Macro Porous Polymer Extraction Systems (MPPE)

VWS MPP Systems is a hydrocarbon removal water treatment specialist and a member of Veolia Water Solutions & Technologies

www.vwsmppsystems.com
MPPE process (1)

Water

Steam

Extraction

Stripping

Condenser

Settler

Hydrocarbons

Condensed steam recycle

Water/hydrocarbons

MPP SYSTEMS
MPPE process (2)

- Organics and water
- Condensed water recycle
- Heavy Organics for reuse
- Light Organics for reuse
- Clean water

Diagram details:
- Extraction
- Stripping
- Condenser
- Separator
- Steam flowpaths

MPP SYSTEMS
MPPE Extraction versus AC-adsorption

- Toluene supersedes Benzene
- More “other” molecules requires more Activated Carbon
- Sensitive for fouling

- Molecules do not interfere
- More “other” molecules require not more MPPE
- Not sensitive for fouling
MPPE

Typical extraction curve

Average concentration during cycle = 1/3 end of cycle concentration
MPPE Features

- High reduction factor
- Reduction factor independent of inlet concentration
  99\% = 100 \text{ ppm} \rightarrow 1 \text{ ppm} \text{ but also } 100 \text{ ppb} \rightarrow 1 \text{ ppb} (predictable modelling)
- Flow/ Inlet concentration flexibility
  - 10\% lower flow \rightarrow 50\% higher inlet concentration possible
  - lower inlet concentration: higher flow possible
- Robust against water environment (surfactants, salts, pH range 3 - 9 etc.)
- Capacity & operational flexibility
  - turn up / down ratio 0 to 150\% of design capacity
  - Batch wise operation; Immediate performance at start up
- No waste stream (no use of chemicals), no air emission
- 100\% recovery of water and hydrocarbons (~100\% pure for (re)use)
- Spent MPPE material is cleaned off-site and ready for reuse

MPP SYSTEMS
<table>
<thead>
<tr>
<th>Aromatic and Aliphatic Compounds</th>
<th>Halogenated/Chlorinated Compounds</th>
<th>Poly Aromatic Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Monochloromethane</td>
<td>PCBs</td>
</tr>
<tr>
<td>Toluene</td>
<td>Dichloromethane</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>Trichloromethane</td>
<td>Acenaphthylene</td>
</tr>
<tr>
<td>Xylene(s)</td>
<td>Tetrachloromethane</td>
<td>Acenaphthene</td>
</tr>
<tr>
<td>Cumene</td>
<td>Dichloroethane (1,1 &amp; 1,2)</td>
<td>Fluorene</td>
</tr>
<tr>
<td>Limonene</td>
<td>Trichloroethane</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>Tetrachloroethylene</td>
<td>Anthracene</td>
</tr>
<tr>
<td>Cresol(s)</td>
<td>Chloroethylene</td>
<td>Fluoranthene</td>
</tr>
<tr>
<td>Higher alkylated phenols</td>
<td>Dichloroethylene</td>
<td>Pyrene</td>
</tr>
<tr>
<td>Octanol</td>
<td>Trichloroethylene</td>
<td>Benz(a) anthracene</td>
</tr>
<tr>
<td>Nonanol</td>
<td>Tetrachloroethylene</td>
<td>Chrysene</td>
</tr>
<tr>
<td>Decanol</td>
<td>Trichloropropane</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>Hexane</td>
<td>Chlorobutadiene</td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>Hexachlorobutadiene</td>
<td></td>
</tr>
<tr>
<td>MIBK</td>
<td>Monochlorobenzene</td>
<td></td>
</tr>
<tr>
<td>TetraHydroThiophene</td>
<td>Dichlorobenzene</td>
<td></td>
</tr>
<tr>
<td>CS2</td>
<td>Chlorobenzenes</td>
<td></td>
</tr>
<tr>
<td>Tetramethyltetrahydrofuran</td>
<td>Chloroaphtalene</td>
<td></td>
</tr>
<tr>
<td>MTBE / ETBE</td>
<td>Hexachlorocyclohexane</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Monochlorophenol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dichlorophenol, Trichlorophenol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dichloro-di-isopropylether</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dioxines</td>
<td></td>
</tr>
</tbody>
</table>
MPPE

