale clean-up started in 1997.

The Hradcany air base clean-up is the most important long term project financed by the Czech Ministry of Environment. It belongs to the world's largest "in situ" bioremediation projects.

The site is a part of the Bohemian Cretaceous Basin, the most important resource of high quality groundwater in the Czech Republic. The endangered aquifer is the only source of drinking water in the region. The presence of extensive contamination limits future use and revitalization of the site.

The geological profile of the site is the following: upper layers (0,5 - 3 m) are formed by Quaternary river sediments (sands, gravels), the aquifer is represented by middle to fine grained Middle Turonian sandstone with thickness from 67 to 75 m. The base of the aquifer is formed of Lower Turonian siltstones and marlites with thickness about 75 m. Groundwater table depth varies from 3 to 8 m under surface.

In 1997 the volume of contaminated soil in the 28 ha area was estimated to be 490 000 m^3. The maximum pollution is present in the smear zone - the soil layer influenced by fluctuation of the groundwater table. Average thickness of the contaminated soil is 1,75 m and its depth varies between 3 - 10 m below the surface. In this layer the average concentration of total petroleum hydrocarbons (TPH, infrared detection) was 8.800 mg/kg. The total amount of TPH, which was released into soil and groundwater, was estimated on 7.150 tons. At the start of the clean up the free oil phase (LNAPL) was frequently present in the wells in the thickness over 0,5 m. Pollution consisted mainly of jet fuel (70%), with admixture of gasoline and diesel.

CLEAN-UP LIMITS

The clean-up limits was given by The Czech Ministry of Environment, based on the results of risk assessment as follows:

- Oil hydrocarbons (TPH infrared) in soil   5000 mg/kg
- Oil hydrocarbons (TPH infrared) in groundwater   5 mg/L, absence of LNAPL
- BTEX in groundwater   1 mg/L

DISTRIBUTION OF POLLUTION

Several principal source zones of petroleum pollution were identified at the site – three storage areas and the jet fuelling depot. The pollutants migrated great down gradient distances due to more than 20 years of massive fuel leakages in source areas and high

permeability of sandstones. The contamination was first detected in 1986, when the eastern plume reached the river bank, which distance from the storage area was approx. 2 km. The plume shape was partly controlled by highly permeable beads of Quaternary fine gravels, where the predominant flow of pollutants and groundwater occurred. The horizontal contamination extent in 2000 is on fig. 1, (result of soil sampling, regular sampling grid 20 boreholes/ha, averages of smear zone).

The vertical extend of pollution was found deeper below groundwater table level (GWL) during clean-up monitoring, than was expected in 1997. It reached 2,5 m below GWL in the source areas and was found in 1,5 m depth below GWL in the areas of pollutants transport. The thickness of the smear zone found on the site is not only the result of GWL fluctuation (it is only 0,75 m), but it is caused by a gravitational penetration of fuels after extreme leakages, which occurred in a relatively short period of time – see fig. 2.

