Haemers® technologies

Final Report

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Haifa Bay

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2	*14-11-23*	*A. Vandekerckhove*		*J. Haemers*	*Update emission standards*

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2 INTRODUCTION

2.1 Purpose

The purpose of this document is to report on the laboratory and field work performed on the AKKO contaminated materials to assess the feasibility of thermal desorption for treating said contaminated materials.

As the materials contain mercury, organics solvents of various nature as well as mixed contaminations, the method chosen was to start with a laboratory project where mercury impacted soils were heated to different temperatures and resident times, to assess what was achievable as clean-soil targets with these specific soils.

In a second step, a full-scale small project (i.e. a project that has all characteristics of what a full scale would be, but applied to small quantities of soil) was set-up on site. The purpose of this project was to verify that:

1. Heating to the target temperatures (set by the laboratory tests) could be achieved
2. Heating-up to those temperatures would not cause additional air contamination at the site
3. Vapors could be recovered and handled properly without exceeding air emission standards
4. Heating and treating soil containing high mercury as well as high organic contaminants was feasible as well.

2.2 Report structure

The report will cover the laboratory work as well as the field work done, then present the results of both before drawing conclusions as to the feasibility of the Ex-Siu Thermal Desorption technology for the full-scale treatment of the contaminated materials on the Akko site.

3 PROJECT CHRONOLOGY

3.1 Laboratory phase

Table 1 summarizes the different steps for the laboratory test.

Date	Operations
January 13th, 2022	Sample reception ('S' and 'O')
January 17th, 2022	Start-up of first kinetic laboratory test
January 24th, 2022	First test end
January 28th, 2022	2 samples sent to Agrolab (analysis of total mercury)
February 4th, 2022	Reception of the results from Agrolab
February 7th, 2022	13 samples sent to i2Analytical (mercury speciation)
February 8th, 2022	Start-up of the second kinetic laboratory test (300°C)
February 11th, 2022	Samples of the second test sent to Agrolab and i2analytical
February 16th, 2022	Sample reception ('E' and 'C')
February 17th, 2022	Reception of the results from i2analytical
February 18th, 2022	Third kinetic test of the samples E and C
February 22th, 2022	Samples of the third test sent to Agrolab
February 25th, 2022	Reception of the analysis results from Agrolab (third test) and i2analytical (second test)
February 24-25th, 2022	Primary draft report
March 1st, 2022	Secondary draft report
March 8th, 2022	Reception of speciation and leachability from i2analytical (tests 3 and 4)
March 9th, 2022	Third draft report

Table 1. Project chronology of laboratory phase

3.2 Pilot phase

Date	Operations
December 1st, 2021	Start of the engineering phase
December 12th, 2021	Authorization to process
December 20th, 2021	Beginning of the mobilization of the equipment
January 17th – 21st, 2022	Thermal pile building up
February 21st, 2022	Reception of the vapor treatment equipment

February 15th, 2022	Validation of the thermal pile
March 17th, 2022	Start-up of 50 of the burners
March 24th, 2022	Start-up of the remaining burners
April 20th, 2022	Stop the heating phase
May 15th, 2022	Stop of the vapor system
June 15th, 2022 – July 7th, 2022	Thermal pile and vapor treatment unit dismounting
July 28th, 2022	First draft of report
August 8th, 2022	Second draft of report

Table 2. Project chronology of the pilot test on-site

4 LABORATORY PHASE

4.1 Nature of the contaminant

4.1.1 Sampling and nature of contaminant

The investigation of the contaminated soils of the Electrochemical Industries site at Haifa Bay revealed a pollution with chlorinated solvents (mainly trichloroethylene and perchloroethylene) and mercury.

The soil remediation of TCE/PCE by Thermal Conductive Heating (TCH) has been often used to treat volatile such trichloroethylene (TCE) and tetrachloroethylene (PCE). The target temperature is typically between 90 and 99°C, which does not require to evaporate all water content.

By contrast, the desorption kinetics of mercury are not as well documented as those of TCE/PCE. It is mainly explained by the mercury species. Indeed, mercury (Hg) is a natural element that is commonly found in the environment in 3 different forms: (1) metallic (or elemental), (2) organo- and (3) inorganic. Each form has different physicochemical properties. As example, elemental mercury is liquid and has a boiling point of 352°C, whereas mercury sulphide is solid with a boiling point of 582°C.

Most mercury forms are highly toxic to highly exposed humans, even low exposure can affect the central nervous system. However, specific human activities were contributing to a widespread mercury contamination. Due to his health-hazard, 130 countries agreed to the United Nation's Minamata Convention for reducing the emission and use of Hg (Xu J., 2015).

Therefore, this report essentially focuses on the kinetic behaviour of the mercury. The samples used for this study are given in table 3 (see appendix I). The mercury decrease in function of the temperature and the duration was investigated through 4 tests. The initial concentrations of mercury, including specifications, are also depicted in the table 3.

Test reference	Operating procedure	Sample reference	Total mercury conc.	Organo-mercury species conc.	Inorganic mercury conc.	Elemental mercury conc.	Unit
Test 1	Protocol 1	O	6,777[1]	176	1584	5017	mg/kg DM
Test 2	Protocol 2	O	6,777	176	1584	5017	mg/kg DM
Test 3	Protocol 2	C	120	9	61	15	mg/kg DM
Test 4	Protocol 2	E	43	2	27	7	mg/kg DM

Table 3. Test references: temperature, duration, and initial concentrations

4.1.2 Elemental mercury

The properties of mercury (Hg) are listed in the table 4.

	Quantity	Unit
Atomic mass	200.59	g/mol
Density	13,579.04	kg/m³
Heat capacity	138.8	J/kg.K
Thermal conductivity	8.34	W/m.K
Boiling temperature	356.73	°C

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[1] Average concentration between DEME Group (see appendix I) analysis and blank sample (see appendix II – Blank). Both have been analyzed by I2analytical, an agreed laboratory.

Heat of vaporization	295	kJ/kg
Oxidation state	0 (Hg), I (Hg^{2+}), II (Hg^{1+})	-
Vapor pressure	See figure below	-

Table 4. Mercury properties

The figure 1 represents the variation of the saturation pressure of mercury with temperature.

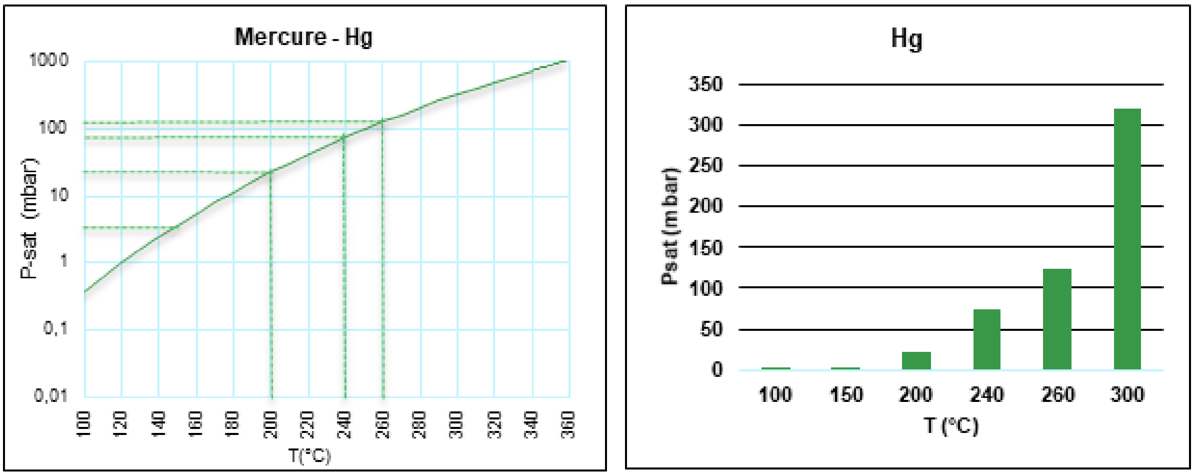


Figure 1. Variation of the saturation pressure of mercury with temperature

The saturation pressure (Ps) of mercury increases considerably with temperature:

1. P(sat) = 0.4 mbar at 100°C;
2. P(sat) = 4 mbar at 150°C; at 150 °C mercury is 10 times more volatile than at 100°C;
3. P(sat) = 22 mbar at 200°C, at 200°C mercury is 60 times more volatile than at 100°C;
4. P(sat) = 124 mbar at 260°C; at 260°C mercury is 330 times more volatile than at 100°C;
5. P(sat) = 320 mbar at 300°C; at 300°C mercury is 860 times more volatile than at 100°C.

4.1.3 Organo-Mercury species

They are mainly mercuric compounds. They are of the form CxHy-Hg-Z (Z= S, O, Na...). Some bacteria can transform inorganic mercury compounds into organic mercury compounds. The organic mercury compounds can be easily absorbed by plants and animals.

4.1.3.1 Monomethylmercury

It is produced by anaerobic bacteria that interact with inorganic mercury in marine sediments and fresh waters. It binds to proteins in fish muscles and thus enters the food chain.

4.1.3.2 Dimethylmercury

It is a volatile liquid. Aerobic and anaerobic bacteria produce this molecule from inorganicmercury compounds. It is soluble in ethanol and diethyl ether. In acidic solution it hydrolyses to monomethylmercury derivative.

4.1.3.3 Methylmercury chloride

This is a compound (solid) that is readily soluble in fat. It is not readily eliminated by the body.

4.1.3.4 Physic and chemical properties

The table below indicates the different organo-mercury species.

Form	Chemical substance	Chemical formula	Melting point (°C)	Boiling point (°C)
Liquid	Methylmercury	$(CH_3Hg)^+$	-	-
Liquid	Dimethylmercury	$Hg(CH_3)_2$	-43°C	87-97

Solid	Methylmercury chloride	CH3HgCl	170°C	-
Solid	Mercury acetate	Hg(C2H3O2)2	179	-
Solid	Mercurous acetate	HgC2H3O2	-	-
Solid	Phenylmercury proprionate	C9H10HgO2	-	-
Solid	Phenylmercury acetate	C8H8HgO2	148-153	-
Solid	Phenylmercury oleate	C24H38HgO2	-	-
Solid	Thiomerosal	C9H9HgNaO2S	232-233	-
Solid	Mercurous carbonate	Hg2CO3	-	Breaking down from 130°C
Solid	Mercuric carbonate	HgCO3.2HgO	-	
Solid	Mercuric oxychloride	HgCl2.3HgO	-	Breaking down from 260°C
Solid	Mercuric silicofluoride	HgSiF6.HgO.3H2O	-	-
Solid	Phenylmercury nitrate	C6H5HgNO3	176-178	

Table 5. Organo-mercury species; forms, chemical substances, formula, melting and boiling points

4.1.4 Inorganic Mercury

Mercury in the mercuric state forms stable compounds with nitrogen, chlorine, bromine, iodine and sulfur; it also forms compounds with oxygen and fluorine, but the bonds in these are easily broken.

4.1.4.1 Mercuric halogens

As examples of mercuric halogens, the following may be mentioned:

Form	Chemical substance	Chemical formula	Melting point (°C)	Boiling point (°C)
Solid	Mercuric fluoride	HgF2	-	Breaking down from 645°C
Solid	Mercuric chloride	HgCl2	276	304
Solid	Mercuric bromide	HgBr2	237	322
Solid	Mercuric iodide	HgI2	259	350

Table 6. Mercuric halogens species – forms, chemical substances, formulas, melting and boiling points.

Note that mercury (II) chloride and mercury (II) bromide have high solubility in water, respectively 74 and 220 g/l at 20°C.

4.1.4.2 Mercury (II) oxide

Mercury oxide (solid: yellow or red) is obtained by the action of air or oxygen on mercury below 300°C. It is a basic oxide soluble in diluted acids, but not very soluble in water. It decomposes into mercury and oxygen under the effect of light and high temperatures.

4.1.4.3 Mercury (II) sulfur

It is a red solid practically insoluble in water and decomposes at high temperature (>500°C).

4.1.4.4 Mercury (II) sulfate

It is a white solid which decomposes at a temperature above 500°C. It hydrolyses in contact with water.

4.1.4.5 Physical and chemical properties

The table below indicates the different inorganic species.

Form	Chemical substance	Chemical formula	Melting point (°C)	Boiling point (°C)
Solid	Mercury (II) sulfur	HgS	580 (sublimation)	584
Solid	Mercury (II) sulfate	HgSO4	Breaking down from 540°C	
Solid	Mercury (I) chloride	HgCl	302	383,7
Solid	Calomel	Hg2Cl2	385 (sublimation)	-
Solid	Mercury (I) fluoride	Hg2F2	645	650
Solid	Mercury (I) bromide	HgBr	345 (sublimation)	-
Solid	Mercury (II) bromide	HgBr2	-	345
Solid	Mercury (I) iodide	Hg2I2	290	-
Solid	Mercury iodide	HgI	290	-
Solid	Mercury telluride	HgTe	669	
Solid	Mercury selenide	HgSe	996	
Solid	Mercury (II) cyanide	Hg(CN)2	Breaking down from 320°C	
Solid	Mercury fulminate	Hg(CNO)2	150°C	-
Solid	Mercury cyanide fulminate	Hg(CNO)2.aH2O	-	-
Solid	Mercury (II)) nitrate	Hg(NO3)2	79	-

Table 7. Inorganic mercury species: forms, chemical substances, formula, melting and boiling points.

4.2 Kinetic tests

This study is the very first step of a scaling-up project. It aims at determining the feasibility of thermal desorption on the soils provided, by defining the temperature and time necessary to reduce as much as possible the concentration of the pollutant in the soil. In addition, this laboratory pilot will aim to provide the client with a global vision of the technique's ability to reach the objectives set in terms of pollutant content reduction, but also of the nature of the products obtained after treatment.

4.2.1 Operating procedure – Protocol 1

First, all rocks with a diameter above 20 mm are excluded from the samples. Then, about 300 g of soil are put in adequate containers (350 ml).

The thermal treatment is executed in open air in electric ovens (power: 2000 W), preheated to the adequate temperature. The containers are put in the ovens at different temperatures and the samples are taken out of the oven at different times.

In detail, 12 samples (300 g each) for soil polluted by **mercury** were prepared for the test. Four electric ovens (F1-F4) were used for the test: F1=200°C, F2=220°C, F3=250°C and F4=260°C.
Three samples are placed in each oven and the last one (EP0) is put aside to define the initial state of the soil. One sample is taken out of the oven after 24, 72 and 168h the heating phase is carried out in electric ovens. A fan creates the negative pressure in the vapor network and blows the remaining vapours into the activated carbon filters “before being released in the atmosphere”.


Figure 2. Test set-up of protocol 1

4.2.2 Operating procedure – protocol 2

The treatment is designed in a setup reproducing on a reduced scale the thermal conduction treatment process that will be carried out on site. The soil is placed in a thermally insulated metal container (± 10 l) and heated by conduction with an electric resistance placed in the centre of the container.

The electrical resistance is controlled by a temperature controller in the ON / OFF mode, which allows the temperature of the resistor to be set to reach the target temperature. A perforated vapor tube is located at about 7 cm from the heating element. The vapor tube is connected to a refrigerant tube which condenses the vapours that are recovered in a round-bottom flask. A fan creates the negative pressure in the vapor network and blows the remaining vapours into the activated carbon filters before being released in the atmosphere.

Figure 3. Equipment set up of protocol 2

The evolution of the temperature in the soil is monitored using several K-type thermocouples placed in the soil sample at various positions. These temperatures are recorded continuously using a datalogger box. The figure 4 describes the temperature monitoring points in the soil.

At the end of the test the soil samples are cooled and then are sent to an aggregated soil analysis laboratory. The initial state is given by the non-treated samples.