Markets / Applications

- **Industry**
  - Offshore
  - Oil & Gas
  - Petrochemical
  - Chemical
  - Pharmaceutical
  - Coatings
  - Electronics

- **Governmental**

<table>
<thead>
<tr>
<th></th>
<th>No. of units</th>
<th>CAPEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Offshore produced water</td>
<td>20%</td>
<td>70%</td>
</tr>
<tr>
<td>Industrial waste water</td>
<td>35%</td>
<td>15%</td>
</tr>
<tr>
<td>Groundwater</td>
<td>45%</td>
<td>15%</td>
</tr>
</tbody>
</table>

- **Customers e.g.**
  - TOTAL
  - Gaz de France
  - NAM (Shell/Exxon)
  - Statoil
  - Woodside
  - Shell
  - Dupont
  - Degussa
  - Albemarle
  - AkzoNobel
  - Philips
  - Woodside
  - Western Refining
  - Inpex
  - LMBV
MPPE Offshore Demo unit 1
MPPE Demo unit 1
MPPE Shell Prelude FLNG
MPPE Separator
Groundwater challenges

- Varying broad and complex compositions
  - Aromatics
  - Poly aromatics
  - Heavy halogenated / chlorinated
  - Light halogenated / chlorinated
  - Other e.g. CS\textsubscript{2}
- Low effluent levels
- Presence of
  - Iron (hydroxide formation)
  - Humic acids
  - Salt(s)
  - CaO / MgO
- Remote (unmanned) locations

**MPPE**

- Simultaneous 99.99% removal
- Flexible
- Robust
- Remote control
Diosynth Oss (NL)
groundwater treatment

- Pharmaceutical raw material supplier
- Flow rate 40 m³/hr

Composition:
- Benzene & Toluene 50 ppm
- DCM 2 ppm
- TCM, DCE, TCE 8 ppm

Discharge:
- Benzene & Toluene <0,1 ppm
- DCM <0,5 ppm
- TCM, DCE, TCE <0,1 ppm

- Iron 48 ppm, Ca 65 ppm
- Since December 1995
Problem:
- Small irregular heavy waste stream (2,000 ppm EOCL, BTEX)
- Big fluctuating waste / ground / surface water stream (5 ppm EOCL, BTEX)

Solution:
- MPPE for removing non polar / toxic organic compounds
- Biotreatment for removing polar and Nitrogen compounds

Specific details:
- Total flow: 15 - 20 m³/hr (90 gpm)
- Effluent in Rotterdam harbour
- Components: BTEX, chlorinated hydrocarbons
- N and polar compounds
- >99% removal
- Operational since 2001
MPPE

LBC MPPE with Bio-treatment

MPP SYSTEMS
MPPE

Schwarze Pumpe Site

- Former Brown Coal Site (Power & Chemical)
- 2 years intensive testing
- 5 MPPE units
- ≥ 99% removal of BTEX & PAHs
- Re-infiltration of purified water
- Enhanced DNAPL & LNAPL removal
Five MPPE units, LMBV, Schwarze Pumpe Germany

- Groundwater since 2004
- Flow rate 20 m³/hr
- BTEX 233,000 µg/l (ppb)
- Naphthalene 500 µg/l (ppb)
- PAHs 153 µg/l (ppb)
- > 99% removal
- Performance guaranteed
Two MPPE units, LMBV, Lauchhammer Germany

- Groundwater Dec. 2010
- Flow rate 3 m³/h
- BTEX 30,000 → 150 ppb
- PAHs 500 → 15 ppb
- Remote location including office; heating/airco; pump network control
GERMANY PLANT RUHRGEBIET

- Groundwater 1999
- Flow rate 120 m³/h
- Chlorinated 600 → 6 ppb
  & aromatic HC
- Treated water is reused as cooling water in the plant.
### Groundwater (summary 1)