Figure 1: Horizontal TPH contamination extent at Hradcany air base in 2000

500 m   ———— TPH average in soil above 5000 mg/kg
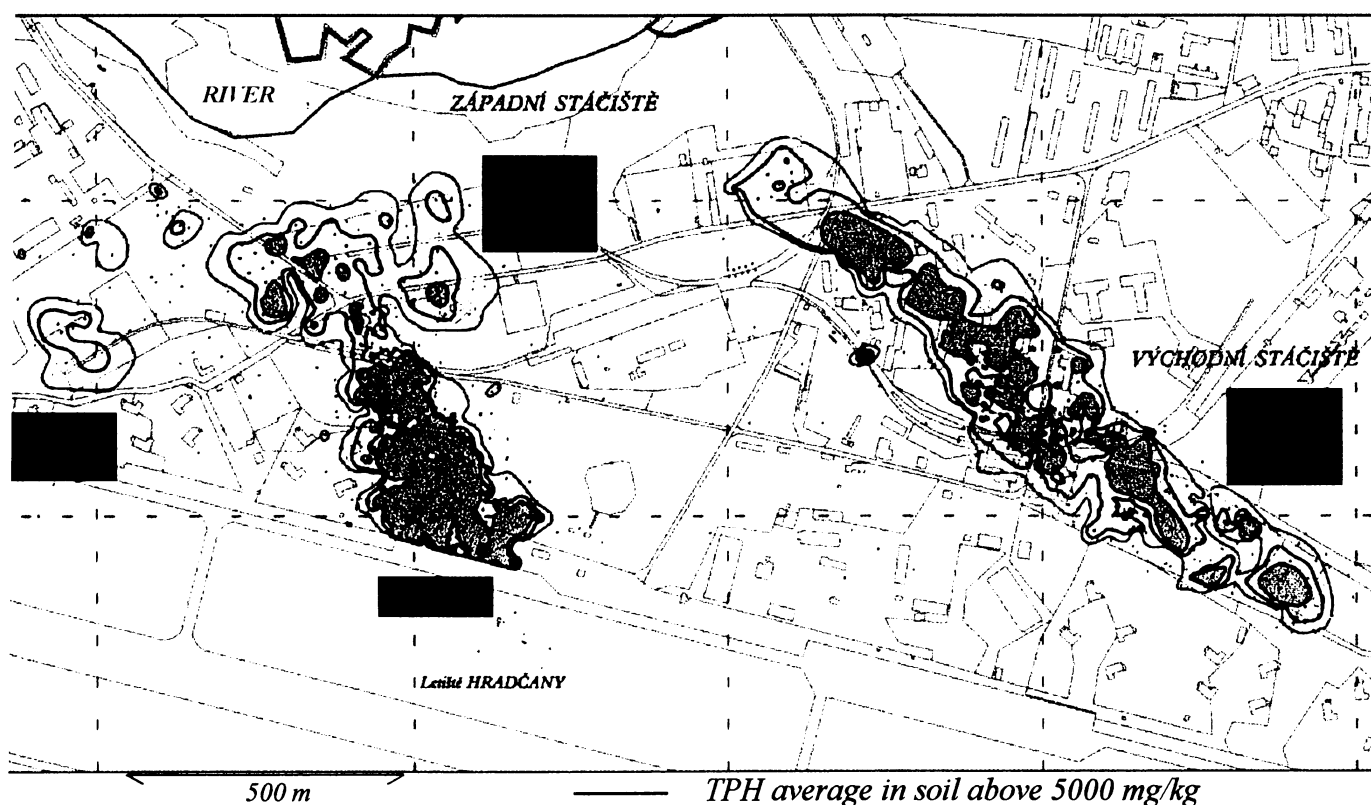
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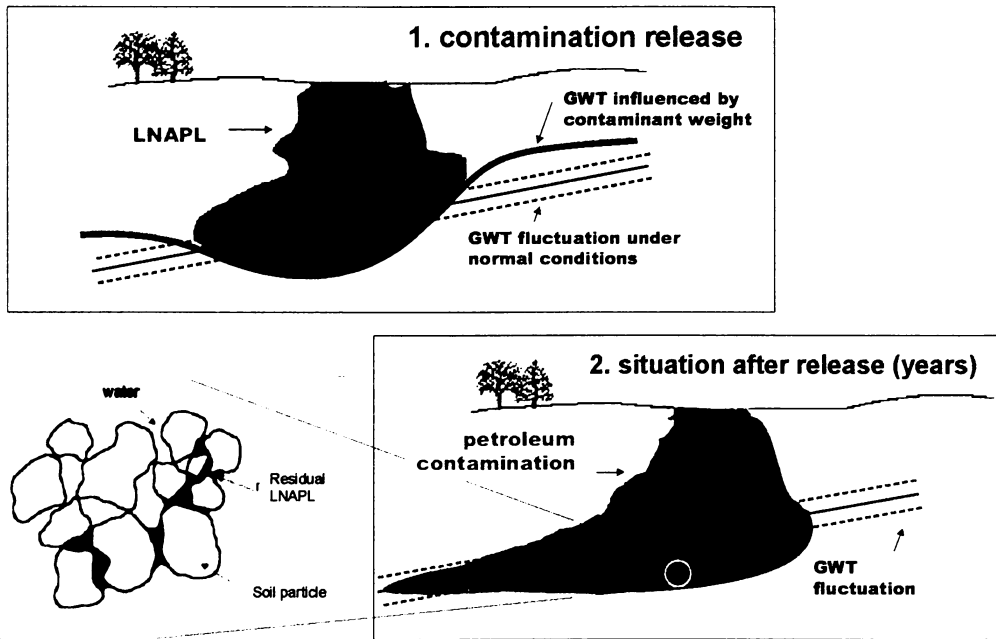*Figure 2: Scheme of gravitational penetration of LNAPL under GWT*

Fig. 3 shows the average distribution of pollution in the soil profile at the start of the clean-up.. The figure of contaminant's distribution is based on results of detail soil sampling, with infrared detection of TPH mass. Soil samples were taken in regular grid and in 0,5 m depth intervals. The possibility of cross contamination from the upper to the lower part of soil profile was eliminated by means of downwards moving casing during drilling.

Fig. 3 represents results of 900 soil samples in an area of 12 hectares in 2000 – 2001. The Fig. 2 shows, that 85 % of pollutant content is concentrated below GWT. The unexpected depth of the pollution caused initial underestimation of the site pollutants balance, which resulted in partly insufficient clean-up technology design in the most contaminated parts of the site (detailed description in section 7).

