

VOCs Remediation by the Use of Two Phase Extraction (TPE) at a Petrochemical Site

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A full scale Two Phase Extraction (TPE) remediation system was designed, installed and still operating at a petrochemical site located in north-eastern Italy. Main aim of the treatment is to simultaneously draw down shallow groundwater and to remove contaminated soil vapor from vadose zone (at least 2600 m³ of treated soil). Even considering only gaseous contamination, until the time frame this paper is referred, more than 25 kg of VOCs were removed from soil and treated. Although groundwater remediation was not a specific object of the project continuous pumping out accelerated improvement of the saturated zone quality. Treatment operations started-up on February, 2014 and it is supposed soil clean-up goals will be reached after 10 operating months.

1. Site description

The whole TPE remediation system is constituted by three different treatment/control package units, which have been installed over three different operational area, formed by five Thiessen polygons named PSS-A45, PSS-A50, PSS-D37, PSS-D47 and CR4-B3. In Figure 1 planimetry of the petrochemical site area interested by remediation actions is reported.

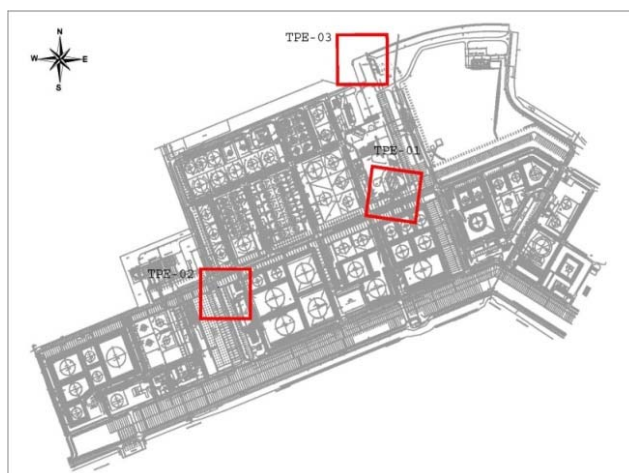


Figure 1: Planimetry of the petrochemical site where the three TPE units are located. Red squares approximately indicate Thiessen polygon and treatment control package units approximate position.

Thiessen polygons definition occurred during soil and groundwater investigation campaign in 2005 aimed to characterize petrochemical site. Investigations activities revealed diffused contamination with VOC and hydrocarbon, included chlorinated hydrocarbon, as PCE, TCE and VC, and BTEX. Contamination nature is certainly due to petroleum refining and chemicals synthesis activities since late 60's. Actually is not possible identify one or more specific activities accountable for contamination. In order to better address remediation design and operation management during wells drilling operation, in 2013 October, with more details soil was characterized. Pollutants concentration in soil was found to be very high, reaching within vadose zone even 1000 mg/kg of dry soil for hydrocarbon, 200 mg/kg of dry soil for chlorinated solvents and 100 mg/kg of dry soil for BTEX. As an example analytical soil characterization along depth of three different extraction wells, from three different polygons, are reported in Figure 2. In figure it is identified the specific extraction well results are referred to, it also reported sampling depth interval.

