4th CCMS/NATO Workshop on “Management of Industrial Toxic Wastes and Substances Research”

Advanced monitoring techniques of hazardous wastes

Book of Proceedings

Ioannina
26-27 August 2006
"MANAGEMENT OF INDUSTRIAL TOXIC WASTES AND SUBSTANCES RESEARCH"

Advanced monitoring techniques of hazardous wastes

26-27 AUGUST 2006

Ioannina, Greece
 Participating Institutions / Organizations

NATO Committee on the Challenges of Modern Society (CCMS)

Greek General Secretariat of Research and Technology (GSRT)

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Mrs. Eleni E. Oikonomou

Funding Organizations

NATO Committee on the Challenges of Modern Society (CCMS)
Greek General Secretariat of Research and Technology (GSRT)
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CHROMIUM REDUCTION FROM INDUSTRIAL WASTEWATER

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University of Ioannina, Seferi 2, 30100 Agrinio, Greece

ABSTRACT

The purpose of the present study was to estimate Cr(VI) reduction through biological mechanisms in pilot-scale trickling filters by chromate-reducing bacteria originating from industrial sludge. The effects of different operating modes and different filter media types (i.e. gravel and plastic) on the reduction rate of Cr(VI) were studied. Process was simulated via a mathematical model. Model predictions were found to correspond very closely to experimental quantitative observations of Cr(VI) reduction at both pilot-scale trickling filters used.

INTRODUCTION

Cr(VI) is toxic, carcinogenic and mutagenic to animals as well as humans. The discharge of Cr(VI) to surface water is regulated to below 0.05 mg/l by the U.S. E.P.A. [1] and the European Union [2], while total Cr, including Cr(III), Cr(VI) and its other forms is regulated to below 2 mg/l.

At the present study, the use of mixed aerobically grown indigenous cultures attached on the support media of a pilot-scale trickling filter resulted in Cr(VI) reduction was examined. The effect of the operating mode and the feed Cr(VI) concentration for very high concentrations were studied. A dual-enzyme kinetic model was used to simulate biological Cr(VI) reduction.

EXPERIMENTAL SECTION

The pilot-scale trickling filters consisted of a Plexiglas tube, 160 cm high and 9 cm i.d. This pilot-filter height is typical of a full-scale industrial filter. Since it is the loadings per unit cross-sectional area that matter, no scale-up was necessary. Two different support materials were used for the experiments. The first type was hollow plastic tubes, 1.6 cm internal diameter, and specific surface area 500 m²/m³ and filter porosity 0.8. The second type was calcitic gravel, mean diameter 5.5 mm, specific surface area 1059 m²/m³ and filter porosity 0.4. The depth of the support media was about 143 cm in both cases (Fig. 1). The working volumes of the reactors after several
operating cycles were about 7.5 l and 3.3 l respectively. The formation of sediments caused fluctuation on the working volumes of the reactors. Chromate sediments were removed during the backwashing procedure from the entire volume of the reactors. After backwashing, the trickling filters reach a new steady state within two hours.

Throughout all experiments water temperature was fairly constant at about 28±1°C (ambient temperature 26°C). The pH ranged from 7.2 to 8.87 and the concentration of the dissolved oxygen in the liquid phase was physically maintained at a near constant level of 4.5 mg of DO /l. During all experiments Cr(VI), pH, temperature, and DO concentration measurements were made on a daily basis according to Standard Methods for the Examination of Water and Wastewater [3].

Fig.1. Pilot-scale trickling filters arrangement for Cr(VI) reduction from industrial wastewater and detail from the support materials used.

RESULTS AND DISCUSSION

Samples of industrial sludge were taken from the Hellenic Aerospace Industry S.A, in order to grow bacterial strains able to reduce Cr(VI). For the preparation of the enrichment of indigenous bacteria and the immobilization, the procedure described in Dermou et al.[4] was followed. The pilot-scale trickling filters were operated as batch reactors for a period of about 50 days, to ensure attachment of the bacterial culture to the support media and development of a biofilm layer, while organic carbon was used in excess. After several operating cycles under this operating mode the filter filled with gravel media resulted in a reduction rate of 0.11 gr Cr(VI)/d (Fig. 2a).

The reduction of Cr(VI) to Cr(III) was followed by the formation of sediments, which caused obstruction of the flow along the filter depth (partial or complete pore clogging) and consequently insufficient exploitation of the entire filter volume. In order to overcome sediment formation and make better use of the entire filters, SBR operating mode with recirculation was applied to the reactors. The filters were loaded
with nutrients and Cr(VI) to a final concentration of 30 mg/l. After several operating cycles the period was reduced to only 40 min for the filter with gravel media resulted in a reduction rate of 3.7 gr Cr(VI)/d (Fig. 2b).