Figure 3: Distribution of TPH pollution in the soil profile (2000 –2001)
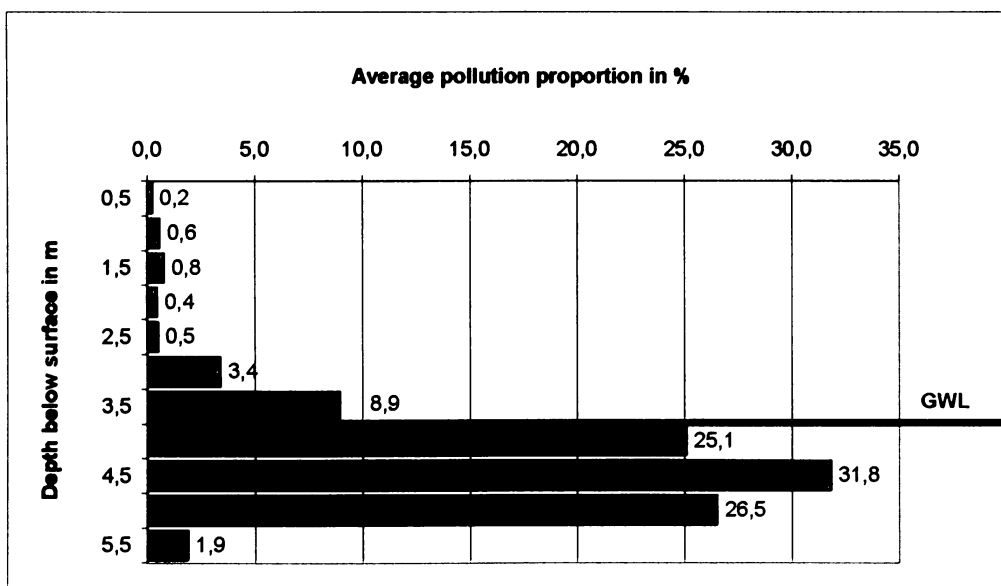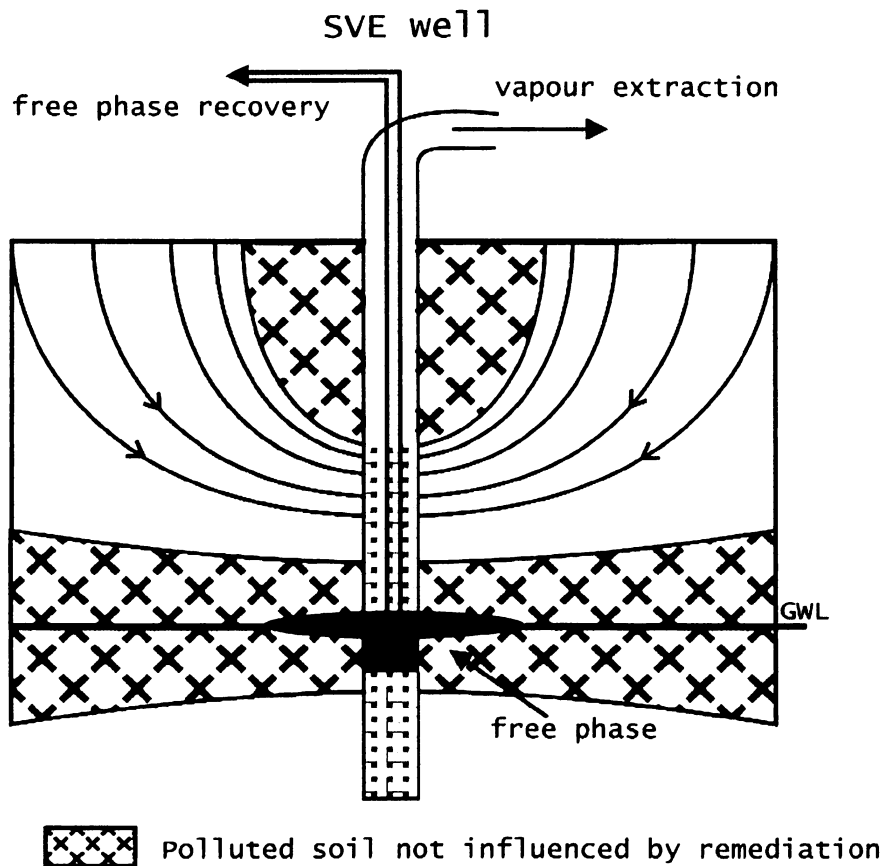
CLEAN-UP TECHNOLOGY

A combination of several clean-up technologies is used on the site. Both physical and biological methods have been implemented. Remedial works are divided into two stages.

The first stage employs soil vapor extraction (SVE) and recovery of LNAPL by vacuum pumping (bioslurping), for scheme of technology see fig.4. The main aim of this stage is maximum removal of free oil phase. In addition, volatile compounds are removed from unsaturated zone by venting.

Figure 4: Clean-up stage I. The schematic layout of SVE and vacuum extraction

SVE well

free phase recovery   vapour extraction

GWL

free phase

⊠ Polluted soil not influenced by remediation

The main remediation method is in situ aerobic biodegradation on the site. Biodegradation activity of indigenous aerobic microorganisms is stimulated by oxygen delivery and nutrient amendment. Petroleum hydrocarbons are used as a source of carbon and energy by soil bacteria and are transformed to harmless substances – water, biomass and carbon dioxide.

Air sparging (AS) and nutrient amendment (N, P and K) are implemented for support of soil microorganisms in the second stage (see Fig. 5). The aim of the second stage is removal of limiting conditions for aerobic bacteria in the whole contaminated soil profile.

