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## CONTAMINATION AND ENVIRONMENTAL REMEDIATION OF FORMER MISSILE SITES NEAR LIEPAJA

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### Introduction

Activities carried out at former Soviet military bases in Latvia have resulted in the discharge of various toxic substances into the environment. Since the abandonment of these bases, local residents have been able to access these lands for agriculture, forestry and recreation. Consequently, there is a high risk for exposure to the soil and water which is contaminated with toxic chemicals with the resultant impacts to human health. Large scale clean-up operations are required in order to return this land to profitable or safe use. A joint project was set up in Canada and Latvia to carry out the environmental assessment and remediation of sites at former military bases at Barta and Tasi, located in the coastal zone near Liepaja (Latvia).

During the site assessment conducted at former military bases at Barta and Tasi, soil and water samples were found to be contaminated with varying concentrations of the xylidine-based missile fuel SAMIN and oil products. The estimated level of oil product contamination (by mineral oil and grease analysis) reaches 6,000-7,000 ppm, while the xylidine contamination reaches a few thousand ppm (in some places more than 20,000 ppm). Xylidines have been found to be toxic at concentrations as low as 2 ppm by inhalation and skin contact; however xylidines are valuable intermediates in many industry processes. Therefore, the main research objective of this project is to improve the quality of these coastal sites by focussing on the development of remediation technologies to clean-up the xylidine contaminated soil and water through the development of a nondestructive xylidine concentration and recovery process.

### Materials and methods

The materials utilized for this research project was spiked soil and water samples and contaminated soil and water samples from the site. Spiked samples were used to narrow the range of operating parameters for these tests before the actual soil and water samples were used for parameter optimization.

Spiked water samples produced by adding specific amounts of 2,4 xylidine or 2,5 xylidine to deionized water. A soil comparable to that at the site in Latvia, was produced by mixing 70% sand, 10% black earth, 10% peat and water in a ball mixer. This soil was then spiked by adding a xylidine/methanol solution. The methanol was then evaporated by air drying at room temperature. Contaminated soil and water samples were received from former Soviet military bases in Latvia and were refrigerated until use.

The analysis of the xylidine and oil products were performed by gas chromatography /FID. A rapid analytical method for spiked sample determination using a UV-VIS spectrometry was developed. This method is based on the reaction of xylidine with a reagent to shift the absorbance signal from the UV region towards the visible zone of the spectrum. The colouring agents used were para-dimethylaminobenzaldehyde and trisodium pentacianoamino ferroate.

## Results and discussion

The technologies investigated for the decontamination of the soil were : soil washing, solvent extraction, and low temperature thermal desorption (LTTD).

In soil washing an aqueous solution is used to solubilize and separate contaminants from soil. Although soil washing is technically easy to conduct and comparably cost effective, its application is limited, as shown in table I, for use at this sites by the low solubility of xylidine in water and its slow dissolution rate. As a result, it is necessary to use large volumes of water and to repeat the washing process several times to reach acceptable target levels of xylidine in the processed soil. In addition Barta's soil contains a large amount of fine dispersion silt, whose presence renders the outlet stream very difficult to filter and interferes with the subsequent concentration process. Solvent extraction from the soil matrix using a methanol permits a greater than 90% recovery of the xylidine, but solvent recovery from the soil is costly and the processed soil often requires farther treatment such as LTTD to remove the solvent.

Table 1  
Final concentrations and efficiency of removal of xylidines from soil

Water/soil ratio L/kg	Conc. of xyl. in the soil(ppm) at the washing time			Efficiency of removal of xylidines, %		
	30 min	120 min	24 h	30 min	120 min	24 h
3	5512	3624	1958	11.5	41.8	68.6
4	4354	2832	1710	30.1	54.5	72.6
5	3870	2544	1295	37.9	59.2	79.2
6	3642	2068	866	41.5	66.8	86.1
7	2768	1831	847	55.6	70.6	86.4
8	2685	1565	710	56.9	74.9	88.6

Although xylidine boiling point is between 213<sup>0</sup>C and 228<sup>0</sup>C, our research indicates, as shown in table 2, that effective and relatively fast xylidine removal is possible by heating the soil to temperatures which are lower than the boiling point. For the xylidine recovery optimization of this low temperature thermal desorption (LTTD) process, it is necessary to have at least 10% water in the soil. Steam acts as a carrier gas which serves to enhance the xylidine desorption and also lessens its destruction/oxidation by reducing the oxygen concentration in the desorption unit. The gaseous emissions from the LTTD process can be condensed to obtain a relatively concentrated xylidine-water solution/emulsion without the carry-over of the finely dispersed silt from the soil. By applying a partial vacuum, it is possible to desorb the oil contamination in addition to the xylidine.

For ground water remediation, research was done utilizing steam-stripping. Good results have been obtained by this process for concentrating xylidine. More complete xylidine recovery and higher xylidine concentrations, as shown in table 3, are achieved with higher initial concentrations and higher feed/steam ratio values. A pH adjustment step is required before the steam-stripping process in order to maximize the recovery of the xylidine in the column tops stream. Also, enhanced recovery of the xylidine is possible by preheating the feed stream. The residual xylidine in the column bottoms stream is destroyed using an advanced oxidation processes (AOP).