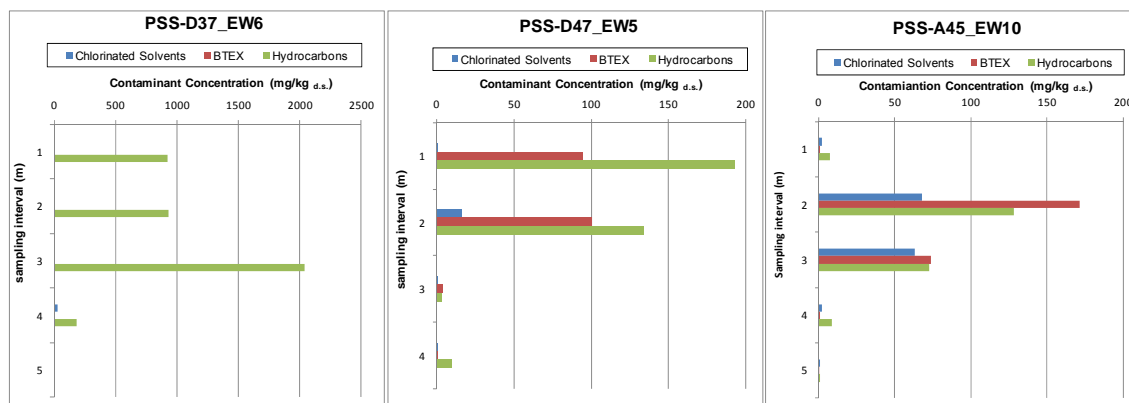


Figure 2: Three typical soil analytical results from drilling operations carried out in three different polygons

Since analytical characterization was fully exhaustive including a large number of compounds, to simplify analytical results depiction pollutants are gathered into three main classes: Hydrocarbons, Chlorinated Solvents and BTEX. Results plotted in Figure 3 evidence pollution heterogeneity over the different area, both in terms of concentration and in terms of pollutant classes distribution. A second outcome from surveys is that the areas is mainly characterized by shallow contamination. Contaminants are in the majority located within first 1-2 meters, in some cases reaching the third meter depth. Site sediments was also characterized during drilling operation. Stratigrafical sequence identified an upper layer mostly formed by heterogeneous matrixes from industrial activities, even containing sand, gravel and rocks from ground level to 1.4÷8.6 m, with 4.6 m mean thickness. A second silty/clay layer was identified from 1.4÷8.6 to 3.0÷12.6 m, with 2.4 m mean thickness Underlying the silty/clay layer a mostly sandy layer was identified until to 10÷20 m below ground level. First saturated zone is composed by a very shallow groundwater, located within the upper layer described above, and overlaying the silty/clay layer, which assure confinement towards first groundwater.

2. Technology description and system design

TPE is typically applied characterized by weak to low soil permeability through vacuum application to enhance hydraulic gradient. Vacuum, applied vacuum to extraction sealed wells screened in the zone of interest, generates both soil vapor and groundwater extraction, and consequently induces water table lowering. Liquid flow rates are increased due to the increased pressure gradient applied on the system. As a consequence of the increased vadous zone thickness a greater exposition of the contaminated soil is addressed. This fact allows to remove both volatile contaminants as sorbed and residual phase above and below water table (Baldwin et al., 2009). Especially when capillary fringe and smear zone are heavily impacted TPE resulted particularly effective to remove pollutant mass. Consequently TPE addresses contamination in both the saturated and vadose zones, remediating dissolved, vapor, residual, and non-aqueous phases of contamination. TPE affects mass removal by volatilization, dissolution, and advective transport (Aglietto et al. 2003).

Remediation strategy involved installation of three different treatment/control package units, being each unit installed on a different area. The three units hereafter will be identified as TPE-01 (2 blowers), TPE-02 (3 blowers) and TPE-03 (4 blowers). The units were respectively installed to treat the following polygons: PSS-D47, PSS-A45 and PSS-A50, PSS-D37 and CR4-B3.

During drilling operation a total amount of 39 geognostical surveys were realized and successively equipped with fenestrated suction pipe as extraction wells. Wells depth ranged from 2 to 6 m below ground level, while suction pipes were installed at a depth ranging from 1 to 5 meter below ground level. Extraction wells are distributed on the five polygons as follows:

- PSS-A45 n.10 extraction wells
- PSS-A50 n.7 extraction wells
- PSS-D37 n.7 extraction wells
- CR4-B3 n.7 extraction wells
- PSS-D47 n.8 extraction wells

Additionally in each polygon were also installed 4 monitoring wells, for a total amount of 20. The 4 wells were placed at radial increasingly distance from centred extraction point, 4,8,10 and 15 m.