- Ranges of tested temperature : 250°C – 450°C

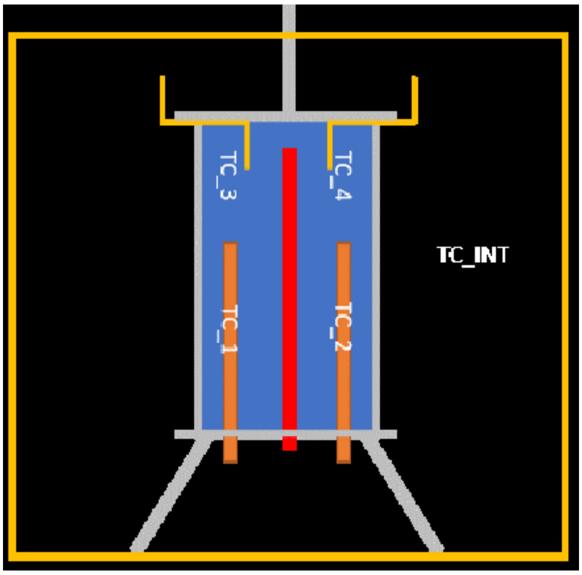


Figure 4. Temperature and monitoring points in the metal container of protocol 2

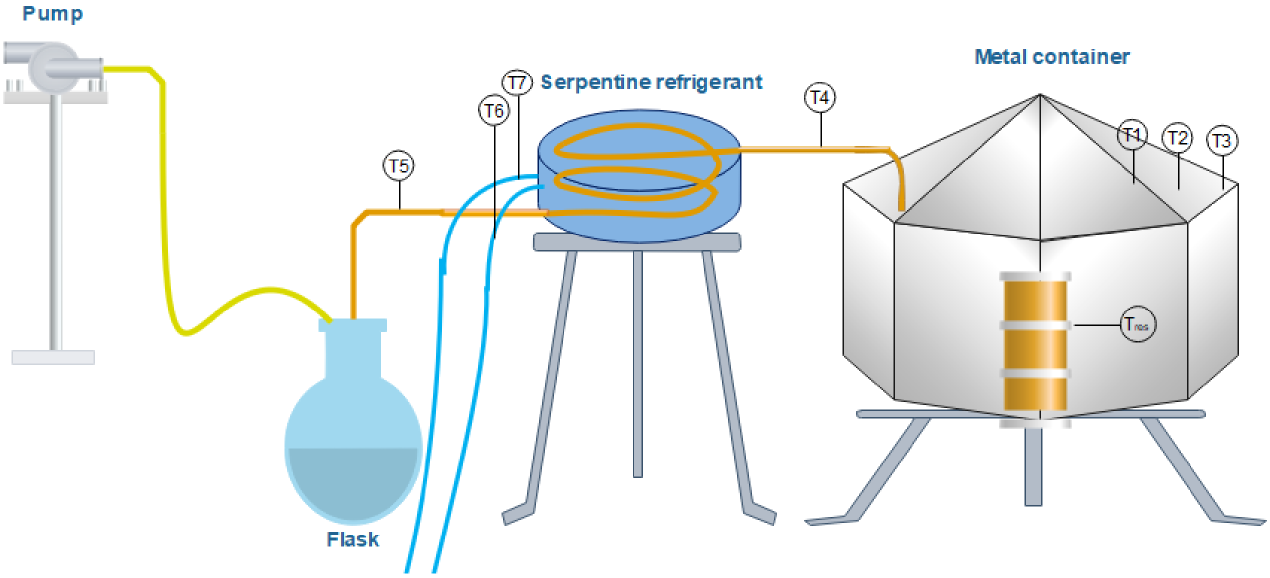


Figure 5. Equipment and monitoring details of protocol 2

4.2.3 Soil analysis methods description

The heated samples were analysed by 2 different agreed laboratories: (1) I2analytical and (2) Agrolab West B.V.

Laboratory	Analysis duration	Analysis method description	Accreditation Status	Measures
I2Analytical	Transport + 7 days	Determination of metals in soil by aqua-regia digestion followed by ICP-OES	ISO17025	Total mercury
I2analytical	Transport + 7 days	Determination of speciated mercury in soil by Millennium Merlin Analyzer	Internal method	Organo-mercury species; Elemental mercury; Inorganic mercury
Agrolab West B.V	Transport + 1 day	Determination of metals in soil by mineralisation followed by XRF	compliant with NEN 6950 (A) (Mineralisation according to NEN 6961, measurement according to NEN-ISO 16772) (A)	Total mercury

Table 8. Analysis method description

4.2.4 Results

4.2.4.1 Test 1

As depicted in table 3, protocol 1 was used to investigate the mercury kinetic behaviour between 200 and 260°C for a sample highly contaminated. Table 9 shows the different temperature and duration investigated, including the internal references.

T(°C)\time(h)	24	72	168
200	4	8	12
220	2	6	10
250	3	7	11
260	1	5	9

Table 9. Nomenclature lists of kinetic samples

The results of test 1 are shown in table 10. The complete laboratory report is given in appendix II and III.

Internal reference	Total mercury mg/kg DM	Organo-mercury species mg/kg DM	Inorganic mercury mg/kg DM	Elemental mercury mg/kg DM
Blank 1	6777	176	1584	5017
4 (200; 24h)	1000	77	634	272
2 (220; 24h)	820	70	318	393
3 (250; 24h)	430	31	294	82
1 (260; 24h)	510	55	322	87
8 (200; 48h)	550	48	368	108
6 (220; 48h)	490	48	271	118
7 (250; 48h)	360	-	-	-
5 (260; 48h)	470	50	296	82
12 (200; 168h)	700	73	437	167
10 (220; 168h)	430	-	-	-
11 (250; 168h)	420	29	284	68
9 (260; 168h)	200	19	128	34

Table 10. Mercury speciation results of test 1

Note that the samples 7 and 10 were sent directly in Agrolab West B.V. for total mercury analysis.

4.2.4.2 Test 2

Protocol 2 was used to investigate the mercury behaviour of a highly mercury contaminated sample at 300°C after 72h.

The results are shown in table 11. The results are shown in the appendices IV (from Agrolab) and V (from I2analytical).

Internal reference	Total mercury mg/kg DM	Organo-mercury species mg/kg DM	Inorganic mercury mg/kg DM	Elemental mercury mg/kg DM
Blank 1	6777	176	1584	5017
Hg30072#1	430	-	-	-
Hg30072#2	360	-	-	-
Hg30072	530	68	347	112

Table 11. Mercury speciation results of test 2

4.2.4.3 Test 3

Protocol 2 was used to investigate the mercury behavior of low contaminated sample at 300°C after 24h.

The results are shown in table 12. Two laboratories have been contacted to do the analyses. Only I2 Analytical was able to do the speciation. Both results are presented here below.

Internal reference	**Total mercury mg/kg DM**	**Organo-mercury species mg/kg DM**	**Inorganic mercury mg/kg DM**	**Elemental mercury mg/kg DM**
C	120	9	61	15
Hg30096-100 (Agrolab)	41	-	-	-
Hg30096-100 (I2 Analytical)	51	3,9	36,8	8,8

Table 12. Mercury speciation results of test 3

It is important to note that the sum of the species resulting from the speciation analyses do not equal the total mercury given in the table. This is because the figures are obtained through two different analyses.

A leachate test has been performed on the sample Hg30096-100. Its results are presented in the Table 13. 10l of water have washed 1kg of sample. The figure presented in the Table 13 is the concentration of dissolved mercury in the water after lixiviation.

Internal reference	**Dissolved mercury in leachates mg/l**
Hg30096-100	1,24

Table 13. Mercury concentration in the leachates of test 3

The complete reports are given in appendix I and VIII.

4.2.4.4 Test 4

Protocol 2 was used to investigate the mercury behavior of low contaminated sample at 300°C after 24h.

The results are shown in Table 14. Two laboratories have been contacted to do the analyses. Only I2 Analytical was able to do the speciation. Both results are presented here below.

Internal reference	**Total mercury mg/kg DM**	**Organo-mercury species mg/kg DM**	**Inorganic mercury mg/kg DM**	**Elemental mercury mg/kg DM**
E	43	2	27	7
Hg30096-40 (Agrolab)	30	-	-	-
Hg30096-40 ((I2 Analytical))	38	2,5	25,6	8,6

Table 14. Mercury speciation results of test 4

It is important to note that the sum of the species resulting from the speciation analyses do not equal the total mercury given in the table. This is because the figures are obtained through two different analyses.

A leachate test has been performed on the sample Hg30096-40. Its results are presented in Table 15. 10l of water have washed 1kg of sample. The figure presented in the Table 15Table 13 is the concentration of dissolved mercury in the water after lixiviation.

Internal reference	**Dissolved mercury in leachates mg/l**
Hg30096-40	0,97

Table 15. Mercury concentration in the leachates of the test 4

The complete reports are given in appendix I and VIII.

4.2.5 Discussions

4.2.5.1 Test 1

This test was carried out on a sample with a high initial mercury content to investigate the desorption kinetics parameters between 200 and 260°C.

The concentrations of organic, inorganic, and elemental mercury, including their associated degradation/elimination rates in relation to the initial concentrations, are depicted in the graph below (see figure 6 and figure 7).

Figure 6. Kinetic test 1 – Mercury concentrations and degradation/elimination rates

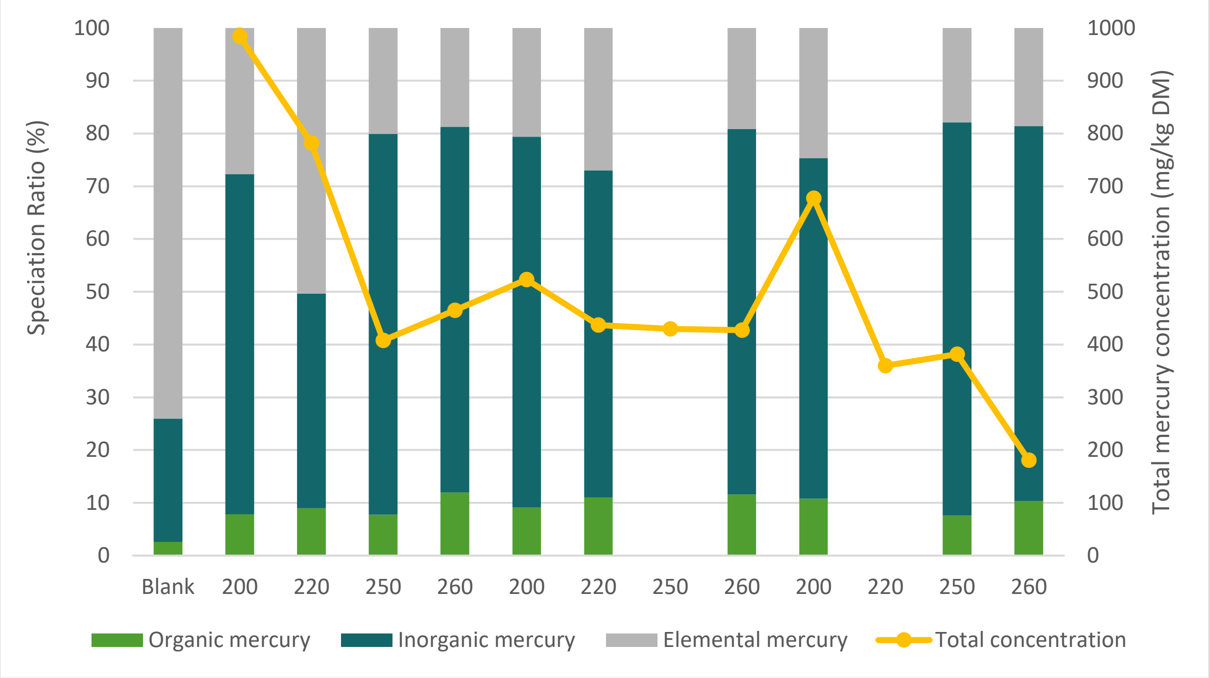


Figure 7. Desorption kinetics results of test 1 – Total mercury concentrations and speciation ratio

The following information is noted:

1. The higher the temperature, the lower the total mercury concentration, regardless of residence time. Note that the total mercury concentration of the sample "260°C – 24h" is higher than the sample "250°C-24h". This result is correlated to the heterogeneity within the initial samples and the uncertainties around the measures (due to the dilution factor – see appendix II).

2. The initial samples have the following ratio: 74% elemental mercury, 23% of inorganic mercury and 3% of organic mercury. The majority species after treatment, with high degradation/elimination rates of total mercury, is inorganic mercury (at least 64%), then the elemental part (average of 20%), and the organic part (10%). This observation may be correlated to the physical and chemical properties of the species. The most frequent organic species are dimethylmercury (II) and methylmercury (II) chloride which have boiling points (respectively 242°C and 92°C) lower than the elemental mercury (353°C).

3. Elemental mercury has a significant elimination rate of respectively 92 and 95% at 200°C and 220°C after 24h, corresponding to a concentration of 272 and 393 mg/kg DM. For a longer treatment time the concentration levels decrease rapidly to reach a value below 100 mg/kg DM, reaching reduction rates above 98%. The sample "260°C-168h" has a reduction rate of 99.33% with a final elemental mercury concentration of 33,58 mg/kg DM.

4. The degradation rates of the organo-mercury species are respectively 56%, 73% and 58% for 24h, 72h and 168h at 200°C, corresponding to a decrease from 176 mg/kg DM to maximum 77mg/kg DM. A trend seems also to be emerging through the residence time- the longer the treatment, the lower the organic concentration. Indeed, a final concentration of 18 mg/kg DM of organo-mercury species is measured after 168h at 260°C, corresponding to 90% of elimination rate.
5. 24h of heating phase at 200°C is sufficient to decrease the inorganic part from 1,584 mg/kg DM to 634 mg/kg DM, so 60% of decrease. Correlated to the presence of chlorinated solvent into the samples, this result involves the presence of inorganic volatile species such as dimethyl mercury chloride,

methylmercury chloride, mercury (I) chloride and mercury (II) chloride. This analysis does not exclude the potential presence of mercury (I) bromide, mercury (II) bromide, mercury (I) iodine, mercury (II) iodine and mercury (II) nitrate.

6. The degradation/elimination rates of inorganic mercury species are between 60% and 95%, directly proportional to the temperature and residence time. The comparison between the samples “200°C-168h” and “250°C-168h” shows a significant decrease of the inorganic concentration. The duration is therefore a key factor to break down/volatilize the inorganic part.

7. The residual concentration of inorganic mercury after 168h at 260°C is correlated to the presence of mercury salt with high boiling points such as mercury (II) sulfur, mercury (II) sulfate and potentially mercury (II) fluoride.

4.2.5.2 Test 2

The second test consisted of determining the degradation/elimination rates of a highly contaminated sample (6,800 mg/kg DM) at 300°C after 72h. The removal rates and the speciation ratio are shown in table 16 and figure 8.

Reference sample	Elimination rate (%)			
	Total mercury	Organo-mercury species	Inorganic species	Elemental mercury
Hg30072	92.17	61.36	78.09	97.77

Table 16. Elimination rate of mercury species after test 2

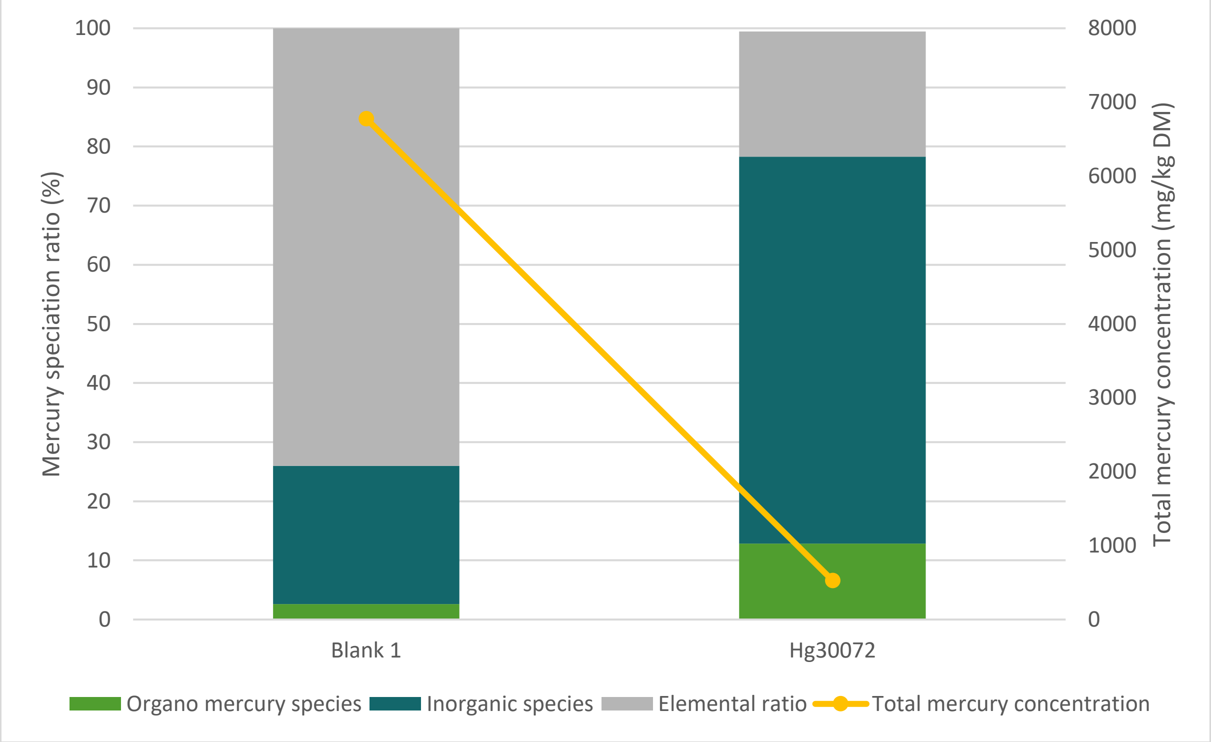


Figure 8. Speciation ration of the sample ‘O’ before and after test 2.