**Halogenated / chlorinated HCs removal > 99%**

<table>
<thead>
<tr>
<th>Company</th>
<th>Year</th>
<th>Flow (m³/h)</th>
<th>Concentration (µg/l)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merck S&amp;D Oss (NL)</td>
<td>1995</td>
<td>40</td>
<td>250,000</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>Solvay, Amsterdam (NL)</td>
<td>1998</td>
<td>25</td>
<td>100,000</td>
<td>&gt; 99.9</td>
</tr>
<tr>
<td>Degussa Huls/Evonik, Marl (D)</td>
<td>1999</td>
<td>120</td>
<td>600</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lulsdorf (D)</td>
<td>2001</td>
<td>60</td>
<td>13,800</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>AKZO Nobel, Mannheim (D)</td>
<td>1996</td>
<td>18</td>
<td>5,000</td>
<td>&gt; 99.9</td>
</tr>
</tbody>
</table>
### Groundwater (summary 2)

**BTEX and PAHs removal > 99%**

<table>
<thead>
<tr>
<th>Location</th>
<th>Year</th>
<th>m³/h</th>
<th>µg/l</th>
<th>Rem. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flensburg (D), 1998</td>
<td></td>
<td>14</td>
<td>1,083</td>
<td>&gt; 99.9</td>
</tr>
<tr>
<td>Schwarze Pumpe (D), 1998</td>
<td></td>
<td>70</td>
<td>223,000</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>Lauchhammer (D), 2006</td>
<td></td>
<td>6</td>
<td>44,600</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>950</td>
<td>&gt; 99</td>
</tr>
</tbody>
</table>
MPPE Germany

- Groundwater regarded as a high value product
- Clean groundwater only for high value use (e.g. process/potable water) if it can be proven that surface water cannot be economically used
- If contaminated groundwater to be cleaned, it has to be reused as process water before discharged to surface water; otherwise very difficult to get approval
- In Ruhrgebiet MPPE unit applied for contaminated groundwater reuse as process water
- Schwarze Pumpe:
  - MPPE ideal for groundwater treatment of hot spots and re-infiltration to **enhance natural attenuation**
  - Why: toxic hydrocarbon removal and no chemicals added
    - basically groundwater composition is not altered
MTBE / ETBE for lead free Gasoline

- 70’s lead replacement: air improvement
- USA (’92), EU (2002): Groundwater problem
- MTBE:
  - Odour (20-40 ppb)
  - Highly soluble (43 – 50 g/l)
  - Difficult biodegradable (especially with BTEX present)
  - Difficult to oxidize
  - Low sorption property
  - Plumes 1000 -1800 m and larger (gas stations)
- USA: banned in 27 states (2007)
- EU 2005: replacement by ETBE
- ETBE stronger odour and less biodegradable
- Challenge to remove MTBE/ETBE from water
**MPPE for MTBE, BTEX, GROs and DROs removal**

### Analytical results Gasstation Germany (µg/l)

<table>
<thead>
<tr>
<th></th>
<th>In</th>
<th>Out</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>550</td>
<td>&lt; 2 (dl)*</td>
<td>&gt; 99.2 %</td>
</tr>
<tr>
<td>BTEX</td>
<td>1,693</td>
<td>&lt; 1 (dl)</td>
<td>&gt; 99.9 %</td>
</tr>
<tr>
<td>PAHs</td>
<td>49.7</td>
<td>&lt; 1 (dl)</td>
<td>&gt; 98 %</td>
</tr>
</tbody>
</table>

*(dl) = detection limit

### Analytical results Agip Italy (µg/l)

<table>
<thead>
<tr>
<th></th>
<th>In</th>
<th>Out</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>4,860</td>
<td>0.1 (dl)***</td>
<td>&gt; 99.9 %</td>
</tr>
<tr>
<td>BTEX</td>
<td>981.8</td>
<td>0.1 (dl)</td>
<td>&gt; 99.9 %</td>
</tr>
<tr>
<td>GROs*</td>
<td>2,315</td>
<td>&lt; 5 (dl)</td>
<td>&gt; 99.8 %</td>
</tr>
<tr>
<td>DROs**</td>
<td>280</td>
<td>&lt; 5 (dl)</td>
<td>&gt; 98 %</td>
</tr>
</tbody>
</table>