Each treatment/control package unit contains 2 to 4 blower, depending by treatment area extension and the number of the wells installed on each area. Blowers have the aim to guarantee wellhead vacuum and vapor extraction generating low pressure area around each extraction well that assures groundwater and soil gas flux. System was designed to achieve 27 Nm³/h extraction flow from each well, inducing -0.6 bar as maximum vacuum at wellhead. A demister, to separate gaseous and liquid flow, is placed inside the treatment/control package units. The two split flows are separately treated. Water are collected in a tank and send to site groundwater treatment plant, whereas soil gas, after cooling and moisture condensation, is treated through activated carbon filters. In Figure 3 a schematic overview of the main items is reported, in particular scheme in Figure 3 is referred to package operating on PSS-D47 polygon.

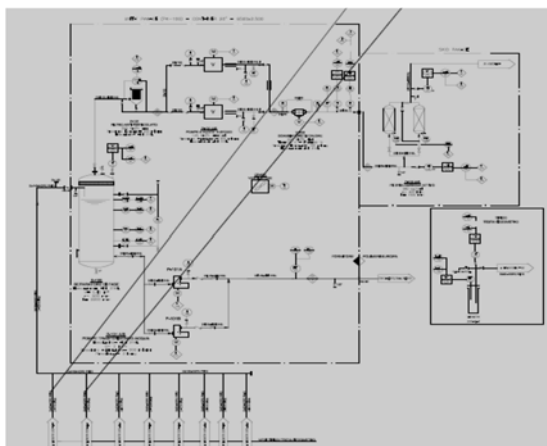


Figure 2: Schematic layout of the extraction system (extraction wells and pipeline), main items and connections between them

3. Technology performance

Operation of the three TPE units started at the end of February, 2014, and currently are still working. Following will be presented first 300 working days. During the whole period operative data were routinely collected with the aim to monitor technology performance. Gas flow rate was continuously monitored through digital sensors installed along pipeline and data collected by remote controlled PLC. The three systems operated at approximately constant flow rate. Average gas flow rate was respectively 328 Nm³/h referred to TPE-01, 335 Nm³/h referred to TPE02, 368 Nm³/h referred to TPE-03. Soil gas extracted was periodically monitored through sampling operation at GAC filters inlet. Vapour emission after GAC filters was monitored to assure law limits fulfilment.

In Figure 4 analytical results from gas sampling are summarized and plotted. In particular it is shown VOCs concentration trend over operative period. Total VOCs concentration was determined as sum of the VOCs concentration determined at each TPE units. In figure is also reported concentration trend of both chlorinated VOCs and BTEX. At the first stage after remediation activity started Total VOCs concentration increased, reaching approximately 40 mg/Nm³ as maximum value. Subsequently concentration rapidly decreased, as effect of soil gas extraction, until approximately the fifth operational month. Consequently to several optimization actions (i.e. gas flow throttle at chosen extraction wells) expected isolated concentration peaks were observed. Anyway each concentration increase was suddenly followed by significant decrease when operative parameters were switched again to normal functioning condition. Some qualitative differences in gas flow composition it is possible to note. For the first five months aromatic compounds concentrations, identified

in figure as BTEX, overwhelmed chlorinated compounds concentration, as chlorinated VOCs. After that period relative ratio were completely inverted, and chlorinated VOCs became the most abundant compounds. Aromatic removal rates outweighed chlorinated removal rates, as several studies observed, and more rapid mass depletion was induced. Aromatic mass decrease reasonable leading to mass removal rate decrease. Anyway a sharp asymptotic trend, typical for TPE application, is not clearly observable. This fact is mainly due to optimization activities on TPE system routinely conducted. This activities was intended to maximize contaminants extraction, and resulted in isolated concentration peaks showed in Figure 4. Thus, excluding those peaks not due to normal system operation, it is possible to note a general decreasing concentration trend to a lower value. This trend is intended as reaching technological limit for the site treatment, suggesting that VOCs removal rate reached steady-state.