Based on the results, the followings are noted:

1. The total mercury degradation rate of test 2 (93%) is lower that the kinetic "260°C – 72h" of test 1 that depicts a degradation rate of almost 97%. This result may be explained by 2 reasons: (1) the heterogeneity within the sample and (2) the difference of protocol. Indeed, protocol 1 includes the heating phase of a jar of 300 ml in a furnace. The temperature within the jar reaches rapidly the target temperature. Protocol 2 includes the heating from the center of a sample of approximately 10l, 5 hours was necessary to bring the whole sample at the target temperature.

2. The elemental mercury concentration is also higher that the kinetic "260°C-72h". The same situation is observed for the organic and inorganic part.

3. The elemental mercury is the most affected by the heating phase: 97% was eliminated.

This result demonstrates the heterogeneity within the samples and the need to increase residence time for the future tests.

Note that the following information was made after the test:

1. Due to the low water content, the level at 100°C was hardly visible. This observation is directly related to the measures from the agreed laboratory (3-5% of initial water content - see appendix II).

2. Crystal formed in the vapor collectors (see figure 9 and appendix VII). This white crystal is soluble in water. Therefore, the main assumption is the formation of mercury (II) chloride in the vapors due to the presence of chlorinated and mercury compounds in the initial sample. The formation of mercury (II) bromide is not excluded due to the physical aspect and the high solubility. The collectors were decontaminated/cleaned in hot water in few minutes.

Figure 9. Picture of white crystal after test 2 heating phase.

4.2.5.3 Tests 3

The third test aimed at studying the kinetic behaviour of samples with low initial contents. Despite the feedbacks from the first two tests, this test could only be carried out over a short period of time – 24h.

The Table 17 depicts the elimination rate for the test 3.

Reference sample	Elimination rate (%)			
	Total mercury	Organo-mercury species	Inorganic species	Elemental mercury
Hg30096-100 (test 3)	58%	57%	40%	41%

Table 17. Elimination rate of mercury species after tests 3

Based on the results, the following observations are noted:

1. The initial concentration of total mercury of samples 'C' (see table 3) is 120 mg/kg, with predominantly inorganic mercury (71%), 18% of the total mercury is elemental mercury followed by organo mercury species with 11%. One can observe that the proportion of the species differs from high and low concentrations sample. The table 18 summarises the ratios of all sample before treatment.

Sample reference	Total mercury ratio	Organo-mercury species ratio	Inorganic mercury ratio	Elemental mercury ratio
O	6777 mg/kg DM	3%	23%	74%
C	120 mg/kg DM	11%	71%	18%
E	43 mg/kg DM	6%	75%	19%

Table 18. Mercury species ratio within initial blank samples

2. The total mercury concentration decreases at 51 mg/kg DM after 24h at 300°C. with a total mercury decrease of 58%. This figure is lower than the one observed in the tests 1 and 2. It cannot be excluded that longer period of heating at this temperature would have resulted in higher global removal rate.

3. In average the degradation ratios are lower than the ones observed within the test 1 and 2. The lower degradation ratio are to be seen in the light of the shorter treatment time (24h) and the lower initial concentration. The organo mercury species are the ones that show the highest degradation ratio (57%) followed by elemental mercury (41%) and inorganic species (40%). Nevertheless, the final concentrations of all species are lower than the one observed in the tests 1 and 2 suggesting the ability of thermal desorption to decrease the mercury concentration at lower values than observed after test 1 and 2.

4. As it can be observed on the table 18, the speciation of the sample before and after treatment are very similar. Where for the test 1 and 2 the drastic decrease in elemental mercury thanks to the heating results in a large dominance of the inorganic species after treatment. In this test, the initial concentration in elemental mercury within the blank 'C' sample was already very low before treatment avoiding an as important elimination rate as for the two first tests. Moreover, the removal rates are similar for all species (see Table 17. Elimination rate of mercury species after tests 3. Nonetheless, the mercury species are largely dominated by inorganic species (74%) after treatment.

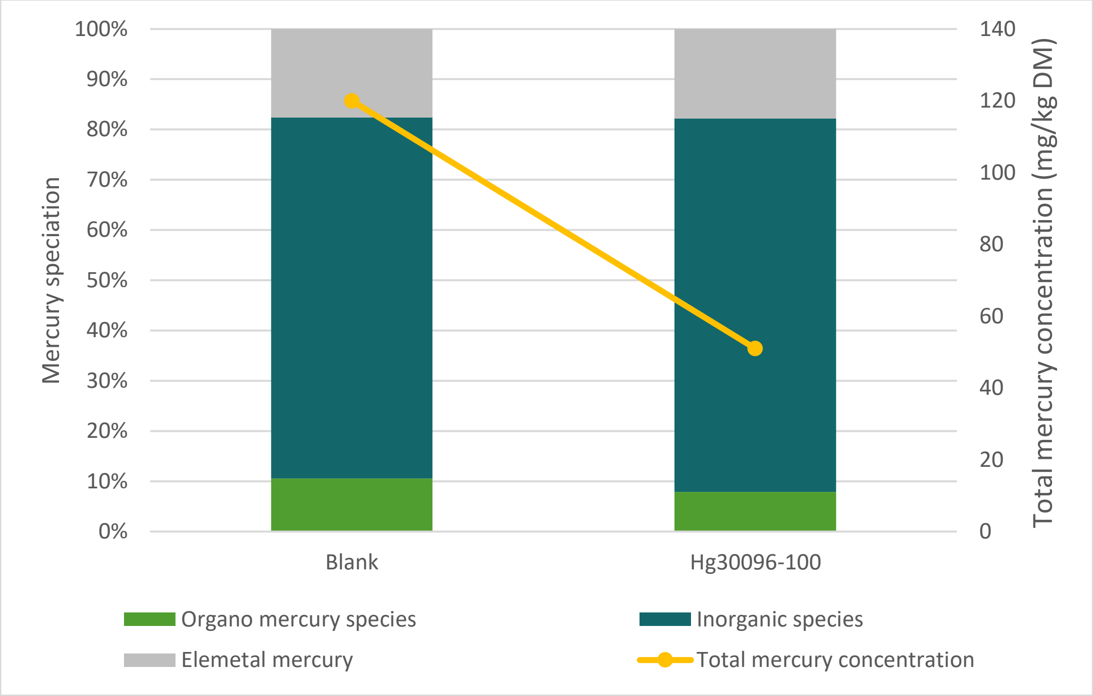


Figure 10. Speciation of the sample C before and after test 3

5. As an assumption and based on the previous results (see test 1), the elemental mercury and inorganic part should be the most affected. However, the measurements on the initial sample indicate 61 mg/kg DM of inorganic mercury, which corroborated to removal of 'light' inorganic species such mercury chloride (II).

6. The residual concentration of inorganic mercury is correlated to the presence of mercury salt with high boiling points such as mercury (II) sulfur, mercury (II) sulfate and potentially mercury (II) fluoride.

4.2.5.4 Leachate test on Hg30096-100

The leachate test is performed over 1kg of sample which is washed with 10 l of water. The dissolved mercury concentration is measured in the leachate and is reported in the Table 13.

Based on the leachate test that has been performed on the Hg30096-100 sample after treatment, the following observations are noted:

1. Out of the initial 51 mg contained in the kg of sample 12.4 mg (24%) have leachate and dissolved in the water.

2. The speciation ratio of the dissolved mercury is proportional to both the initial speciation and the specific solubility coefficient of each species. The sample being mainly dominated by inorganic species it is highly possible that the dissolved phase is also dominated by inorganic species within which, mercury (II) chloride and mercury (II) bromide are the most soluble in water.

4.2.5.5 Test 4

The fourth test aimed at studying the kinetic behaviour of samples with low initial contents. Despite the feedbacks from the first two tests, this test could only be carried out over a short period of time – 24h.

The Table 19 depicts the elimination rate for the test 4.

Reference sample	Elimination rate (%)			
	Total mercury	Organo-mercury species	Inorganic species	Elemental mercury
Hg30096-100 (test 3)	12%	-25%	5%	-23%

Table 19. Elimination rate of mercury species after tests 4

Note that some figures in the table above are negative. This means that the laboratory results showed higher values of concentration after the heating than before highlighting the sample heterogeneity and limitation of the laboratory protocol to mitigate that well known issue with mercury.

Based on the results, the following observations are noted:

1. The initial concentration of total mercury of samples 'E' (see table 3) is 43 mg/kg, with predominantly inorganic mercury (75%), 19% of the total mercury is elemental mercury followed by organo mercury species with 6%.

2. The total mercury concentration decreases at 38 mg/kg DM after 24h at 300°C. with a total mercury decrease of 12%. This figure is lower than the one observed in the tests 1 and 2 and 3. It cannot be excluded that longer period of heating at this temperature would have resulted in higher global removal rate. This figure of 12% is to be interpreted very carefully as this test and its related analyses clearly show heterogeneity in the sample. The higher concentration of organo-mercury species and elemental mercury is indeed the result of heterogeneity of the sample.

3. The final concentrations of all species are lower than the one observed in the tests 1 and 2 suggesting the ability of thermal desorption to decrease the mercury concentration at lower values than observed after test 1 and 2.

4. Just as the test 3 and as it can be observed on the figure 11, the speciation of the sample before and after treatment are very similar. Where for the test 1 and 2 the drastic decrease in elemental mercury thanks to the heating results in a large dominance of the inorganic species after treatment. In this test, the initial concentration in elemental mercury within the blank 'C' sample was already very low before treatment avoiding an as important elimination rate as for the two first tests. Moreover, the removal rates are similar for all species (see table 17). Nonetheless, the mercury species are largely dominated by inorganic species (75%) after treatment.

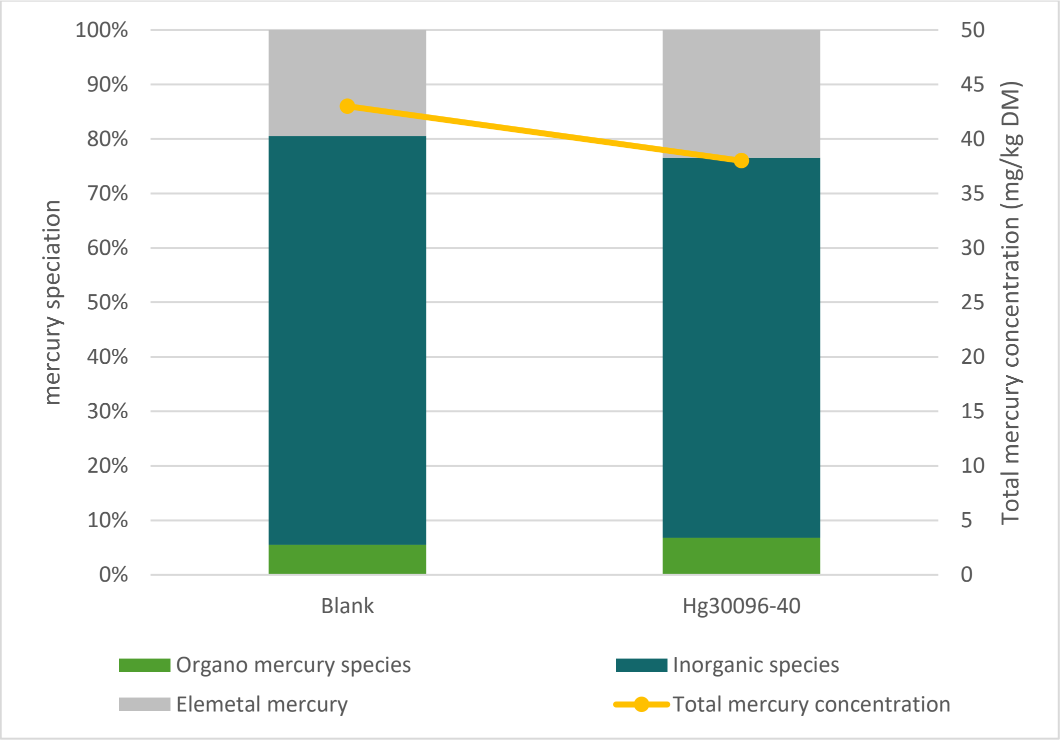


Figure 11. Speciation of the sample E before and after test 4

5. The residual concentration of inorganic mercury is correlated to the presence of mercury salt with high boiling points such as mercury (II) sulfur, mercury (II) sulfate and potentially mercury (II) fluoride.

4.2.5.6 Leachate test on Hg30096-40

The leachate test is performed over 1kg of sample which is washed with 10 l of water. The dissolved mercury concentration is measured in the leachate and is reported in the Table 15.

Based on the leachate test that has been performed on the Hg30096-100 sample after treatment, the following observations are noted:

1. Out of the initial 38mg contained in the kg of sample 9.7 mg (26%) have leachate and dissolved in the water. The proportion of dissolved material is similar to the one observed on the Hg30096-100 sample.

2. The speciation ratio of the dissolved mercury is proportional to both the initial speciation and the specific solubility coefficient of each species. The sample being mainly dominated by inorganic species it is highly possible that the dissolved phase is also dominated by inorganic species within which, mercury (II) chloride and mercury (II) bromide are the most soluble in water.

5 PILOT DEMONSTRATION

5.1 Site location

The project is located in Israël, in Haifa Bay (GPS coordinates: 32°53’56.3” N; 35°05’02.4” E). The following provides a summary of Haemers Technologies understanding of the Site, based on information provided by Tidhar Harel Menivim Partnership (“the final client”) and LDD Advanced Technologies (the consultant). The site is a large disaffected chemical industrial factory made of many decaying buildings.

The location is depicted below.