* GROs = Gasoline Range Organics (C7 - C10)
** DROs = Diesel Range Organics (C11- C27)
*** (dl) = detection limit

Gas station (Germany) 2002

Agip gas station (Italy) 2005
MPPE for MTBE, BTEX, GROs and DROs removal
MPPE applications

- Gasoline Range Organics, GROs
- Diesel range organics, DROs
- Aliphatics (dispersed oil)
- Aromatics / BTEX
- PAHs
- MTBE / ETBE
- Polar compounds and Natural Occurring Matter: Humic acids, Fe, etc.

MPPE technology

Other technologies
Groundwater - MPPE benefits

- High reduction factor (up to 99.99%) independent of inlet concentration
- Flexible with regards to flow & concentration
  - 50% higher influent → only 10% flow reduction
  - Lower influent → higher flow rate / higher capacity
- No Waste, but recovered HCs; No Chemicals; No Off-gas
- No iron removal required
- Humic acid flow through
- Reliable, robust
- Stand alone fully automatic; Remote controlled
- Surfactant or alcohol enhanced DNAP / LNAPL removal
The MPPE system in DNAP removal

DNAPL = Dense Non Aqueous Phase Layer

- Chlorinated hydrocarbons heavier than water forming immiscible fluids. Spread laterally as a function of site geology and trapped by capillary forces in soil pores / residing as a pool
- E.g. TEC, PCE, TCA, low solubility
- Drinking water standards extremely low: ppb range
- DNAPLs can contaminate drinking water supply for many years
- DNAPLs can only be removed by slow dissolution in the groundwater
  A process that can take decades
- When remediation is halted, contaminant levels began to increase after a short period
- MPPE successful in field tests
MPPE in DNAPL removal (1)
MPPE in DNAPL removal (2)
MPPE separation performance > 99.9%

Contaminant removal in two weeks equaled 8 years of Pump and Treat

<table>
<thead>
<tr>
<th>Date</th>
<th>MPP-in</th>
<th>MPP-out</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-08-2002</td>
<td>220,000</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>13-08-2002</td>
<td>233,200</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>15-08-2002</td>
<td>120,000</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>16-08-2002</td>
<td>41,000</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>17-08-2002</td>
<td>19,000</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>24-08-2002</td>
<td>7,600</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>

Solvent flushing Dry cleaner site, Jacksonville - Florida
MPPE

Germany, 2000

Germany, 2000

USA, Florida

MPP SYSTEMS
**MPPE**

Successful DNAPL field tests with MPPE since 1998

<table>
<thead>
<tr>
<th>Location</th>
<th>Country</th>
<th>Solution Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jacksonville</td>
<td>USA</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Alamada, California</td>
<td>USA</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Tampa, Florida</td>
<td>USA</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Schkopau</td>
<td>Germany</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Leipzig</td>
<td>Germany</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Castrop Rauxel</td>
<td>Germany</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Schwarze Pumpe</td>
<td>Germany</td>
<td>Alcohol</td>
</tr>
</tbody>
</table>
Conclusion DNAPL removal

- Surfactant flushing:
  source remediation in weeks / months instead of decades

- Applicable to DNAPL, LNAPL, creosoot, PAKs, min.oil

- Good starting point for biological “after remediation”
Constituents with Environmental Impact (CEI)

- Type of molecules and concentration determine Environmental Impact
  - Toxicity
  - Bio degradability
  - Bio accumulation

- Higher environmental impact of toxic molecules:
  - Higher multiplication factors to reflect environmental impact