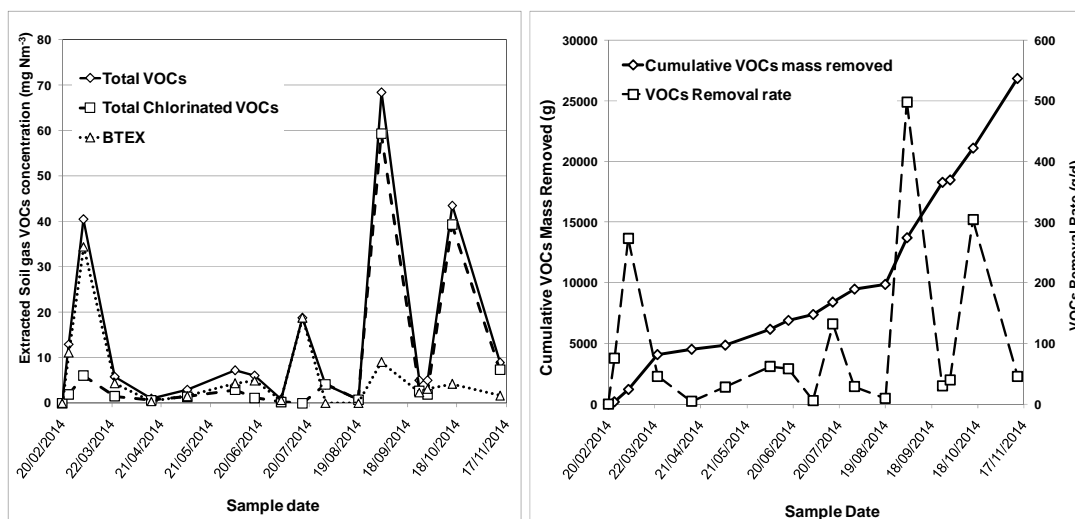


Figure 4: on the left side gas sampling analytical results, diamonds represent total VOCs concentration, squares total chlorinated VOCs and triangle BTEX; on the right side is reported VOCs removal rate, squares, and cumulative amount of VOCs removed

Effects of the optimization activities would be observed more clearly observing soil gas concentration inside each single extraction well instead overall extracted gas flux. Depending on applied vacuum level to specific well different contaminant recall is obtained. This effect is well represented in Figure 5, where VOCs typical distribution in soil gas over remediation area at several stage in the operation time frame is depicted. In particular Figure 5 is only referred to polygon PSS-D47. Additionally groundwater levels is reported too. To allow comparison and correlation between soil gas concentration and ground water levels data elaboration are referred to same period. Base line of both soil gas concentration and groundwater levels are reported in order to evaluate influences of vacuum application on PSS-D47 area. Bottom left portion of the area resulted to be the most contaminated, where EW5 were placed. Soil gas concentration in EW5 was approximately 1,100 mg/Nm³ before vacuum has been applied. In the following months significantly decreased reaching about less than 40 mg/Nm³ in June and approximately 15 mg/Nm³ in August. Continuous vacuum application led to contamination surrounding EW5 concentration decreased of almost 2 order degree. Alternate application of low and high vacuum in some wells (i.e. EW1 and EW3) is accountable for soil gas concentration evolution in time frame. Particularly it is possible to observe increase and subsequently concentration decrease in both wells. Vacuum condition applied at different operation period is also inferable by corresponding groundwater flow field reported in Figure 5. During the operational time frame groundwater flow field is subjected to great variation within treatment area.

3.1. VOCs mass removal

Based on analytical data from sampling and volumetric rates VOCs mass removal rate and cumulative removed mass were calculated. Results of calculations are plotted in Figure 4. Removal rate resulted strictly influenced by the corresponding extracted gas concentration. During the first six months removal rate trend seemed to tend to asymptotic lower value, more evident by observation of the cumulative removed mass curve. Further, due to activities over system parameters, both removal rate and cumulative mass are characterized by isolated peaks, which increased significantly contaminant mass removed.