Figure 12. Site location – google map view

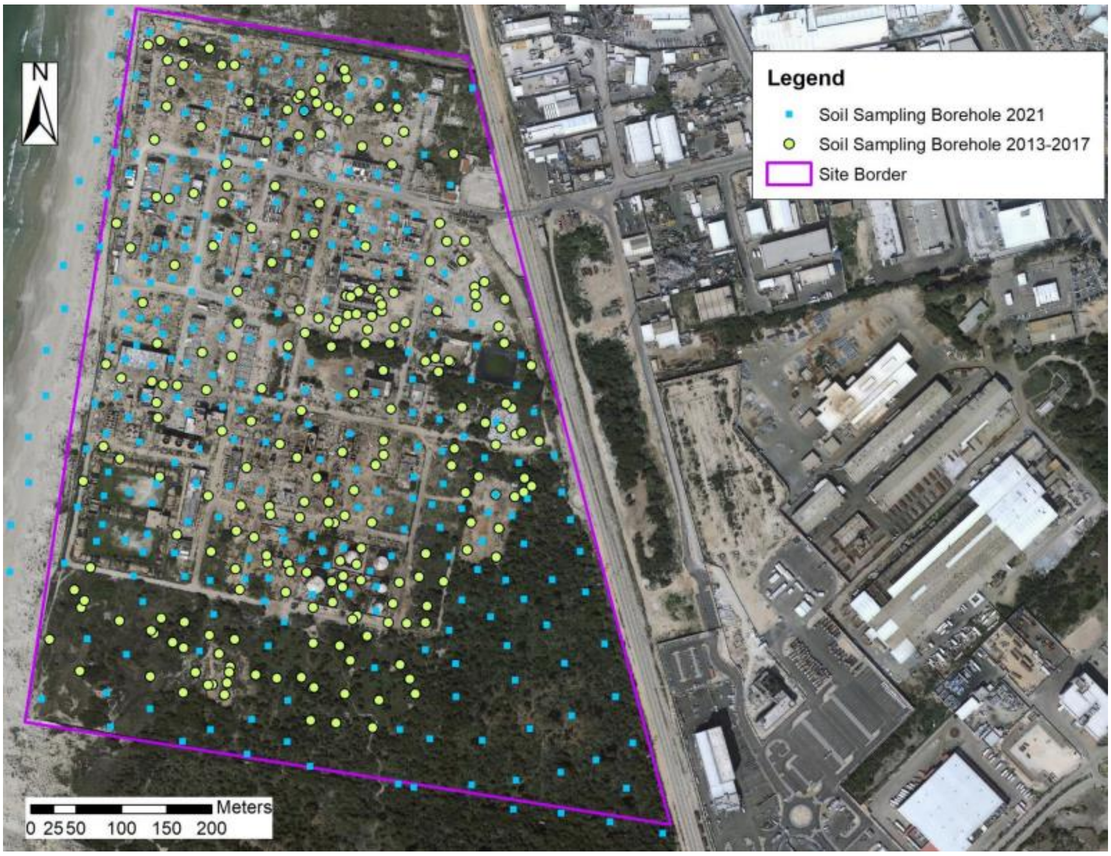


Figure 13. The site – google map view

Figure 14. Pilot location of PAKK

5.2 Material properties

The properties (table 20), the quantities of the pilot (table 21) and the initial concentrations of the contaminated soil (table 22) for the pilot phase are given below.

Item	Quantity	Unit

Average Soil Density	1.600	kg/m^3
Average Porosity*	0.33	V_V/V_T
Moisture Content*	0.10	W_{water}/W_{sol}

Table 20. Relevant properties of the soil to be treated. *Assumed when not provided

Item	Zone 1	Unit
Total Treatment Volume	275	m^3
Total Treatment Mass	440	tons

Table 21 : Quantities of soil to be treated

The soils are from 2 different locations, with unknown ratio. The tables below show the maximum concentrations of the samples, including their target concentrations and boiling points. Details are given in Appendix I.

Compounds	Concentration max. [mg/kg]	Target values for soil after treatment [mg/kg]	Boiling Point [°C]
Total Mercury	5206,0	**416.5 – 455.0**	See p. 17
Mercuric inorganic	Unknown	7.5 – 46.0	
Mercury Elemental	Unknown	307.0	
Methyl Mercury	Unknown	102.0	
Solid Metal			
Arsenic, Inorganic	2,60	16,0	613 (pure)
Barium	0,00	194.000,0	1.897 (pure)
Nickel Soluble Salts	0,00	12.800,0	2,730 (pure)
Zinc and compounds	74,00	30.7000,0	907 (pure)
Copper	100,00	40.900,0	2.562 (pure)
Boron And Borates Only	0,00	204.000,0	4.000 (pure)
Beryllium and compounds	0,50	2.020,0	2.469 (pure)
Vanadium and compounds	3,00	4.920,0	3.407 (pure)
H			
Benzene	0,17	1,5	80
Toluene	0,18	168,0	111
Ethylbenzene	0,92	11,2	136
Methyl tert-Butyl Ether (MTBE)	0,07	110,0	55
Xylenes	0,55	49,7	138
Tetrachloroethylene (PCE)	263,65	20,3	121
Dichloroethylene, 1,2-trans	0,01	667,0	60
Vinyl Chloride	0,01	1,34	-13.4
Trichloroethylene (TCE)	32,48	1,76	87
Dichloroethylene, 1,1	4,30	662,0	32

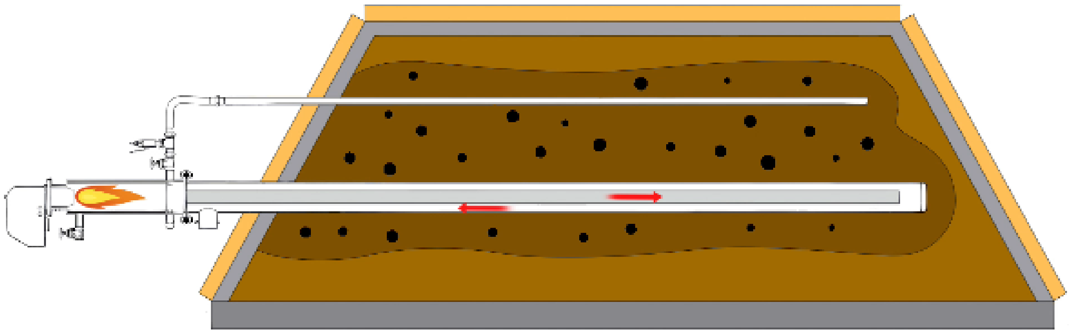
Dichloroethane, 1,2-(EDC)	13,72	0,6	83
Carbon Tetrachloride	0,01	2,0	77
Chloroform	0,38	0,73	61
Dichlorobenzene, 1,4	5,62	4,73	174
Chlorophenol, 2-	0,01	4760,0	220
Chlorobenzene	48,39	145,0	132
Hexachlorobenzene	195,28	0,04	322.2
Hexachlorocyclohexane, Beta-	Unknown	1,12	323
Bis(2-chloroethyl)ether	3,60	0,57	178
Dioxane, 1,4-	0,00	18,7	101
Trichloroethane, 1,1,2-	271,93	2,35	74
Dichloroethane, 1,1-	0,02	8,68	84

Table 22. Initial concentrations, target concentrations and boiling points of contaminant of concerns for the pilot test

5.3 Design

5.3.1 Technology outline

In Haemers Technologies' process (Patent No. BE1024596B1, 2016) polluted soil is heated by conduction under the action of Smart Burners™ developed by Haemers Technologies. More precisely, steel tubes are inserted into the soil to be remediated. Hot gases, generated by Smart Burners™, circulate in the tubes in order to transfer heat to the soil. This results in the vaporization of the pollutants in the soil when their boiling temperature is reached. The vapors emitted are then drawn through perforated steel tubes, called vapor tubes, and are then either treated in a vapor treatment unit or re-injected into the flame generated by the Smart Burners (in the case of hydrocarbons pollution).



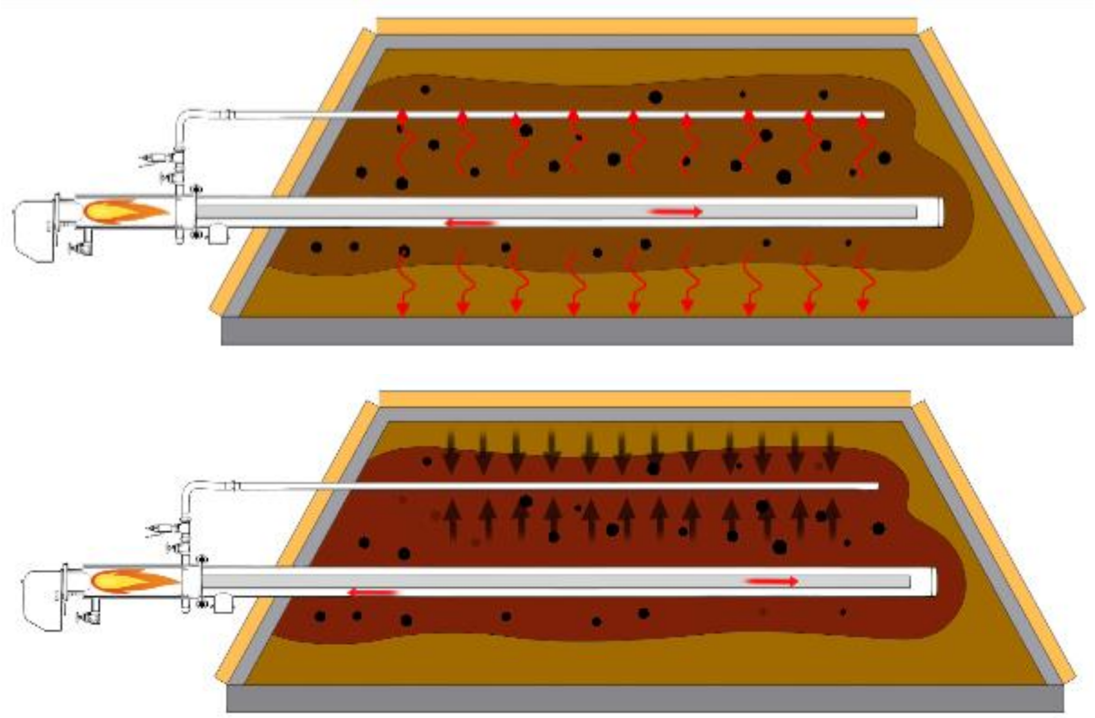


Figure 15. Ex-Situ Thermal Desorption principle

5.3.2 Pilot Design

The ESTD is composed of 15 horizontal heating tubes and 15 exchanger tubes (figure 16). The exchanger tubes recover the combustion gases after their passage through the heating tubes, allowing a second passage through the pile. The fan, located at the back of the pile, drives the combustion gases from the burners through the tube network to the chimney. The combustion gases never encounter the contaminated soil and circulate through the tube network until they are released into the atmosphere. Conversely, the polluted vapors generated by the temperature rise in the pile are collected by the vapor tubes placed inside the pile and connected to a collector, placed in front of the pile, leading the polluted vapors to the vapor treatment unit.

The main goal of treatment is to lower the mercury and VOC/S-VOC concentrations in contaminated soils to target objectives (see table 22) by heating the soil to the target temperature of 335°C.

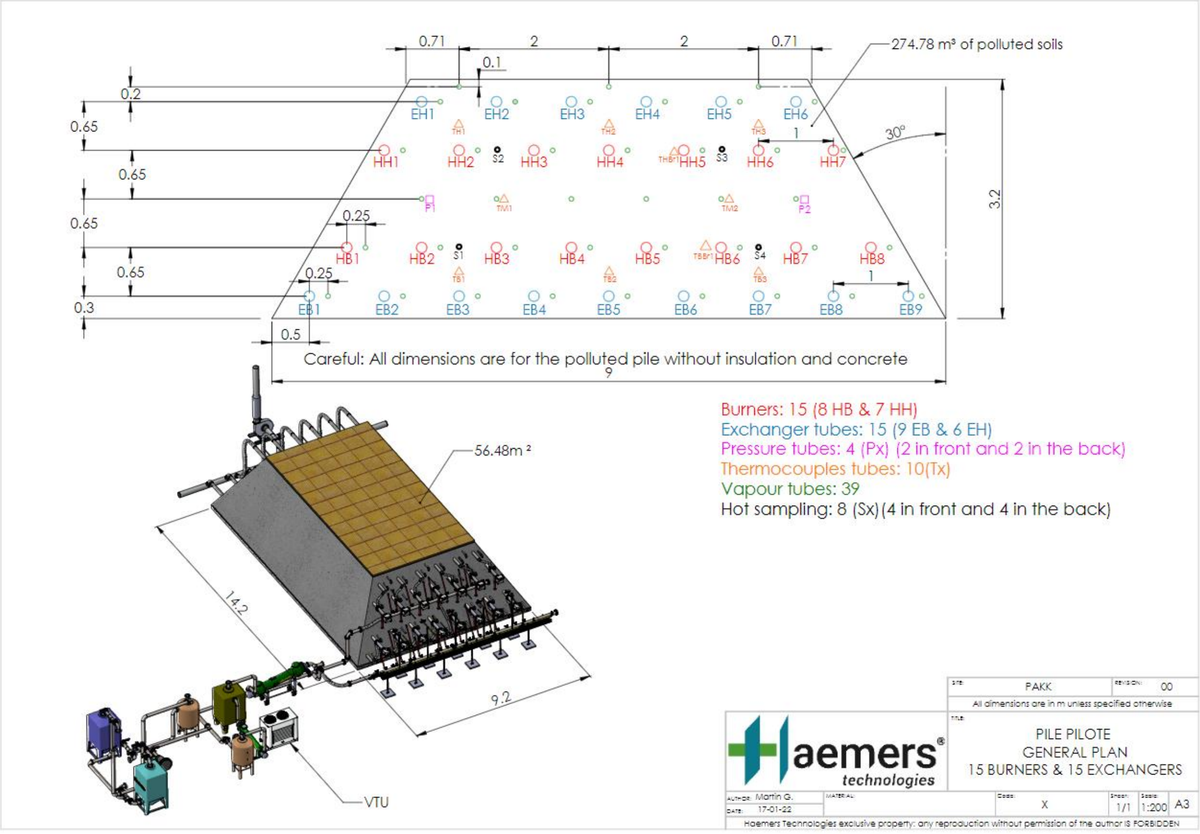


Figure 16. Heating elements disposition

The top of the pile is covered with a layer of gravel, in which more vapor tubes, called secondary vapor tubes, are placed. These secondary vapour tubes are an additional security to avoid any fugitive emission or contamination of the concrete. The whole pile is then covered with concrete and thermal insulation.

The electrical, the exhaust, and the fuel networks are respectively depicted in figure 17, figure 18 and figure 19.

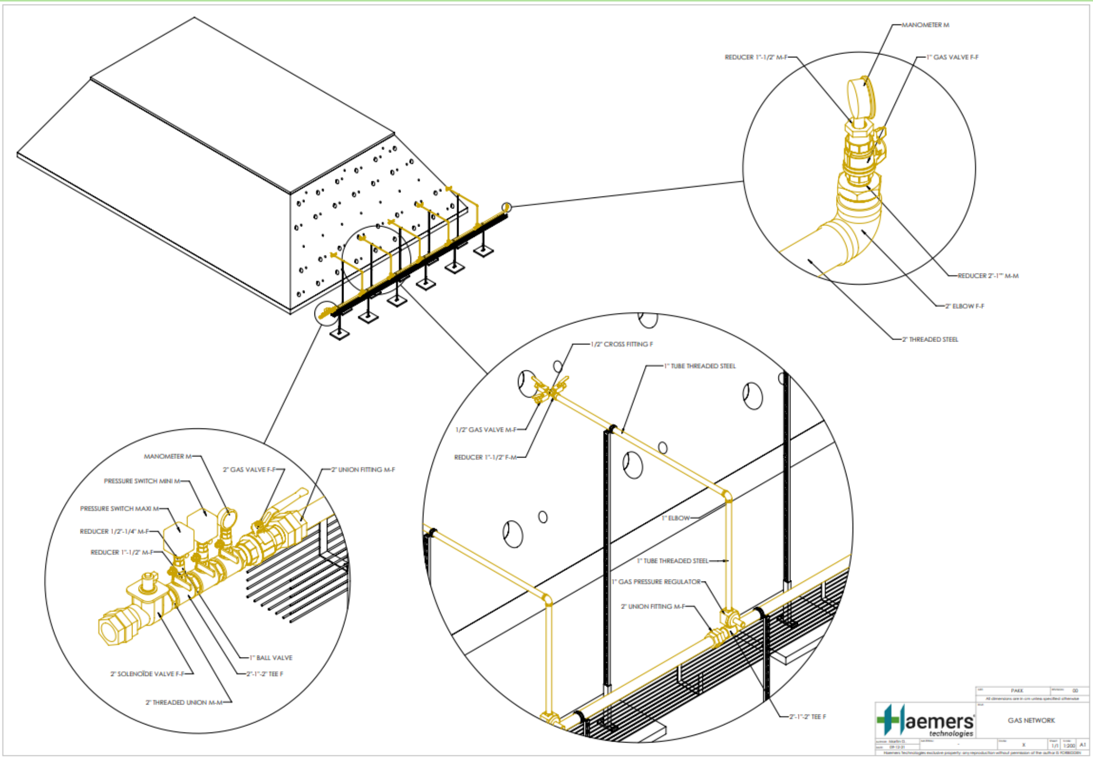


Figure 17. Gas line plan

The electrical supply for the whole installation was insured by a diesel generator. The electrical supply was distributed and controlled by a general electrical box designed by HT (see Figure 18).