Figure 5: Clean-up stage II. The schematic layout of AS and SVE
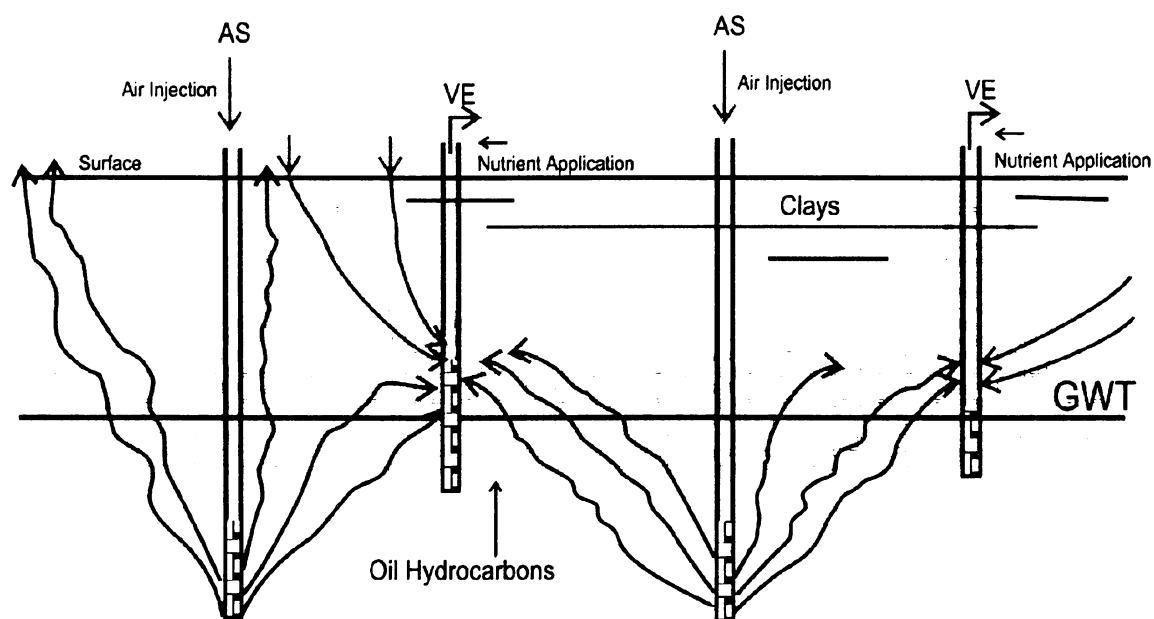
The crucial condition for aerobic biodegradation is a sufficient supply of oxygen. Two systems are used for oxygen delivery - SVE and AS. Ambient air is used as an oxygen carrier. SVE is effective only in the unsaturated zone, for aeration of the saturated zone AS is used.

Microcosms batch laboratory studies showed another important limiting factor for biodegradation at the site - a deficiency of mineral nutrients (N and P), given by the natural geological conditions at the site. The possibility to use synthetic surfactant to improve bioavailability of pollutant was tested, but no or only a slight increase of biodegradation activity rates was observed during laboratory studies.

Effectiveness of SVE decreases relatively quickly. When concentration of volatile TPH in extracted air falls below 1 500 mg/m the SVE system is switched to injection mode (bioventing). Clean up of unsaturated zone ended in 2002 by reaching clean-up limits and since that SVE has been operating only periodically for measuring respiration intensity in saturated and unsaturated zones since.

The clean-up started on 2 ha in 1997. The contaminated area was divided into clean-up fields (0,5 - 2 ha) and the clean-up technology was gradually installed on the site. In 2004 the clean-up system was installed in an area of 27 ha of polluted soil and groundwater. The second stage of the clean up (AS + nutrient application) was under operation on 19 ha, clean-up was completed on the area of 8 ha, 1,5 ha was prepared for installation in 2005. The clean-up technique operated during the year 2004 see in table 1.

Table 1: Installed Clean-up Technology on Hradcany airport (2004)

Technology	No. of wells	No. of engines	unit output
Venting	1620	28 blowers	180 cu.m./hour
air sparging	1680	52 compressors	75 and 180 cu.m./hour
nutrient solution amendment	1200		6 000 m^3 of nutrient solution /year

CLEAN-UP MONITORING

Efficiency of the clean up is monitored by direct measurement of free phase thickness in wells, monitoring of volatile petroleum hydrocarbons concentration in extracted air and monitoring of TPH concentrations (quantitatively and qualitatively) in soil and groundwater.

Measuring of concentrations of respiration gases in SVE system and conducting in situ respiration tests in soil and groundwater monitor biodegradation activity. Concentrations of respiration gases measured in SVE system are used for balancing total biodegraded amounts of petroleum hydrocarbons (based on methodology proposed by Leeson, Hinchee 1997). Quantification of hydrocarbon biodegradation is based on a stochiometric relationship between oxygen consumed/ carbon dioxide produced per kg of metabolized hydrocarbon.

Concentrations of O_2 and CO_2 are measured in SVE system outlets twice a month, which allows observation of changes in biodegradation activity.

Factors influencing biodegradation activity (oxygen content in groundwater and soil air, groundwater nutrient content, pH, temperature) are monitored during the clean-up.

BIODEGRADATION MONITORING RESULTS

Fig. 6 shows results of biodegradation in clean-up fields E and L (2 ha each) in the period 1998 – 2004. The E field was under operation from 1998, the L field from 2001. Fig. 6 shows seasonal changes of biodegradation activity influenced by the groundwater temperature fluctuation and clean-up process. Annual groundwater temperature changes in range 4 - 6 °C, with a minimum in February – March, which is 6 – 8 °C and maximum in August – September, which is 10 – 12°C (see background results in fig. 6).