Fig. 2. Operating cycles of the filter filled with gravel media a) under batch operation, duration of minimum stable cycles: 19h and b) under SBR operation with recirculation.

The continuous operating mode was tested for the filter filled with gravel media. This operating mode (gravity flow) did not improve filter performance. Maximum Cr(VI) reduction rate (1.27 g Cr(VI)/d) was achieved for a volumetric flow rate of 30 ml/min resulting in a retention time of only 1.3 min, while for higher flow rates chromate reduction rate was less.

SBR operation with recirculation proved to be a very effective operating mode resulting in higher reduction rates. Therefore, it was adapted to a new experiment. Aerobically grown mixed cultures were exposed to six different Cr(VI) concentrations of about 5, 10, 20, 30, 50 and 100 mg/l, while the concentration of organic carbon was constant at 400 mg/l, in order to avoid carbon limitations in the bulk liquid. A dual-enzyme kinetic model [5] was used to simulate the experimental results. Equation \( \frac{dCr}{dt} = \alpha + \beta e^{-\gamma t} \) represents the governing model equation that can be used to describe Cr(VI) reduction in pilot-scale trickling filters under SBR operation with recirculation.

Fig 3a and 3b present experimental and predicted profiles of Cr(VI) reduction regarding the time required for complete Cr(VI) reduction. The data points on the graphs represent average values of triplicate experiments. Model fits correspond very closely to experimental observations, while Cr(VI) reduction depends strongly on the
initial concentration forced at the system for both pilot-scale trickling filters. The filter filled with gravel media presented complete Cr(VI) reduction under smaller time intervals. Since enzymatic Cr(VI) reduction takes place mainly at the bulk liquid, the above observation was rather expected due to the smaller working volume of the reactor compared to the equivalent time intervals for the filter filled with plastic media.

Figure 3. Cr(VI) reduction under SBR operation with recirculation at feed concentration of about 5, 10, 20, 30, 50 and 100 mg/l Cr(VI) for the filter with a) gravel support media and b) plastic support material.

The use of two different support materials led to similar filter performances under SBR operation with recirculation (Fig. 4). Plastic media showed slightly better performance compared to gravel media. Moreover, it diminishes operating disturbances during industrial applications, since enables the growth of a thicker biofilm layer and avoids pore clogging. That makes plastic media becomes preferable towards gravel media for industrial use.

Figure 4. Cr(VI) reduction rates under SBR operation with recirculation at various Cr(VI) concentrations for both pilot-scale trickling filers.
CONCLUSIONS

Biological Cr(VI) reduction was proved efficient with the use of pilot-scale attached growth bioreactors and indigenous bacterial population for industrial wastewater effluents treatment. The main conclusions from this work are:

- SBR operation with recirculation proved to be a very effective operating mode, resulting in high Cr(VI) reduction rates.
- Experimental results clearly demonstrated that Cr(VI) reduction depends strongly on the initial Cr(VI) concentration for both support materials tested.
- Experimental results indicated the presence of a) a rapid enzymatic mechanism that is deactivating during Cr(VI) reduction, and b) a slower enzymatic mechanism that remains active during Cr(VI) reduction.
- Model fits were found to correspond very closely to experimental observations for a wide range of Cr(VI) concentrations (5-100 mg/l) under aerobic conditions for both pilot-scale trickling filters used.
- The mathematical model applied could be an excellent tool for Cr(VI) reduction from industrial effluents and the design of corresponding treatment plants.
- Plastic media with high porosity proved to be more efficient for industrial applications than gravel media.
- SBR operation with recirculation for the filter with plastic support media led to significant reduction rate up to 4.8 gr Cr(VI)/d.

REFERENCES

RADIATING ASSESSMENT IN BIOSPHERE TERRITORIES OF THE ISSYK-KUL

Djenbaev B.M., Jalilova A.A., Abdijapar uulu Salamat, Shamshiev A.B., Jolboldiev B.

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Uranium technogenium province of Kadji-Sai is located on a southern coast of the lake Issyk-Kul, in 270 kms from metropolitan city of Bishkek, at height of 1978,9 m above a sea level. The territory is -31,5 sq. kms. The mining industrial complex on processing uranium ore functions from 1948 to 1969, and later on the electrotechnical factory was reorganized.

The oxid of uranium was taken not by a traditional approach, i.e. from the ashes of the brown uranium containing coals of Sogutinskii deposit. The coal extracted on the local mine by a underground way, previously has been burnt with accompanying generation of the electric power, and then the oxid of uranium has been extracted in the in the form of acid from ashes. Waste substances of manufacture and industrial equipment were buried by forming tailing dump, with total amount of uranium waste substances 400 thousand m$^3$. The tailing dump consists of two parts, one part is built up by economic constructions of an electrotechnical factory, and on other part there is ash-dumps, which creates additional loading to tailing dumps [1, 2, 3].