The main power consumptions were associated with the blower; chiller; pumps; burners and monitoring.

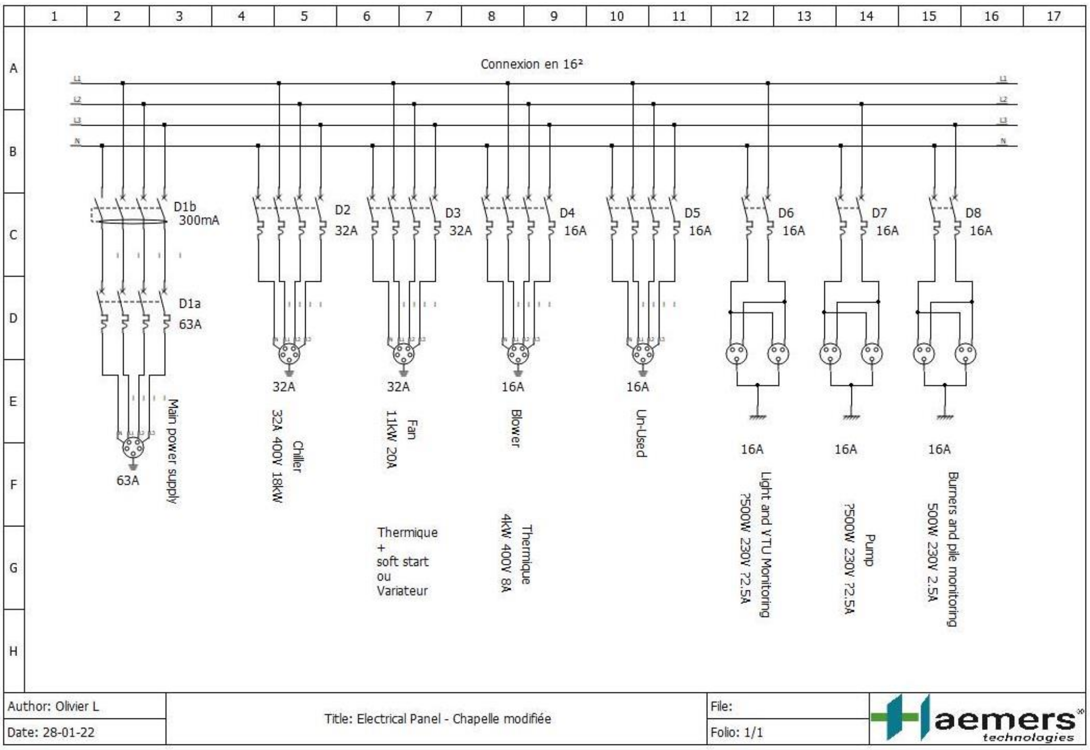


Figure 18. electric layout

The combustion gas exhaust network was built as per specified in HT standard operating procedures and specification. All combustion gases are collected and directed toward the main stack.

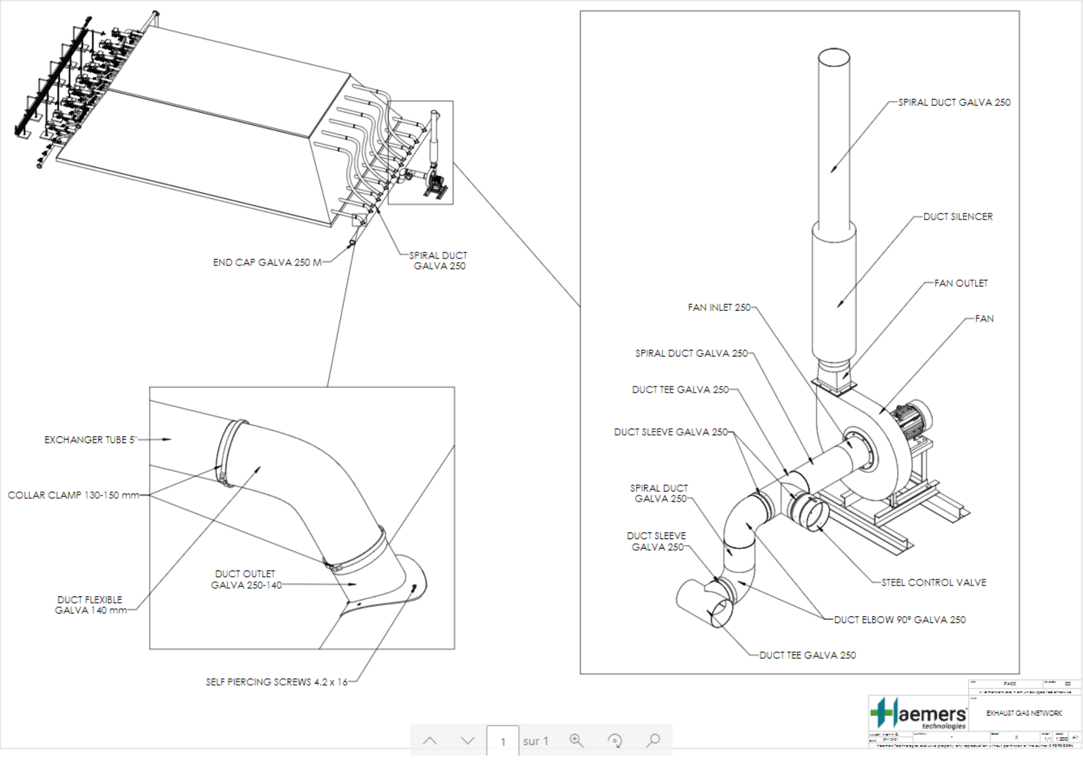


Figure 19. Combustion gas exhaust network

5.3.3 Vapor treatment unit design

The purpose of the VTU (Vapor Treatment Unit) is to handle the contaminated vapors produced in the soil and reduce their concentrations below legal emission standards.

The vapors were vacuumed from the pile and routed towards a Vapor Treatment Unit (VTU) to be properly treated prior to be emitted though the VTU stack. The VTU layout is given in the figure 20.

The VTU is composed of three main steps:

1. Cooling of the vapor: achieved by two heat exchangers in series, one cooled by water, the other by a cooling fluid (60% glycol) (cooled by a chiller).

2. Condensation: mainly achieved by two knock out tanks. Moreover, each element of the VTU was connected to a network of pumps and tanks to collect all the condensate product.

3. Adsorption: All vapors that were not condensate were adsorbed on two activated carbon filters in series. One of them was specially designed for VOC's adsorption, the other for Mercury. The filters line was doubled to be able to switch from one line to the other for maintenance and safety reasons.

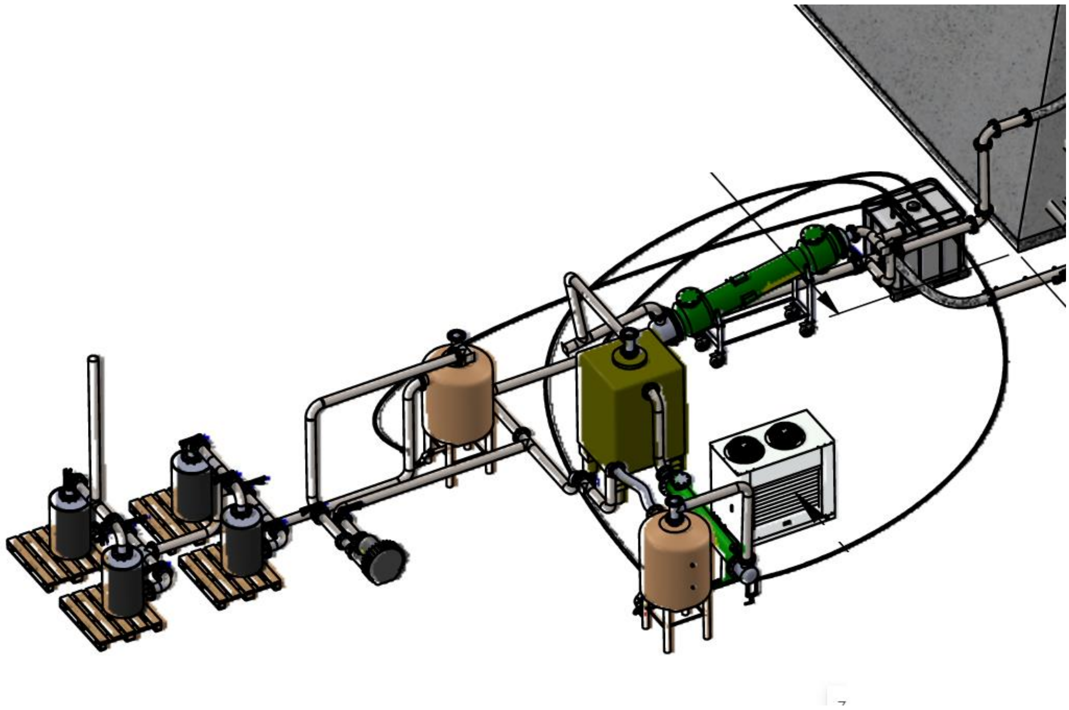


Figure 20. Vapor Treatment Unit (VTU) design for the AKKO pilot

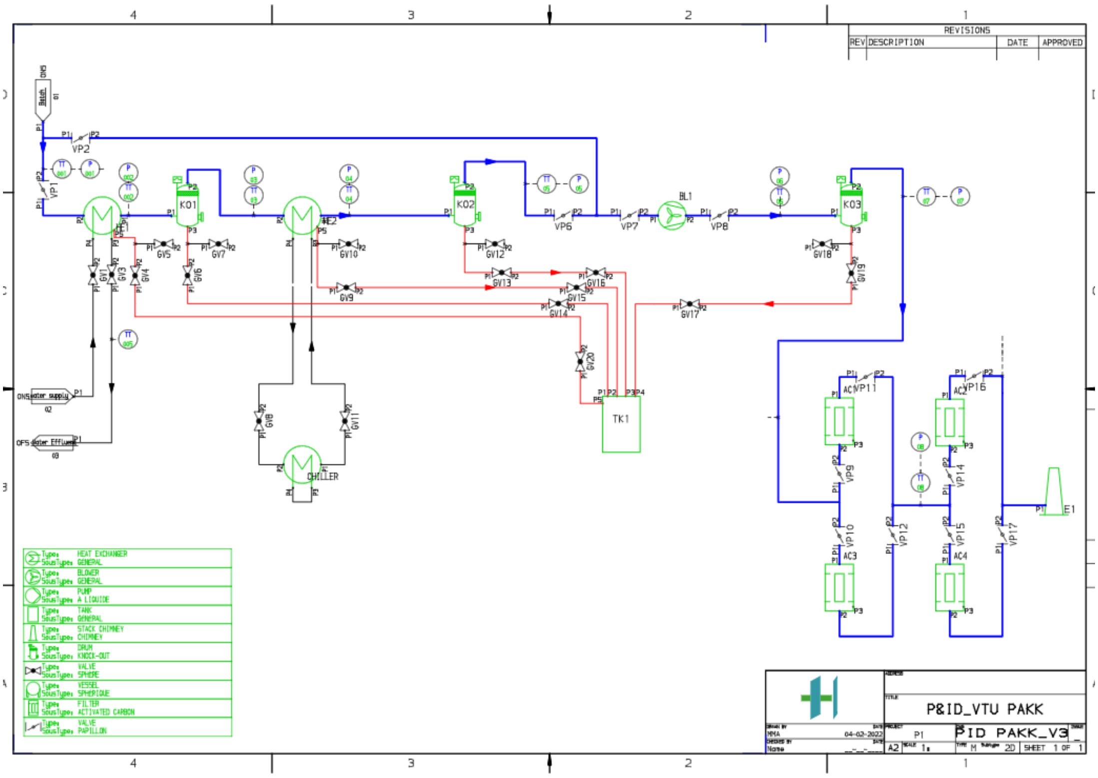


Figure 21. VTU P&ID

5.4 Installation and Preparation

5.4.1 Pile building

The building of the pile begun mid-January and was carried out in 4 days.

The pile was built with two distinct materials from the site. Half of the pile was composed with soil contaminated with a complex cocktail of SVOC the other half with heavily Mercury contaminated soil (see table 22). The two materials were laid, layer by layer over the whole pile surface. Due to the site condition and the constraint of this operational step, one cannot exclude the mixing of the two materials during the building resulting in a soil contaminated with a cocktail of Mercury and SVOC.

The building phase are shown in the figures below.

Figure 22. First layer of draining bed

Figure 23. Second layer of of draining bed of thermal pile

Figure 24. First layer of contaminated soil on the draining bed of the thermal pile

Figure 25. Installation of the first layer of heat exchanger tube

Figure 26. Building phase of the thermal pile

Figure 27. Picture of the pile after building-up

The pile design is given in figure 28. The total volume of the pile was of ~275m³ (see as built plan in figure 28).

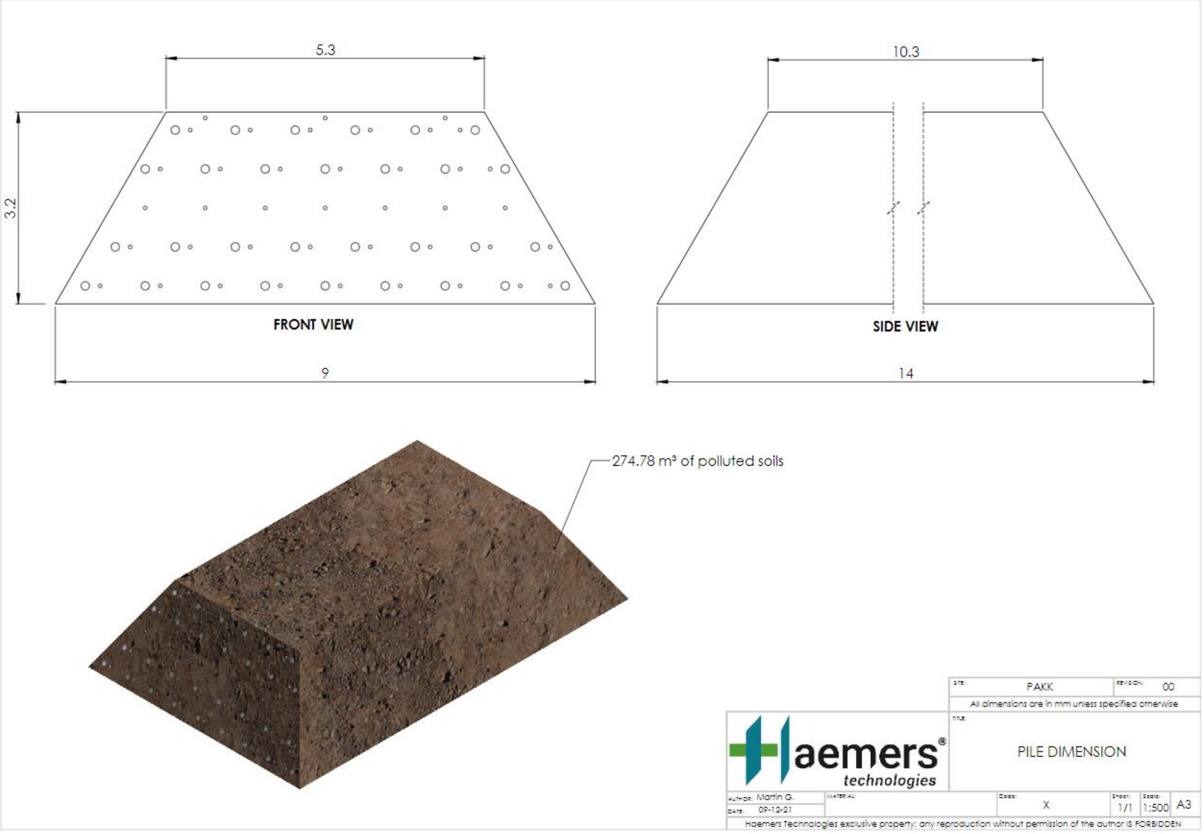


Figure 28. As built dimensions

Then, concrete slab was poured on the pile and insulation was installed on the top to limit the heat losses.