The average groundwater temperature rises significantly (by 4 – 6°C) in clean-up fields in comparison to background groundwater temperature (see fig. 6). A significant rise is observable even during the clean-up, together with the rise of the biodegradation activity. The cause of increasing temperature is a low efficiency of bacterial metabolism, when a portion of metabolic energy is released in a form of waste heat.

Point *in situ* measurements of groundwater temperature shoved increase up to 25 °C in areas with high biodegradation rates (see picture 7), which represents increase to the background temperature to more than 13 °C.

Groundwater temperature was found to be important factor influencing the biodegradation activity and also being an indicator of intensity of the bioremediation process.

Fig. 6 further shows changes of specific biodegradation rates caused not only by the temperature fluctuation, but also by the clean-up operation. Implementation of AS and nutrients on the whole E field took place in 1998 and 1999. Optimization of conditions for indigenous aerobic bacteria resulted in high specific biodegradation rates observed in 2001 – 2003 period. A significant decrease of amount of TPH biodegraded was observed in 2003. It indicated substrate limitation in final clean up stage. The field content of TPH in groundwater and soil was resampled and operation of clean-up was shut down in part of it. The clean-up was focused on the most contaminated part of the E field, which brought a rise of specific biodegradation rate in 2004.

The L field shows a different situation. The clean-up technology (AS and nutrient amendment) was fully implemented in 2001 in the field and a rise of biodegradation rate followed immediately. But vertical contamination extent was underestimated in the L-field and significant oxygen deficits appeared in the field. AS output was doubled in the L field in Spring 2004 and it resulted in more than two-fold increase of specific biodegradation rates observed in the field in that year.

The point biodegradation rates are also measured in soil air and groundwater on the site. The changes of respiration gases content in soil air and dissolved oxygen in groundwater are measured in respiration probes and selected boreholes after aeration shutdown. Oxygen depletion rates are recalculated on amounts of petroleum hydrocarbons removed from soil – to format mg TPH/kg soil/day. The measured values of biodegradation rate in soil and groundwater vary in range 0.5 – 12 mg/kg/day, with average 3 mg/kg/day. The value of a point biodegradation rate serves as an indicator of the biodegradation process in a particular part of the site.

Figure 6: Specific biodegradation rates and temperature in clean-up fields (2 ha each)
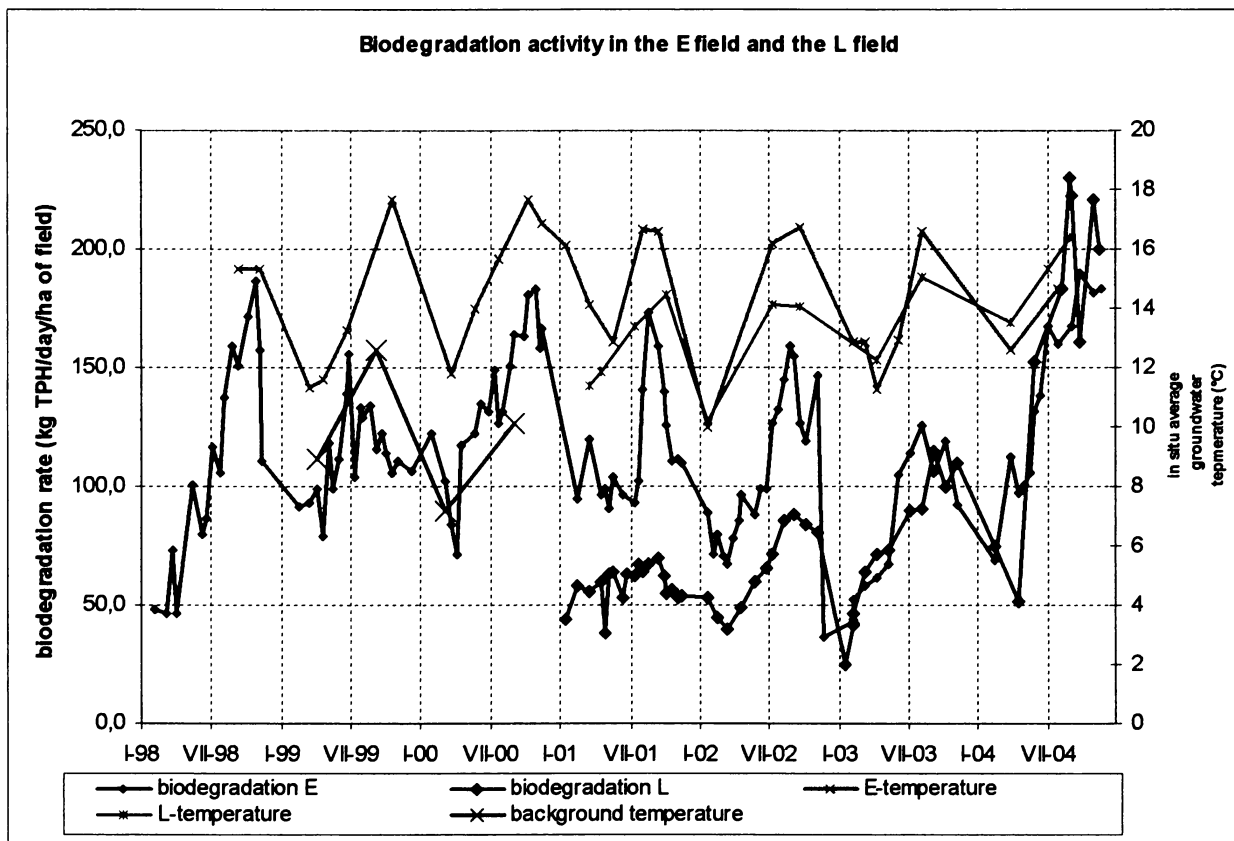
LESSONS LEARNED