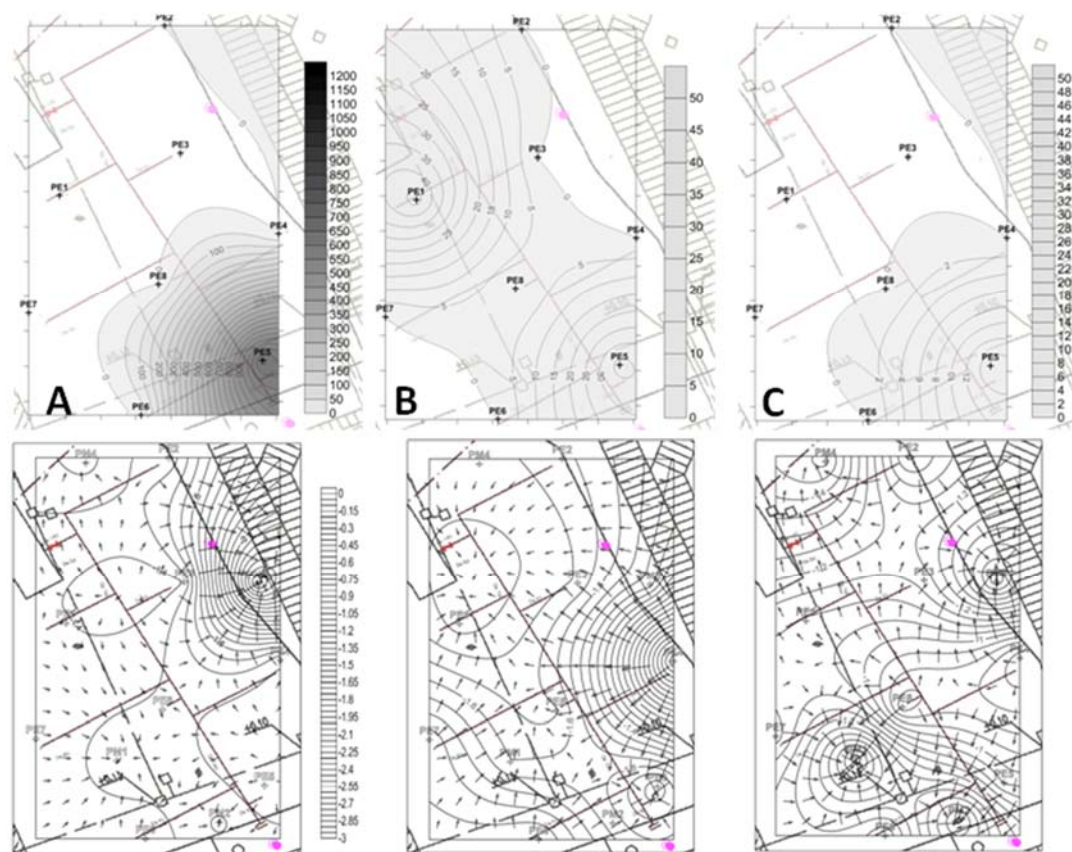


Figure 5: VOCs distribution in soil gas over remediation area at several stage in the operation time frame A) Base line; B) June; C) August. Corresponding groundwater levels are reported

Table 1

(mg/kg d.s.)	Goals	PSS-D47 S1	PSS-D47 S2	PSS-D47 S3	PSS-D47 S4	PSS-D37 S1	PSS-D37 S2
Cloronitrobenzenes	80	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Benzene	18	< 0.01	0,02	1,10	0,01	< 0.01	< 0.01
Ethylbenzene	150	< 0.01	< 0.01	71,40	17,90	0,09	0,05
Toluene	300	0,01	0,03	2,28	0,01	0,02	< 0.01
Benzo(a)antracene	10	< 0.01	0,12	0,11	0,02	0,69	0,05
Benzo(a)pirene	10	< 0.01	0,14	0,07	0,04	0,40	0,08
Benzo(b)fluorantene	10	< 0.01	0,09	0,10	0,03	0,45	0,06
Benzo(k)fluorantene	18	< 0.01	0,04	0,04	0,01	0,15	0,02
Benzo(g,h,i)perilene	30	< 0.01	0,14	0,16	0,08	0,54	0,11
Dibenzo(a,h)antracene	10	< 0.01	0,05	0,06	0,02	0,34	0,04
Indeno(1,2,3-c,d)pyrene	5	< 0.01	0,10	0,12	0,04	0,46	0,07
Pyrene	100	< 0.01	0,25	0,27	0,04	1,22	0,08
Dichloromethane	18	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Vinyl Chloride	1	< 0.003	0,49	0,24	< 0.003	0,01	< 0.003
1,2-Dichloroethane	40	< 0.01	0,04	0,10	< 0.01	0,02	< 0.01
1,1-Dichloroethene	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Trichloroethene (TCE)	25	< 0.01	< 0.01	0,81	0,05	0,27	< 0.01
Tetrachloroethene (PCE)	38	< 0.01	< 0.01	5,45	< 0.01	0,17	0,02
1,2-Dichloropropane	8	< 0.01	< 0.01	0,97	< 0.01	< 0.01	< 0.01
Light Hydrocarbons (C<12)	500	< 1.0	10,90	122,00	< 1.0	182,00	< 1.0
Heavy Hydrocarbons (C>12)	6000	18,00	63,00	149,00	33,00	655,00	18,00