Two gas tanks of 5.000l were installed underground by the client. The main gas line (from the tanks to the pile) has also been build-up by the client. HT has built the rest of the line deserving every individual burner according to its standard plan and specification (see Figure 29)

The electrical, exhaust, gas and vapor networks are then built up (see figure 30, figure 31, and figure 32).

Figure 29. On site gas line

Figure 30. Front of the pile (corresponding to the back of the VTU on the left on the picture)

Figure 31. Front view of the pile with the networks and signalisation

Figure 32. Back of the thermal pile corresponding to the stack of the exhaust gas from the Smart Burners™

A diesel generator was installed to supply electricity to the treatment (see.

Figure 33. Diesel generator. Green tank: diesel tank, white container: generator

5.4.2 Vapor treatment unit and condensate tank installation

The vapor treatment unit and condensate tanks were installed in one week. The VTU is composed of two heat exchangers, a tank of liquids, a pump, three knock-out, a chiller, a blower and four activated carbon tanks. Despite the presence of COCs and mercury concentration in the soils the vapors can be treated by the same VTU. In order to do so, four activated carbon barrels are placed in series, the two first ones for the chlorinated contaminants and the two last ones to neutralized mercury compounds.

As to avoid condensate accumulation inside the VTU and create pressure issues different syphons (with 1” tubes) have been placed at each low point present in the VTU.

As we were dealing with mercury the installation had to be completely sealed/airtight to avoid any health risk.

Figure 34. First heat exchanger of the VTU for the AKKO pilot process

Figure 35. Chiller connected to the second heat exchanger

Figure 36. Knock-out to recover the condensate entrained in the flow

Figure 37. Activated carbon barrels in series to trap the non-condensable VOC and mercury vapors

Figure 38. Condensate tanks in front of the pile

5.4.3 Monitoring of the pile and the vapor treatment unit

Two main parameters were monitored within the pile itself throughout the whole project. All parameters monitored were compiled into a report which was daily communicated to the client.

5.4.3.1 Temperature monitoring

Ten thermocouples' tubes were installed within the pile. 3 thermocouples were installed at different depth within each tube for HT to be able to have a live visualisation of the temperature. The thermocouples are linked to raspberries which then sent all the data to a database. The temperature data are therefore acquired remotely and continuously. The thermocouples layout is given in the Figure 39 and are represented by the orange triangles. As a rule, the thermocouples are place at the 'cold point' (i.e., the further location between a triangle of heating element).

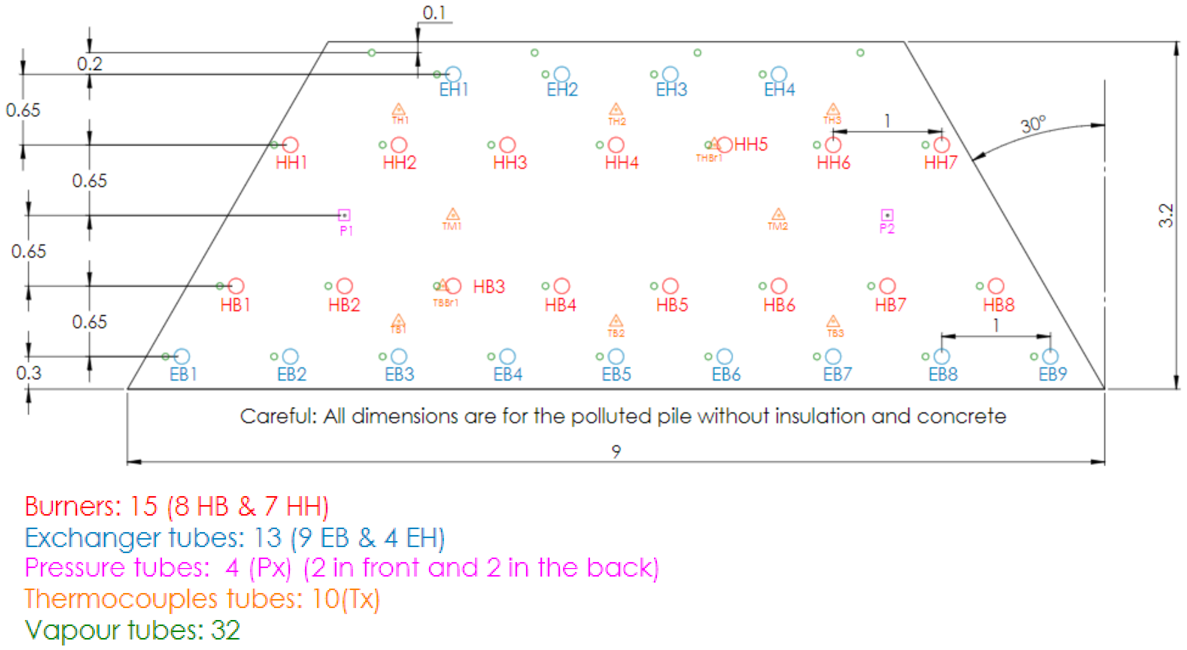


Figure 39. Tubes layout

5.4.3.2 Pressure monitoring

Four pressure tubes were installed (two on each side of the pile). Pressure tubes allows HT staff to manually measure (with an adapted measuring equipment) the pressure within the pile. The pressure was taken daily at each tube location.

5.4.3.3 Monitoring of the combustion gases

The combustion gases from the burners are collected and emitted at a stack. The stack was monitored daily for various parameters (i.e. O_2, CO_2, CO, CxHy, NOx)

5.4.3.4 Monitoring of vapor treatment unit

The VTU was equipped with 9 measuring locations (see figure 40) which allowed HT's staff to have a precise understanding of the key physic-chemical parameters within it. Each monitoring location was analysed at least once a day.

The VTU stack was particularly monitored to ensure compliant emission for key parameters (Hg, VOCs, CO, aso). All parameters were compiled in a report and communicated daily to the client.

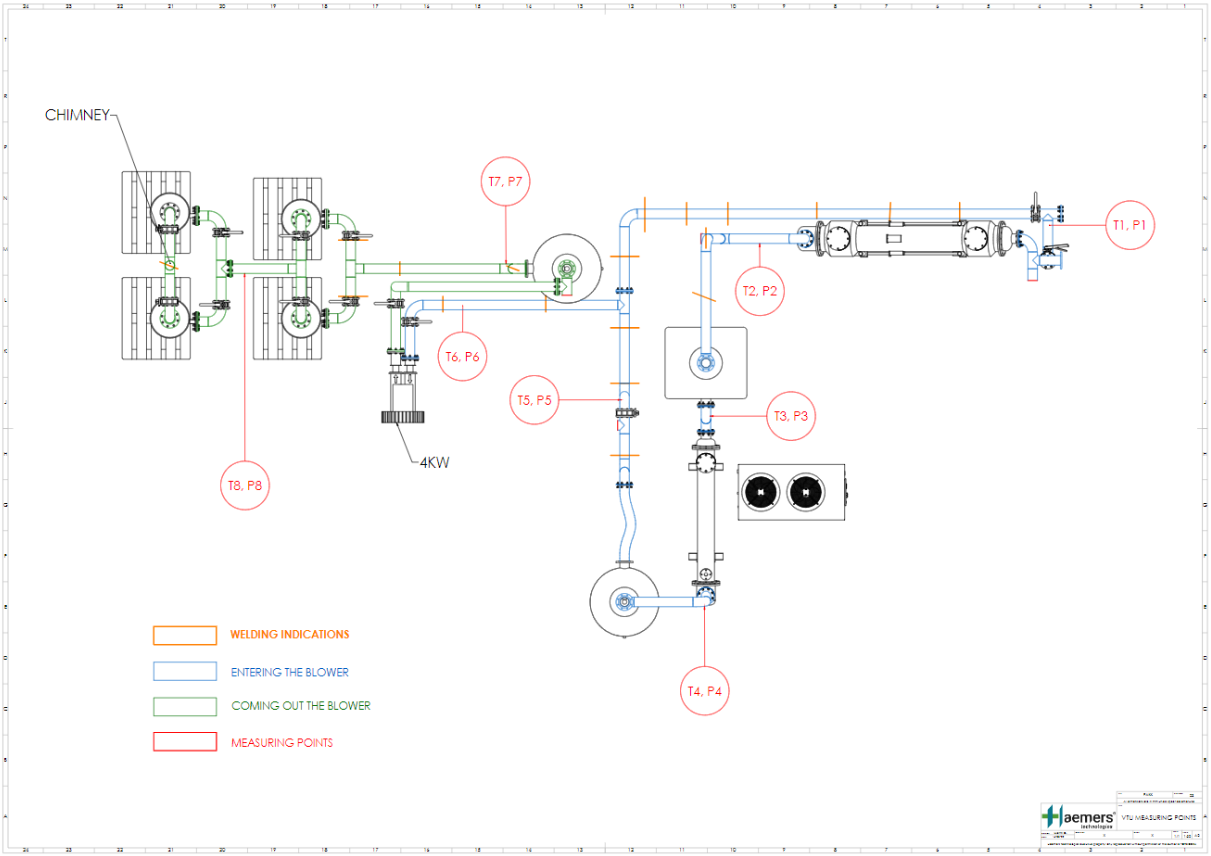


Figure 40. VTU Location for monitoring

5.4.3.5 Ambient air monitoring

Measure of ambient Hg and VOCs were taken daily both at the office location and next to the VTU. All parameters were compiled in a report and communicated daily to the client.

5.5 Treatment Results

This section aims to provide the data of all relevant parameters that were monitored and that helped to evaluate the efficiency and compliancy of the thermal desorption process.

5.5.1 Fuel consumption

The theoretical and practical fuel consumption are given in table 23.

	Quantity	Unit
Theoretical propane consumption	25.000	kg
Theoretical propane consumption per t of soil	56	kg/t
Propane consumption	20.000	kg
Propane consumption per m^3 of soil	45	kg/t

Table 23. Theoretical and practical fuel consumption

The theoretical fuel consumption is higher than the practical consumption. This deviation is directly correlated to the initial water content of the contaminated soil that was initially estimated at 18%. Initial sample showed an average water content of 5%.

5.5.2 Soil temperature

The soil target temperature at the cold point was set to be 350°C. It's important to keep in mind that the graphs of temperature presented here below give the theoretically lowest temperature in the pile as the thermocouples are placed at the geometric centre of a triangle formed by three burners.

The thermocouple tube locations are depicted in the figure 39.

5.5.2.1 Soil temperature grounded by depth (from front to back)

The figure 41 and figure 42 show that the temperature of the soil at the front and the middle of the pile raised quickly over the target temperature. All the thermocouples reached 350°C after approximately a month of heating.

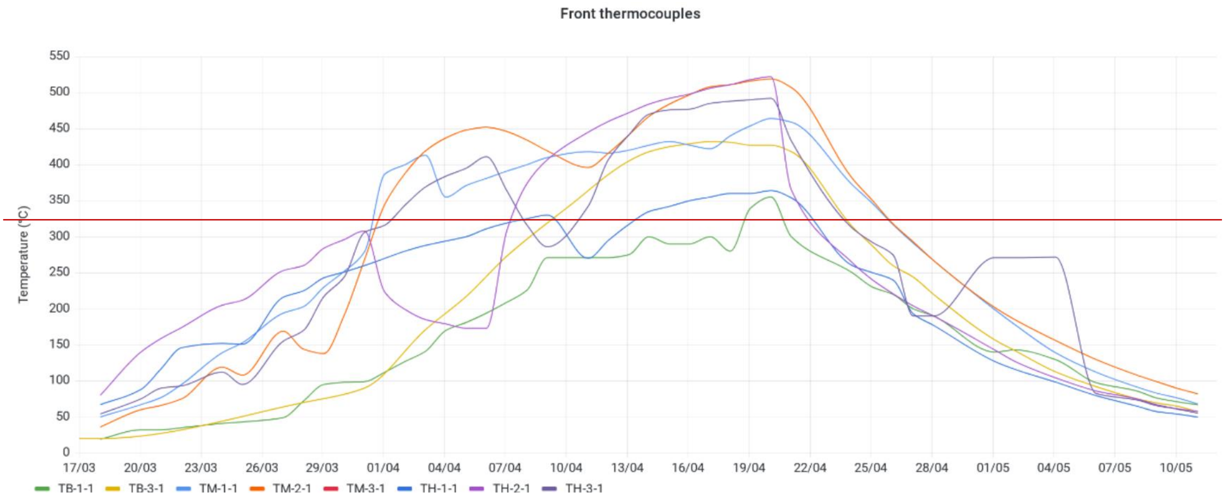


Figure 41. Soil temperature (front of the pile – burner side)

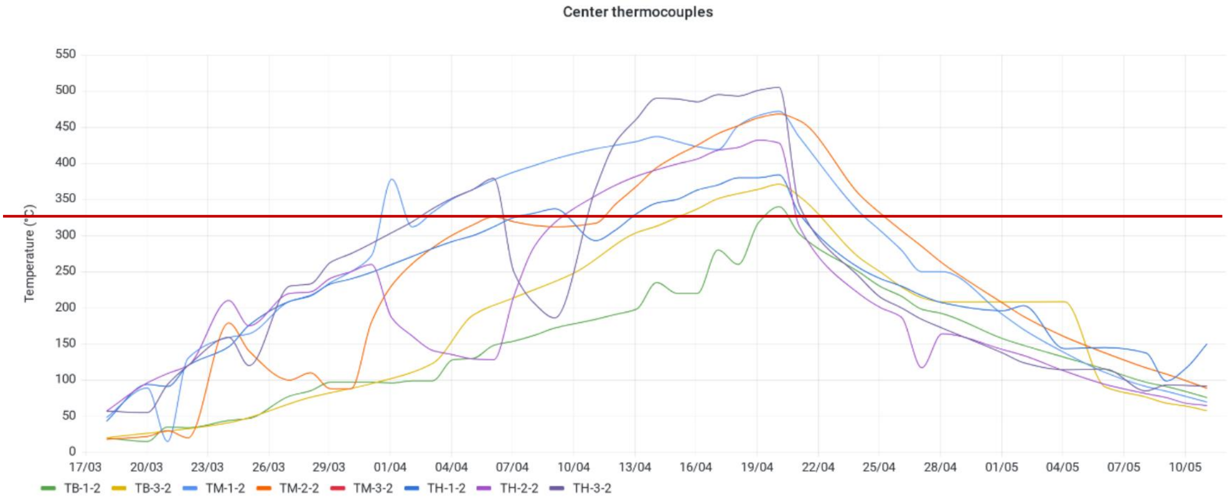


Figure 42. Soil temperature (center of the pile)

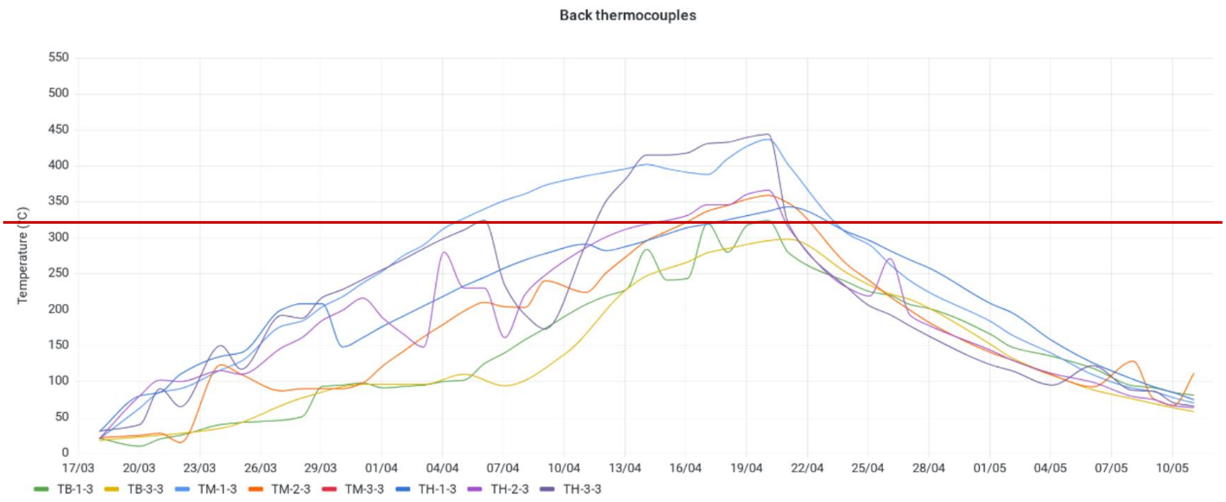


Figure 43. Soil temperature (back of the pile)

The following info is noted:

1. The burners of the top of thermal pile were lit with an offset of 10 days from the bottom line, which explains the slight shift of temperature profile between the thermocouple respectively referred as TB, TM and TH (see locations of the thermocouple in figure 40). The difference is justified by the specific attention given to the treatment of the heavily contaminated vapors with halogenated compounds and mercury species.