Fig. 8 shows clean-up result obtained by soil sampling during four years of bioremediation supported by venting and air sparging. Nearly no contamination remains in the unsaturated zone and in deeper soil layers of the saturated zone after four-year treatment, but high concentrations of TPH, exceeding limits in average nearly 2 times, remain in the middle part of contaminated profile – around GWT. Fig. 8 also shows lack of information in 1998 about contamination of deeper layers, which was obtained later (fig. 2).

At the start of the clean-up it was anticipated that for reaching the clean-up limits in the soil (5000 mg TPH/kg) it would be necessary to remediate approx. 60 % of the total amount of petroleum hydrocarbons. Later, the soil sampling proved, that for reaching of clean-up limits in soil around GWL it would be necessary to remove at least 80% of pollutants. This is caused by the fact, that biodegradation supported by air sparging does not remove contamination thoroughly from the contaminated layers in saturated zone, but treats contamination consequently from the bottom of polluted soil interval towards GWL. High

biodegradability of the jet fuel brings about nearly full soil clean-up in lower part of the profile.

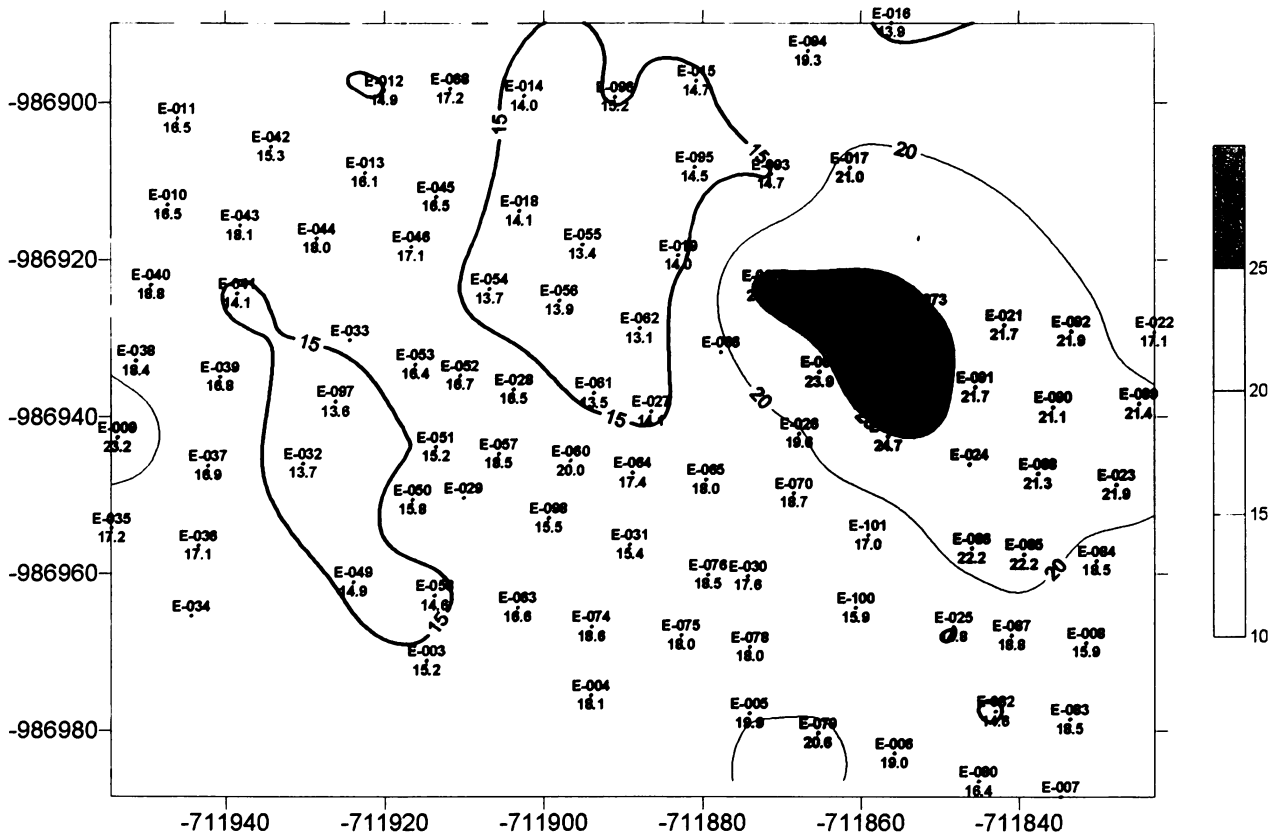*Figure 7: In situ groundwater temperature in the E field, November 1999, a 1 ha part*