Table 2

(mg/kg d.s.)	Goals	PSS-D37 S3	PSS-D37 S4	CR4-B3 S1	CR4-B3 S2	CR4-B3 S3	CR4-B3 S4
Cloronitrobenzenes	80	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Benzene	18	0,01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Ethylbenzene	150	0,05	0,04	0,06	0,10	0,11	< 0.01
Toluene	300	0,03	0,01	0,01	0,01	< 0.01	< 0.01
Benzo(a)antracene	10	0,07	0,17	0,16	0,14	0,14	0,10
Benzo(a)pirene	10	0,19	0,20	0,25	0,23	0,14	0,12
Benzo(b)fluorantene	10	0,14	0,14	0,22	0,23	0,10	0,10
Benzo(k)fluorantene	18	0,05	0,08	0,08	0,08	0,04	0,04
Benzo(g,h,i)perilene	30	0,22	0,27	0,33	0,30	0,16	0,17
Dibenzo(a,h)antracene	10	0,09	0,22	0,13	0,12	0,05	0,06
Indeno(1,2,3-c,d)pyrene	5	0,18	0,21	0,26	0,24	0,12	0,12
Pyrene	100	0,20	0,22	0,28	0,21	0,35	0,18
Dichloromethane	18	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Vinyl Chloride	1	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
1,2-Dichloroethane	40	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1,1-Dichloroethene	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Trichloroethene (TCE)	25	0,09	0,18	0,01	< 0.01	< 0.01	< 0.01
Tetrachloroethene (PCE)	38	0,03	0,10	0,06	< 0.01	< 0.01	< 0.01
1,2-Dichloropropane	8	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Light Hydrocarbons (C<12)	500	4,00	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Heavy Hydrocarbons (C>12)	6000	247,00	582,00	133,00	64,00	81,00	29,00

Table 1-2: Analytical surveys results compared to remediation goals relative to different compounds

3.2. Remediation goals evaluation

Based on the above consideration on September 2014 geognostic surveys were realized on the PSS-D47, PSS-D37 and CR4-B3 areas. Four surveys in each polygon were realized to evaluate possible soil remediation goals fulfilment, or to determine residual contamination levels. In Tables 1-2 are reported only compounds provided by the remediation project as marker to define remediation goals. The majority of the considered compounds determined are below analytical detection limit, whereas remaining compounds entirely fulfilled remediation goals.

As a consequence of the surveys campaign findings remediation certification was demanded, and currently permission to begin certification procedure is awaited. Certification procedure will involve treatment system shut-down and concentration rebound evaluation through three consecutive monthly surveys with the same procedure used for activities described above.

4. Conclusions

During the first 300 operative days TPE treatment system had hallowed extraction of more than 25 kg of contaminants from soil. During operation even groundwater quality was improved. A fine tuning of the functioning parameters allowed a greater contaminant mass removal in a shortened time frame. Geognostic surveys carried out after less than 7 working months confirmed good management system plant turning as results the complete remediation goals fulfillment.

References

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