2. One can observe that the back of the pile (figure 43) took a little bit more time to reach the target temperature and that a lower percentage of the soil reached the target temperature. Nevertheless, all the thermocouples reached at least 300°C.

3. The plateau of 100°C (which is normally clearly seen on other project) has very rapidly been overcome which is the result of a generally low moisture content and a dense network of burners and exchanger tubes (mean distance between burners = 1m).

4. The temperature profile highlights a slight heterogeneity in the temperature profile along the heating tube. Indeed, the closer the contaminated soil are to the Smart Burners™, the higher the temperature at the cold point. Please also note that the thermal pile was built in 2 days due to time constraints, The perfect positioning of the heating tubes and thermocouple tubes may fluctuate slightly and accentuate certain observations.

5.5.2.2 Soil temperature grounded by layer (from bottom to top)

The soil temperature grounded by layer are depicted below (see figure 44, figure 45 and figure 46).

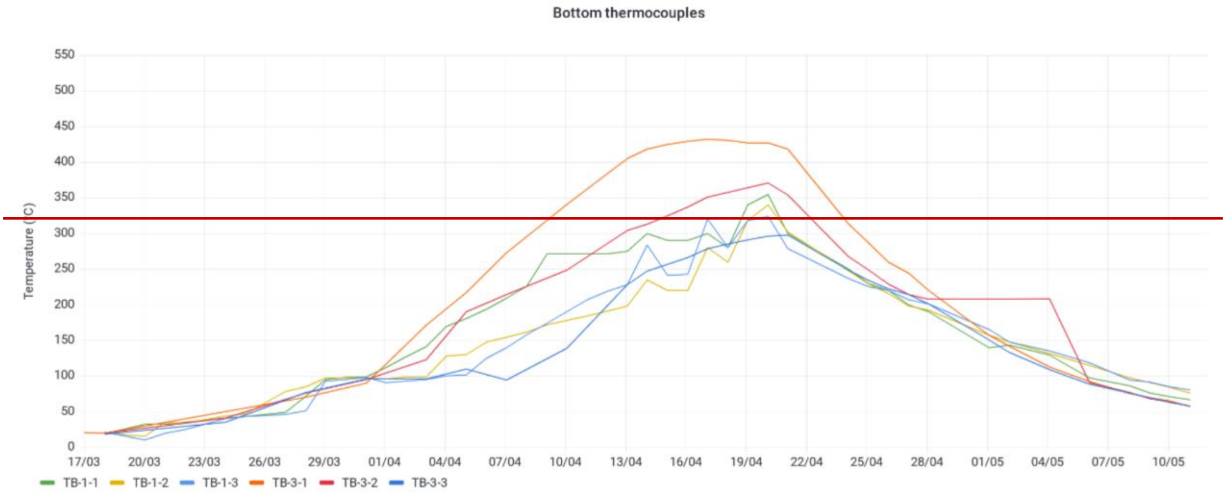


Figure 44. Soil temperature (bottom of the pile)

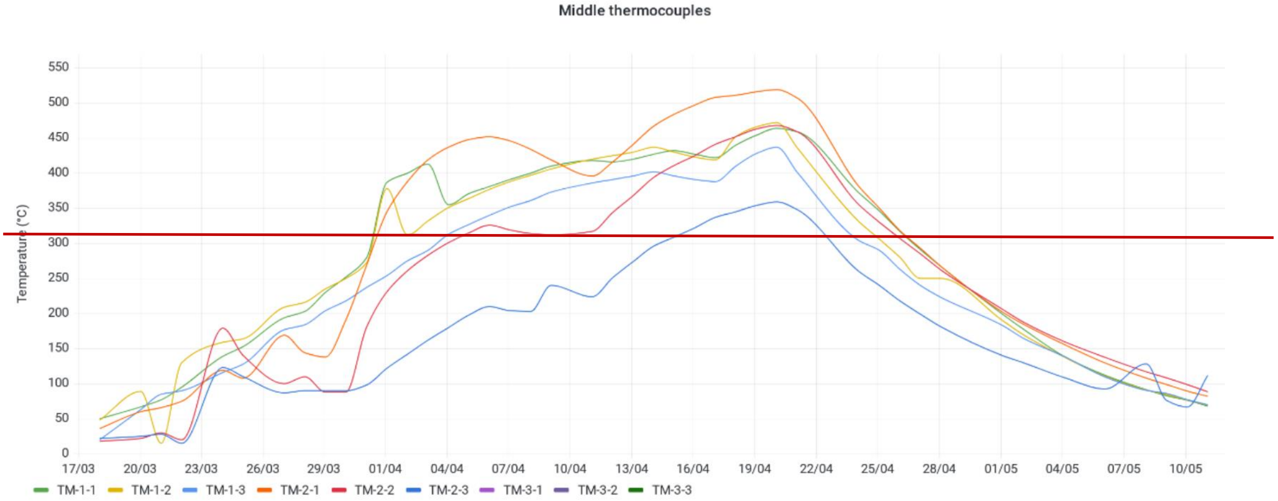


Figure 45. Soil temperature (middle of the pile)

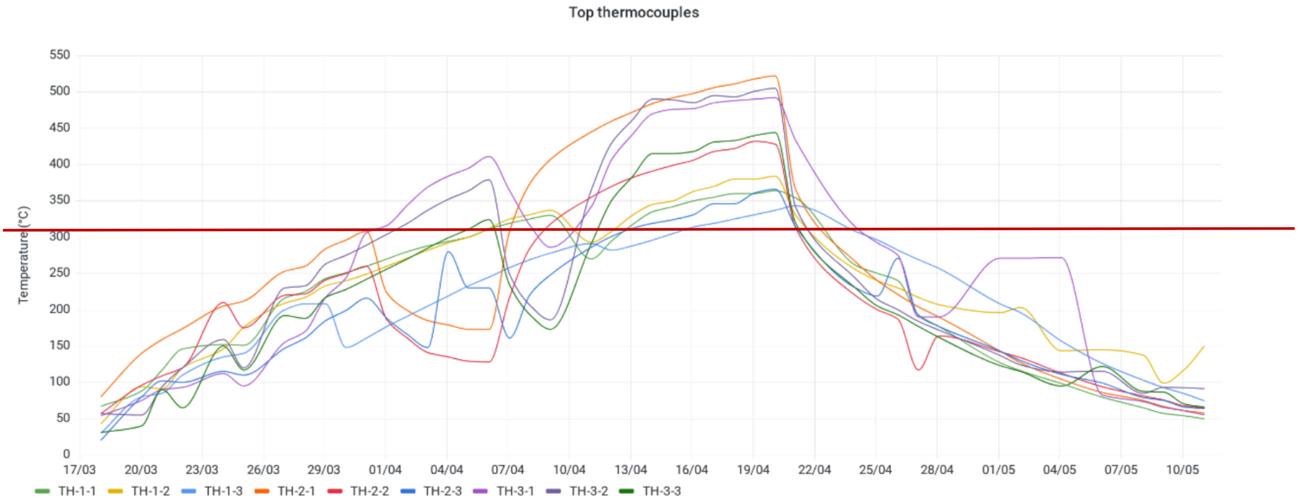


Figure 46. Soil temperature (top of the pile)

The following info is noted:

1. It can be observed on that the centre and the top layers heated more than the bottom one. Due to main blower failure, the back up one had to be installed. The backup blower was a little bit under

designed therefore HT could not allow to heat the whole pile at once (potential production of fumes). Therefore, the heating of the lower row of burners had been limited or absent for the time most of the higher layers released its contamination content.

2. The offset start-up of the burners is well marked on the temperature profile.

3. All thermocouples reached at least 300°C.

5.5.3 Pressure monitoring

Monitoring in pile air pressure in important to guarantee that no fugitive vapors exit the pile into the surrounding atmosphere. As depicted in figure 47, the pressure in the pile remained negative, insuring a slow but constant flow from the pile to the VTU. If the treatment had continued with the first blower, the vacuum could have been a little stronger to accelerate the desorption by pulling the equilibrium of the contaminant toward the vapor phase.

No events of fumes or high VOC/Hg in the ambient air have been seen, which highlights the proper vacuum and treatment of all vapors.

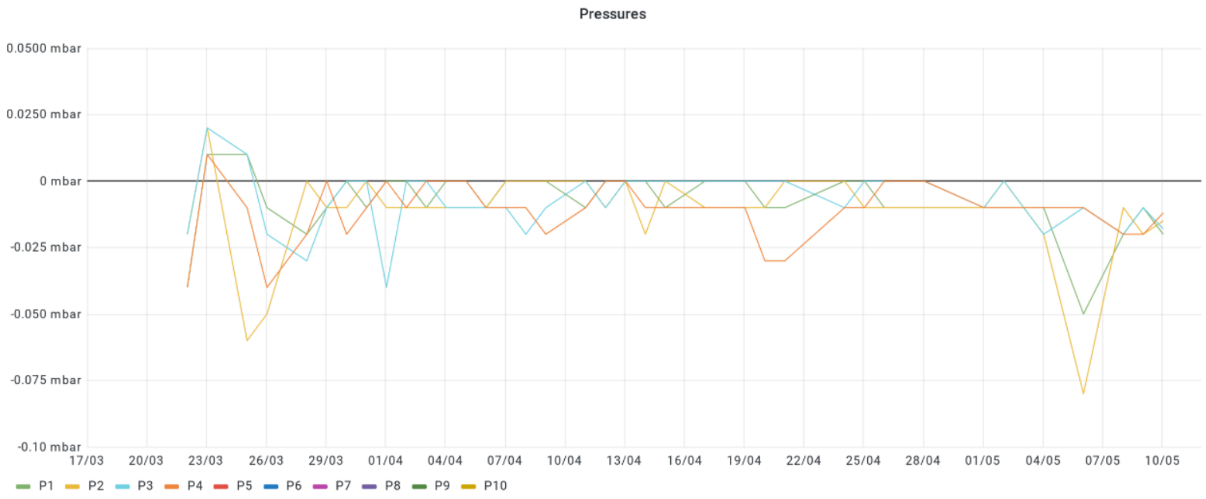


Figure 47. Pressure within the pile during the treatment

5.5.4 Emission control

5.5.4.1 Combustion gases emission

Except from two spikes resulting from unproper burner set up (restart because of general electrical shut down), the measured parameters showed results within limits throughout the whole heating phase (see figure 48).

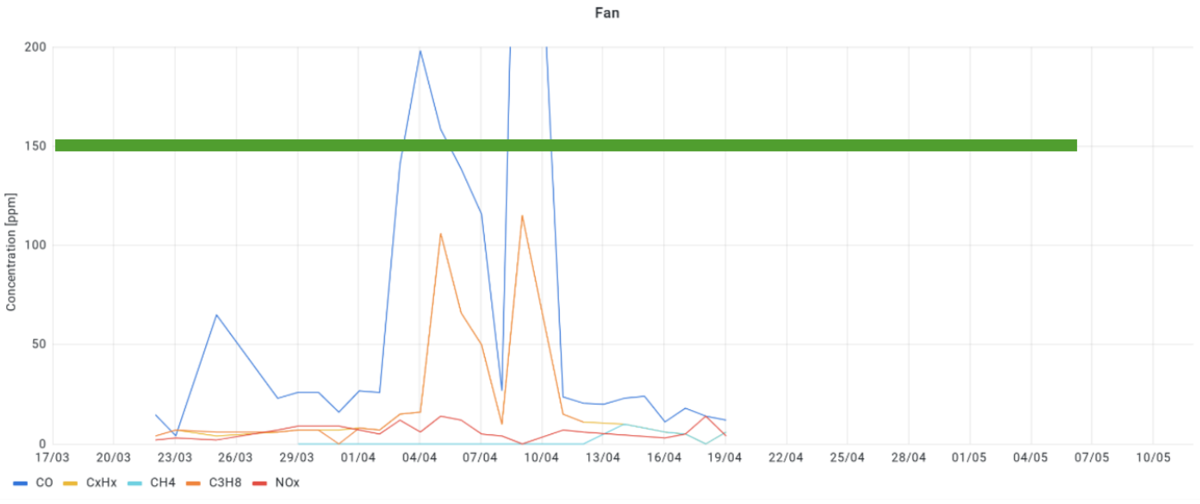


Figure 48.Chemical parameters at the combustion gases stack. Green line: CO standard level

5.5.4.2 VTU emission

The mercury concentration at the VTU stack has been monitored daily and the data are given in the figure 49. One can observe a certain heterogeneity in the concentration at the stack throughout the project.

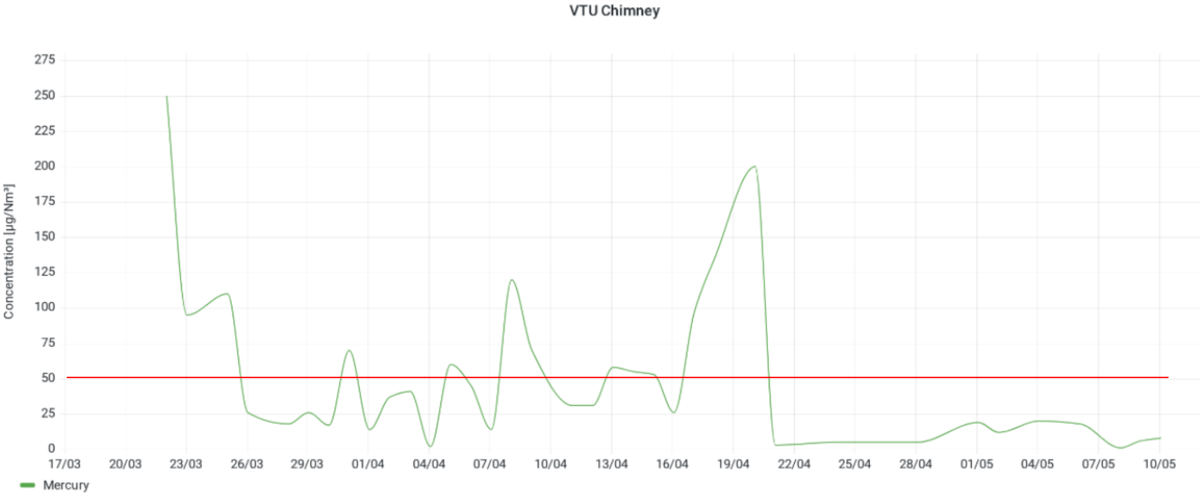


Figure 49. Mercury emission at the VTU stack. red: Mercury standard emission limit[2]

The following info is noted:

1. At the beginning, high elemental mercury concentration was measured at the stack. The first measures were above the norms and were correlated to the flexible pipe used to measure it. Indeed, the silicone hoses are quite porous and tend to trap mercury. The trapped mercury is then released and leads to overestimation. An HDPE hose was then used and proved this hypothesis.

2. Although the average mercury concentration is below 50 mg/kg, few peaks are observed on March 31st, April 5th, April 9th, April 13th and April 19th. These peaks are directly correlated to the design of the GAC (granular activated carbon) and the cooling effiency of the vapors. Indeed, the GAC is designed to treat between 200 and 2.000 Nm³/h. As the flow was close to 200 m³/h, preferential paths were created, which accentuated the localized saturation. Direct measures consisted of mixing the GAC to avoid preferential paths.