Table 2  
Removal of xyldine from soil using LTD

time of exposure min.	conc. of xyldines(ppm) in the soil at different temperatures, °C					
	140	160	480	200	220	240
0	4806	4806	4806	4806	4806	4806
5	3456	2503	2147	1018	479	87
10	1531	717	428	222	63	7
15	834	441	93	20	13	2
30	332	103	22	6	2	0

Table 3  
Concentration of xyldine using steam-sripping

Feed/steam ratio, L/kg	Final xyldine concentrations at the top of column at different initial conc., ppm			
	1098	692	239	133
1.9	2434	1252	599	305
3.6	4200	1916	1062	507
5.3	5158	2341	1285	617
8.5	6044	3611	1537	1055

Advanced oxidation research was conducted on the destruction of spiked 2,4 xyldine and 2,5 xyldine solutions utilizing UV photolysis, UV/hydrogen peroxide, photo- Fenton's reaction and dark Fenton's reaction. The results of the photolysis research indicate that the oxidation of 2,4 and 2.5 xyldine requires a similarly prohibitly long residence time to non-detect levels. The results of the hydrogen peroxide-UV experiments indicate a trend of decreasing exposure time required to achieve non-detect levels of xyldine with increasing hydrogen peroxide concentrations. The Fenton's reagent research indicates the enhancement of Fenton's reagent with UV light and faster oxidation of both 2,4 and 2,5 xyldine with increasing  $Fe^{2+}$  ion concentration. The best results, as shown in table 4, have been achieved with UV/hydrogen peroxide and photo-Fenton's reaction.

Table 4  
Advanced oxidation of 2,5 xyldine water solution

Time of exposure min	Option of treatment						
	UV*	UV HP** -10	UV HP-200	UV HP-500	UV HP-1000	UV HP-1000 FR*** -50	UV HP-1000 FR-50
0	94	123	123	131	156	90	90
2	88	84	103	85	81	77	58
4	80	55	62	45	46	76	48
6	74	42	44	0	0	70	0
8	71	36	36	0	0	67	0
10	67	30	29	0	0	63	0
15	58	24	0	0	0	0	0

\* UV - ultraviolet light; \*\*HP - hydrogen peroxide, ppm; \*\*\*FR - Fenton reagent.

The remediation process of xylidine-contaminated soil and ground water will be based on the following flow diagram (Fig.1):

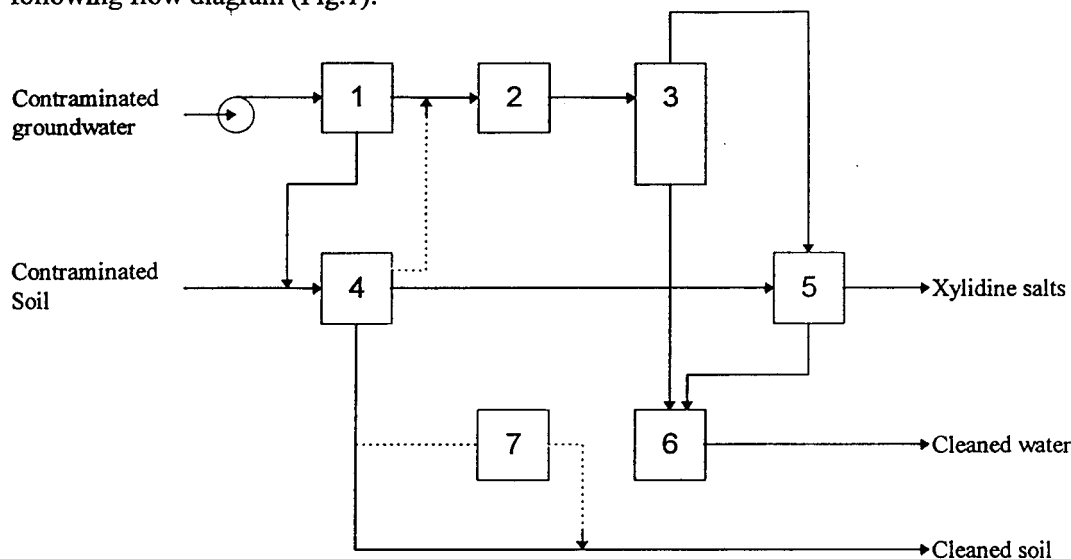


Figure 1. Flow diagram of remediation process

1. Filtration 2. pH control 3. Steam-stripping 4. Low temperature desorption  
5. Chemical treatment 6. Advanced oxidation process 7. Bioremediation

The diagram illustrates the processing of the solids from the ground water-filtration in the LTTD unit and the condensate from the soil after LTTD using the steam-stripper. The product stream from LTTD and steam stripping processes is a concentrated xylidine and oil product solution, the oil products are removed in the chemical treatment process by solvent extraction and xylidine recovered in form of xylidine salts. The residual xylidine and oil products in the column bottoms flow and in the water after the chemical treatment is destroyed using AOP. As the xylidine concentration in the soil will be significantly lower after low temperature thermal desorption, bioremediation can be used as a polishing step for the contaminated soil.

A method has been developed for recovery of the xylidine in concentrated form from the process water which accumulates after the soil has been treated by low temperature desorption or after the ground water has been treated by steam stripping. The method is based on the ability of the xylidine to form salts with various organic dicarboxylic acids. These salts have variable solubilities in water and other polar solvents depending on the xylidine isomer. The best results have been obtained by using phthalic acid. The solubility of 2,5-xylidine phthalic acid salt in water is more than 10 times the solubility 2,4-xylidine phthalic acid salt, and this allows the two isomer to be separated.

## Conclusion

The research conducted under this joint Latvian- Canadian project has lead to the development of a treatment process for xylidine-contaminated soil and water. The outputs for this process are xylidine salts, cleaned water and cleaned soil.

The developed method, producing xylidine phthalic acid salts allows the recovery of xylidine in a concentrated form and their separation into isomers after treatment of the xylidine-contaminated soil and water.