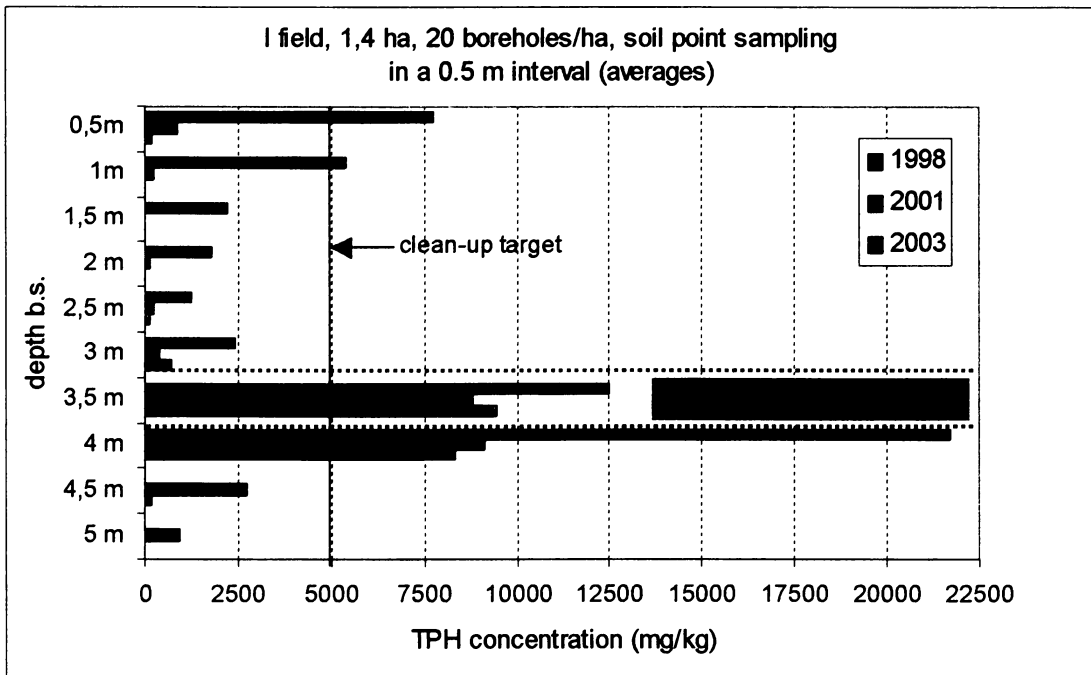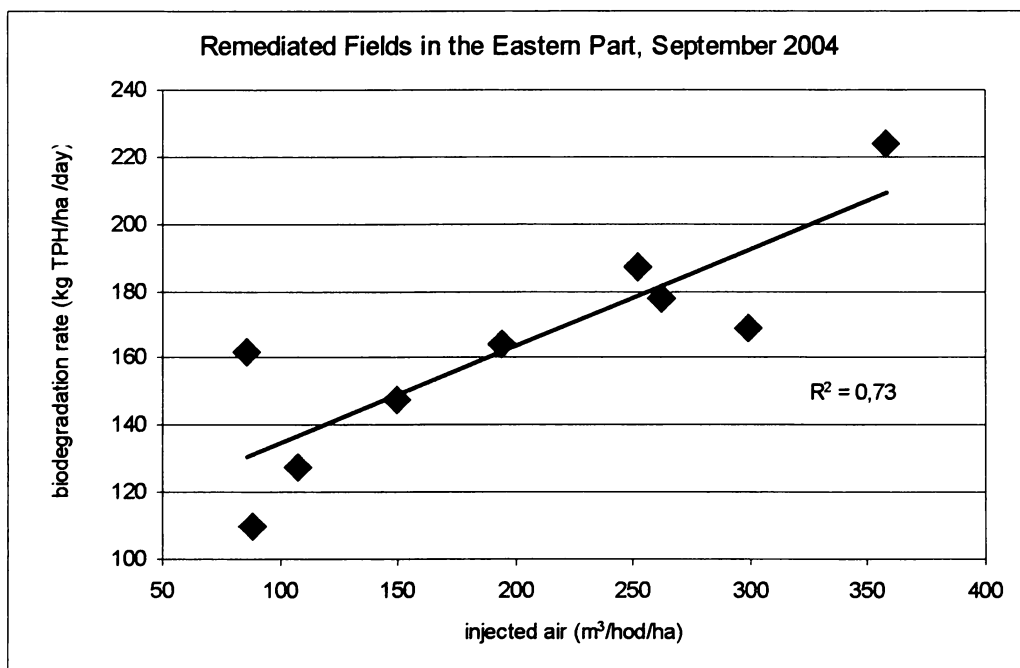*Figure 8: Changes in vertical THP soil content distribution during clean-up*

Figure 9: Correlation between the AS air output and observed biodegradation rates

This findings lead to the decision to increase the air flow rate to single air sparging well from 10 to 20 m³/hour. In addition, the original drilling net of air sparging wells (15x15 m) was doubled (7x7 m) in areas of high concentrations of pollutants. The closer spacing of air sparging wells and increase of air rate per well in general is recommended by Johnson et al., (2001). The main strengthening of AS output took place in Spring 2004. The increased air flow rate (i.e. oxygen input) resulted in proportional increase of amount of biodegraded pollutants, see Fig. 9.