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[2] Based on legislation D.LGS 152, April 3rd 2006

The emission standards are given in the following table:

Compounds	Emission standards
NO_x	200 µg/Nm^3
VOC[3]	300 mg/Nm^3 - 100 ppm

Table 24. Emission standards at the VTU

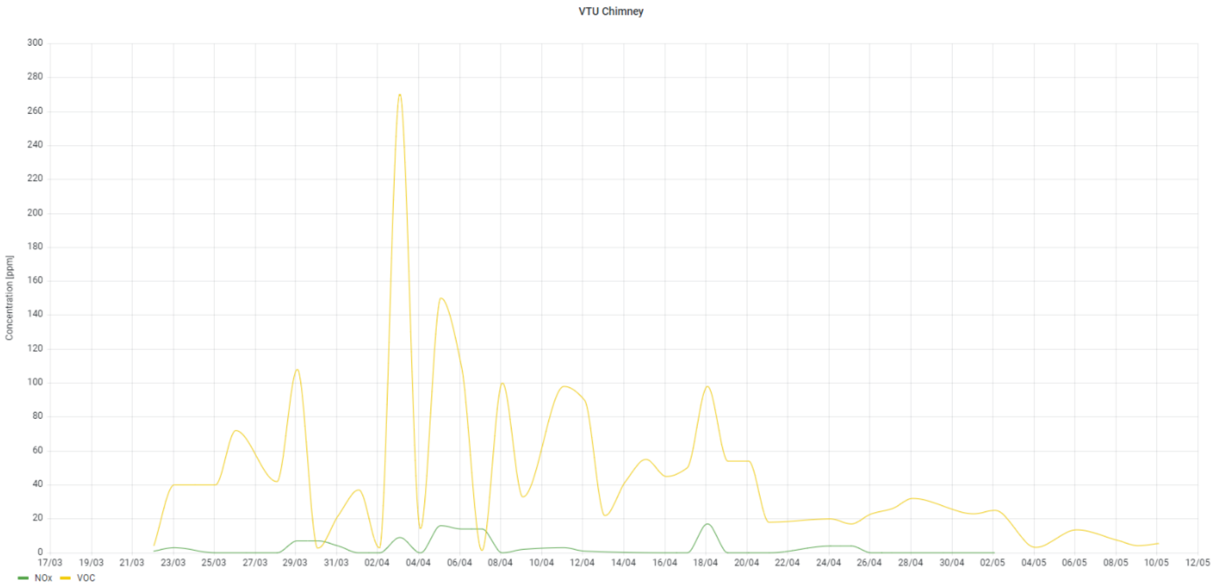

Figure 50. Chemical parameters at the VTU stack

The following info is noted:

1. The concentration of VOC met the emission standards all over the project, except on April 3rd, 2022 and April 5th, 2022. These values are directly correlated to the low flow of vapors circulating through the GAC, which accentuate the creation of preferential paths. Those preferential path caused localized saturation that required replacing the GAC. This issue will be considered during a full-scale project.

2. NOx emissions are significantly below the standard emission all over the project.

5.5.4.3 Ambient air emission

The ambient air emissions have been monitored during the treatment, as shown in *figure 51* (Mercury) and *figure 52* (VOC’s).

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[3] Based on legislation D.LGS 152, April 3rd 2006

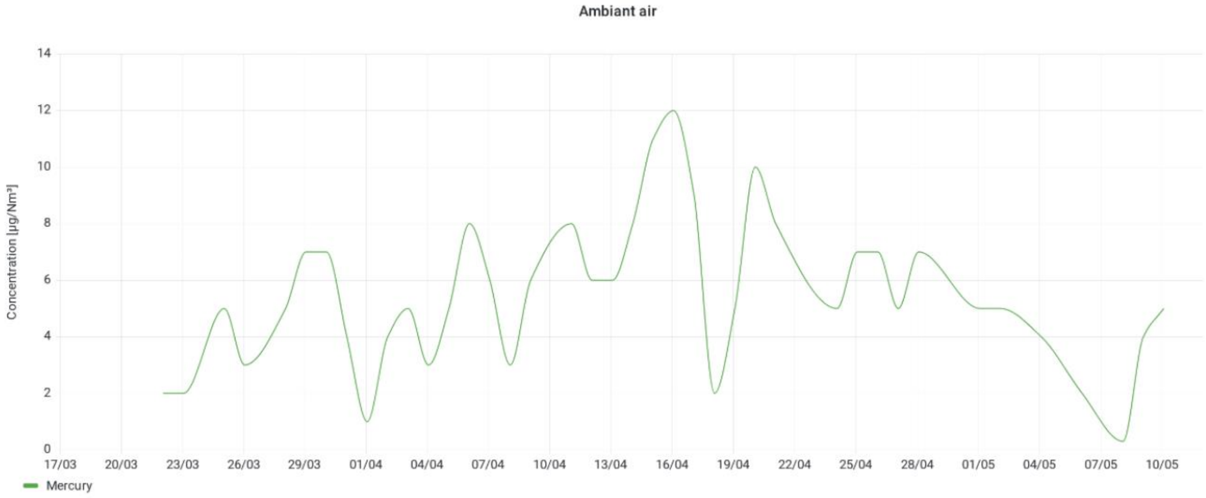

Figure 51. Ambient Hg concentration (vicinity of VTU)

As shown in appendices XX, XXI, XXII and XXII, the concentration in the ambient air correspond to the background level.

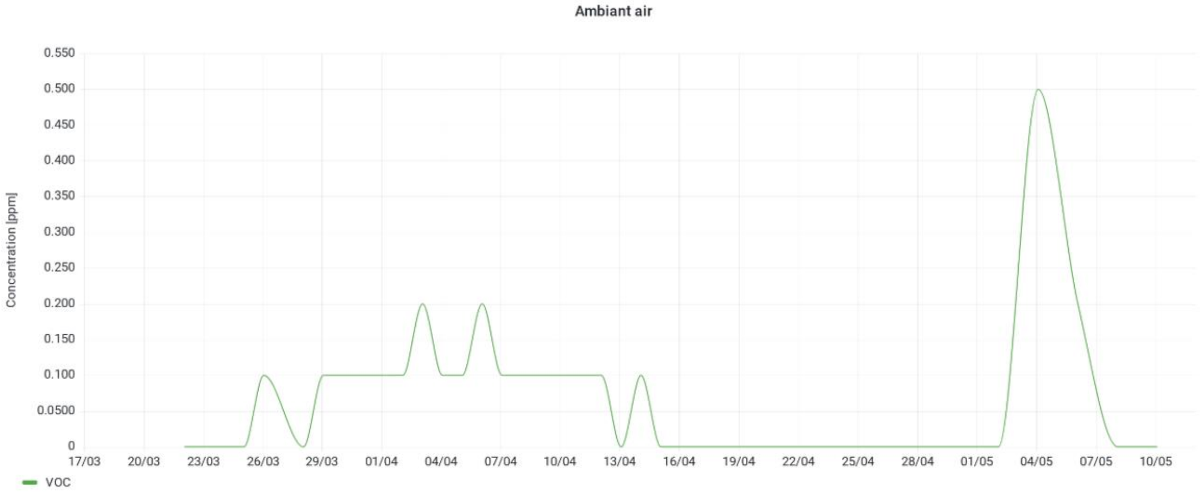

Figure 52. Ambient VOC concentration (vicinity of VTU)

As shown in appendices XV, XVI, XVII and XVIII, the concentration in the ambient air correspond to the background level.

These results demonstrate that the treatment does not affect the ambient air and the neighborhood.

5.5.5 Soil concentrations

5.5.5.1 Total mercury

The results are depicted in the table below in function of their location within the thermal pile. Note that only representative results are given in the table (i.e. the results at the center of the pile). The results are given in

Sample reference	Location	Total mercury concentration mg/kg DM
C7	Center deep low	1,4
C8	Center deep low	2,1
C9	Center deep high	76,8

C10	Center deep high	51,6
D7	Center deep low	584,4
D8	Center deep low	848,3
D9	Center deep high	124,2
D10	Center deep high	8,7

Table 25. Total mercury concentration after treatment in function of the location

The following info is noted:

1. Most samples have total mercury concentrations above the target (see table 22 – total mercury concentration target between 7.53 and 46 mg/kg). These highs values are directly related to the premature shutdown process due to tight schedule. Indeed, the ignition of the burners was held back for almost 3 months (i.e., COVID situation, closing borders, customs, aso).

2. D7 and D8 that are located at the bottom of the thermal pile are very high. This analytical anomaly is likely correlated to the delay in starting the burners of the bottom line.

3. The kinetic test highlighted the desorption kinetic in function of the mercury speciation. Elemental mercury and organic mercury are the most affected species thermally. Therefore, the final concentrations are likely composed of inorganic compounds (sulfur mercury).

Based on these results, a volume of 15% is estimated to be reprocessed during a full-scale.

5.5.5.2 VOC and S-VOC

The soil COV and S-VOC concentrations are given in table 26 (see

Compound	Initial max conc. [mg/kg]	target values for soil after treatment [mg/kg]	Final conc. [mg/kg]
Benzene	0,174	1,51	<0,006
Toluene	0,177	168	<0,006
Ethylbenzene	0,924	11,2	<0,100
Methyl tert-Butyl Ether (MTBE)	0,067	110	<0,004
Xylenes	0,550	49,7	<0,050
Tetrachloroethylene (PCE)	263,650	20,3	<0,05
Dichloroethylene, 1,2-trans	0,006	667	<0,006
Vinyl Chloride	0,008	1,34	<0,004
Trichloroethylene (TCE)	32,475	1,76	<0,005
Dichloroethylene, 1,1	4,298	662	<0,006
Dichloroethane, 1,2-(EDC)	13,721	0,6	<0,006
Carbon Tetrachloride	0,010	2,01	<0,008
Chloroform	0,377	0,728	<0,003
Dichlorobenzene, 1,4	5,620	4,73	<0,010
Chlorophenol, 2-	Not measured	4760	Not measured
Chlorobenzene	48,385	145	<0,006

Hexachlorobenzene	195,279	0,0387	Not measured in representative area
Hexachlorocyclohexane, Beta-	Not measured	1,12	Not measured
Bis(2-chloroethyl)ether	3,602	0,569	<0,006
Dioxane, 1,4-	Not measured	18,7	Not measured
Trichloroethane, 1,1,2-	271,933	2,35	<0,006
Dichloroethane, 1,1-	0,023	8,68	<0,006

Table 26. VOC and S-VOC concentration before and after treatment

The following info is noted:

1. The table contains only the concentrations in the representative area (i.e. center of thermal pile).
2. Although the hexachlorobenzene was not measured in the center of the thermal pile, all VOC and S-VOC compounds are below the target concentrations.

5.6 Dismounting phase

The dismantling steps are detailed in the appendices XXIV, XXV and XXVI. The pictures below show few steps of the dismounting of the thermal pile.

Figure 53. Concrete slab removal on the pile

Figure 54. Mercury recovery in a tank from the vapor collectors

Figure 55. Dismounting of the thermal pile

Figure 56. Dismounting of thermal pile

6 CONCLUSIONS

6.1 Laboratory phase

Four kinetic tests were conducted to determine the effect of thermal desorption in function of time and temperature treatment on mercury contaminated samples from the Akko site.

The first test concerns the study of kinetic curve on soil highly polluted by mercury between 200 and 260°C, while the second regards the behaviour at 300°C of highly mercury polluted soil. The third and the fourth tests were focused on the behaviour at 300°C of low contaminated soil.

Two leachate tests have been conducted by the accredited laboratory to assess the amount of the remaining mercury after tests 3 and 4 that was able to dissolve into water.

6.1.1 Highly contaminated mercury soil

The results show a significant decrease in total mercury content, with a degradation/elimination rate of 92% after 24h at 200°C. This result is directly correlated to the presence of the most volatile species (dimethyl chloride, methylmercury chloride, mercury chloride and elemental mercury). Indeed, ratio analysis of the initial samples indicates 77% of elemental mercury, which corroborates with the significant decrease.

The ratio analysis (organic, inorganic, and elemental content) of the heated samples highlighted the kinetic behaviour of each part:

1. Elemental mercury is most affected by the heating, with elimination rate of at least 92% after 24h at 200°C. Then the ratio increases until 96% after 168h at 260°C. The relation between residence time and temperature was not validated through the test 2. The main assumption is the heterogeneity of the sample. On the basis of the temperature ranges studied, concentrations below 80 mg/kg DM are achievable. Future tests at 350°C after 168h are therefore necessary to determine the technological limits of a thermal desorption plant.

2. The majority fraction after treatment is the inorganic mercury, despite high degradation rate observed during the different test (more than 70%). The main inorganic species are (1) mercury oxide, (2) mercury chloride and (3) mercury sulfide. The concentration decrease was significant from 200°C, suggesting a significant presence of mercury chloride, the most volatile inorganic mercury species.

3. The minority fraction after treatment is the organic part, with a concentration of 18 mg/kg DM after 168h at 260°C.

6.1.2 Low contaminated mercury soil

The results of these thermal desorption tests showed a proportionately lower decrease in total mercury concentration than for the tests in highly impacted soil. Nevertheless, the tests revealed that:

1. Heating at 300°C, even on a short period of time (24h), still reduces the total mercury concentration. The various tests have highlighted the higher weight of temperature over time on the removal rate of total mercury reassuring the initial assumption based on literature and experience that a treatment at higher temperature than 300°C could reduce even more the total mercury concentration. Indeed the closer to the boiling point the species (see Table 5, Table 6 and Table 7) the higher its removal rates.

2. The speciation's before and after treatment are similar which is the result of equivalent degradation ratios for all species. After treatment most of mercury lays in the inorganic species.

3. The speciation of low contaminated soil after treatment is mainly dominated by inorganic mercury species. The main inorganic species are (1) mercury oxide, (2) mercury chloride and (3) mercury sulfide.

The leachate tests performed on the treated sample (300°C; 24h) showed that approximately 25% of the remaining total mercury dissolve into water and can therefore leave the soil matrix. These results have to be studied in light of a leachate test performed on a blank sample.

As an assumption and based on the previous results (see test 1), the elemental mercury and inorganic part should be the most affected. However, the measurements on the initial sample indicate 61 mg/kg DM of inorganic mercury, which corroborated to removal of 'light' inorganic species such as mercury chloride (II).

6.2 Pilot

A pilot test was performed between January and April 2022. It was carried out on heavily contaminated soil with (1) VOC and S-VOC and (2) mercury. Those soils were gathered in a pile for thermal treatment. After 3 weeks of installation (i.e., mounting of thermal pile, vapor treatment unit and condensate tanks), the system was lit within one week and lasted 30 days.

Although the pilot was not finished due to schedule limits, the following has been demonstrated during the treatment:

1. Ex-situ thermal desorption can successfully treat mixed contaminated soil with mercury and VOC, S-VOC contaminated soils to residential levels for subsequent beneficial use. [4]
2. Haemers Technologies' design has proven to be effective in recovering the mercury and chlorinated vapors.
3. Haemers Technologies' operations have proven to be compliant most of time[5] with air emission and did not affect ambient air quality.

The pilot project demonstrated that Ex-Situ Thermal Desorption with propane burners is a very effective technology for treating this type of contaminated material soils in the most sustainable way.

6.3 Outlook

Based on results, Haemers Technologies is confident about the following performances of Ex-Situ Thermal Desorption at the Akko Site:

1. Target temperature is to be set at 350°C
2. The mercury concentration to carry out the pilot phase were extremely high. Mercury concentration during the full-scale phase are expected much lower.
3. We expect 15 % of treated soil to be above said concentrations and requiring additional (re)treatment as low-concentration soil
4. Thermally treated soil (both for highly and low concentrations) will be compliant with European Waste Acceptance Criteria for Non-Hazardous waste, based on leachate concentrations.

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[4] With a longer heating time, the concentration will reach the target values.

[5] Few mercury peaks were measured above the limits and are directly related to the GAC design that was not fully adapted.

Table of appendices

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