- Qualitative model to show:
  - Constituents with Environmental Impact (CEI)
  - Toxic contents detrimental to bio treatment
  - Technologies on CEI removal
### Total hydrocarbon removal (CEI-view)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ppm</th>
<th>Composition</th>
<th>CEI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersed oil (separable) &gt; 30 µg</td>
<td>&lt; 1 - 100</td>
<td>Oil sep</td>
<td>Oil</td>
</tr>
<tr>
<td>Dispersed oil &lt; 30 µg</td>
<td></td>
<td>Oil</td>
<td></td>
</tr>
<tr>
<td>Toxic dissolved hydrocarbons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Aromatic (e.g. BTEX)</td>
<td>&lt; 1 - 100</td>
<td>AHC</td>
<td>AHC</td>
</tr>
<tr>
<td>- PAHs and NPDs</td>
<td>&lt; 1 - 50</td>
<td>PAHs NPDs</td>
<td>PAHs</td>
</tr>
<tr>
<td>- Halogenated/chlorinated hydrocarbons</td>
<td>&lt; 1 - 100</td>
<td>HHC</td>
<td>HHC</td>
</tr>
<tr>
<td>- Other: TNT, MTBE, CS₂, Dioxines, DCPE</td>
<td></td>
<td>Other</td>
<td>Other</td>
</tr>
<tr>
<td>Biodegradable dissolved hydrocarbons</td>
<td></td>
<td>Polar</td>
<td>Polar</td>
</tr>
<tr>
<td>- Polar: thousands</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Acids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Alcohols (Methanol)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* CEI = Constituents with Environmental Impact

**MPPE SYSTEMS**
MPPE

Environmental aspects of MPPE

- Practically pure separated hydrocarbons for reuse / recycle
- Very low waste of polymer
  - Long lifetime
  - Reuse of spent material
- Low Energy consumption
- No addition of chemicals
- No emission to air
- No sludge formation
- No (chemical) iron hydroxide waste
- Compact equipment; little surface
- Long lifetime of equipment
- Higher chance for water reuse
MPPE for offshore produced water, process / waste and groundwater

- High and guaranteed separation performance
- Separation Performance independent of inlet concentration
- Robust against: peak loads, inhibitors, scavengers, biocides, etc.
- Reliable and easy fully automated operation
- Flexible operation
- Compact / small footprint
- Remote controlled
- Ideal for upstream process integration
- Environmentally friendly, low noise, no sludge
- Performance guaranteed during operational life
MPPE unit Flensburg
MPPE unit Flensburg

BTEX and PAHs
- Since 1998
- Flow rate 14 m³/h
- BTEX 1,083 µg/l
- PAHs 3,948 µg/l
- Removal > 99.9%
MPPE in comparison to other technologies (1)

Vs liquid-liquid extraction

- Extraction liquid immobilized in particles
- Packed bed = higher separation power
- “in situ” separation of extraction liquid and water
  - No additional separation step required for extraction liquid removal
MPPE in comparison to other technologies (2)

Vs Steam stripping

- Less energy consumption
  - MPPE: heating of packed bed
  - Steam stripper: heating of total flow
- Minimal scaling due to e.g. carbonate precipitation
  - Extraction at ambient temperatures
  - Back washing every hour with water and steam
- No polymerization in case of monomer presence
- Smaller size: ¼ height, smaller footprint
- Flexible: high turndown ratio
MPPE in comparison to other technologies (3)

Vs airstripping with activated carbon

- No fouling / scaling
  - Minimal carbonate precipitation
  - Not sensitive for dissolved iron ("anaerobic" operation)
- Long lifetime of packed bed (in situ regeneration)
- No competition / replacement on surface
- Higher separation power
- No polymerization of monomers (e.g. VC, Styrene)
- Less equipment
- Disposal / incineration of spent carbon
MPPE in comparison to other technologies (4)

Vs Sorbents in the water phase
(activated carbon; synthetic sorbents)

- Robust, less sensitive to water environment
  - e.g. solids, surfactants, dispersed oil, humid acids
- No competition / replacement on surface but simultaneous removal of hydrocarbons
- Long bed lifetime / in situ regeneration
- No biological fouling