CLEAN-UP RESULTS

Fig. 10 gives the amounts of petroleum hydrocarbons removed yearly by different technologies from 1997. It is clear, that biodegradation is leading clean-up method at the site.

The reason for the increase of biodegradation in 2004 is essential strengthening of AS, mentioned above. The specific biodegradation rate reached in average 36 tons/hectare/year in the year 2004 in comparison to 27 t/ha/year in 2003. Table 2 gives total amount of petroleum hydrocarbons removed from the site during the whole clean-up.

Table 2: The removed amounts of petroleum hydrocarbons (tons)

Method	1989-1997*	1998	1999	2000	2001	2002	2003	2004	total
LNAPL extraction*	489	35	31	38	42	1,8	0,3	0,2	637
Venting	86	32	11	5	2	2,6	0	0	139
Bioremediation	256	131	191	271	313	406	440	683	2691
Grand total	831	198	233	314	357	410	440	683	3467

* water pumping + dual phase extraction (from 1996)

9

Figure 10: Petroleum hydrocarbons removal in period 1997 – 2004
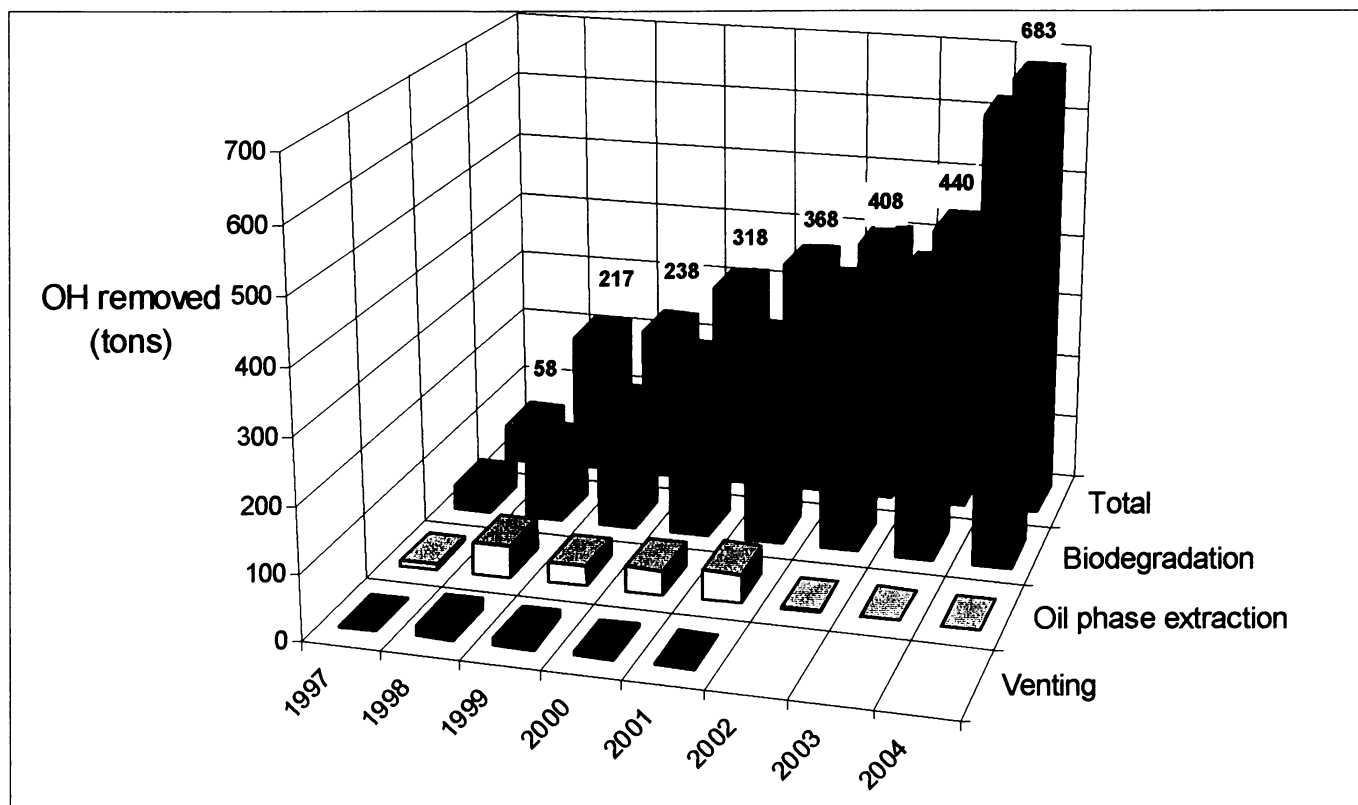
ACKNOWLEDGEMENTS

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