For example, in August, 1998 the insulating layer and dam of Kadji-Sai tailing dump were considerably damaged as a result of cloudburst and other natural influence and as a consequence the ionizing radiation background reached 1700-1800 mc R/hours on the separate parts of the area, that arosed an alarm of a public of the Issyk-Kul and nature protection organizations [6, 12].

Last year the tailing dump of Kadji-Sai with the help of the international projects, (financial sources) are blocked with blanket dirts. Nevertheless, the protective dam under influence of the natural factors and anthropogenous influences on separate parts have begun to collapse, exposed of erode by high waters and mud flows, which result to abiding the radioactive materials on the surface.

The tailing dump with uranium waste substances is located on 2,5 kms to east from an inhabited settlement, but it ) represents ecological threat to the lake Issyk-Kul and nearest settlements because of the natural factors (rains, earth waters, landslips and mud flows. However, after closing the mining industrial complex Kadji-Sai the mass of unabondoned radioactive-industrial waste substances, founded in a coast of tract
Djil-Bulak were exposed to intensive destruction, i.e. transferring its part at a mouth of tract. This phenomenon was conductive because of often cloudburst. For nearly 40 years there was observed the intensive heave of a coastal part in area of industrial court. It became apparent in the formation of terraces in the upper course of tract Djil-Bulak. The radioactive-industrial waste substances still can be met on the kept terraces, put together with ashes material in turn with gravel-galley. The part of radioactive ashes reached to Issyk-Kul, but it was so insignificant as a a drop in the sea for Issyk-Kul (remind, that there are about 100 thousand tons of uranium in the lake contains) [4, 5, 6, 7, 9, 12, 13].

The territory of a province relates to a deserted type, and its climate is characterized as a sharp continentality, with moderate-warm summer and cold a few snowy winter. Monthly average temperature of January is -17-19 °C and July +15+17 °C. Average annual temperature of air varies about 5 °C. Precipitation is totally 200-250 mm per one year, with a maximum in the spring-summer period. As a result of domination of winds there is a strong evaporation of a moisture of ground, the cultivation of only drought stable plants such as Kochia, Eurotia, is possible without irrigation.

Methods of researches. The equipment used during researches, consists of Radon radiometer RRA-01M-03, Dosimeter-radiometer DKS-96, Sampling system POU-04, Photo-electro-colorimeter (SPECOL) etc. Distribution and processing of the received data were made on the personal computer with the help of the special program package.

In the process of performing of researches the selective measurements of a level of radiation on subregion and tails were chosen, the tests of ground, water and plant on various sites for the further research in laboratory conditions are selected.

Researches results. By radiometric shooting it is established, that the level of radiation in the hollow of Issyk-Kul and on both settlements of Kadji-Sai rather low and varies from 15 up to 47 nZv/hour [tab. 1].
<table>
<thead>
<tr>
<th>Places of selection</th>
<th>Pressure</th>
<th>Humidity</th>
<th>t° of air</th>
<th>t° of water</th>
<th>pH</th>
<th>Scale - background on surface of soil</th>
<th>Scale - background at height 1 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Settlement Kara-Oi</td>
<td>709 mm merc.pole</td>
<td>35%</td>
<td>22 °C</td>
<td>18,5 °C</td>
<td>8,5</td>
<td>150-200 nZv/hour</td>
<td>100 nZv/hour</td>
</tr>
<tr>
<td>c. Cholpon-Ata</td>
<td>709 mm merc.pole</td>
<td>35%</td>
<td>22 °C</td>
<td>-</td>
<td>-</td>
<td>200 nZv/hour</td>
<td>- 150 - 200 nZv/hour</td>
</tr>
<tr>
<td>Settlement</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>17,5 °C</td>
<td>150 nZv/hour</td>
</tr>
<tr>
<td>Bulan-Sogotu</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8,15</td>
<td></td>
<td>160 nZv/hour</td>
<td>100 nZv/hour</td>
</tr>
<tr>
<td>r. Kichi Ak-Suu</td>
<td>709 mm merc.pole</td>
<td>44%</td>
<td>22 °C</td>
<td>13,2 °C</td>
<td>7,94</td>
<td>170 nZv/hour</td>
<td>140 nZv/hour</td>
</tr>
<tr>
<td>r.Tup</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18,8 °C</td>
<td>8,12</td>
<td>160 nZv/hour</td>
<td>150-170 nZv/hour</td>
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<tr>
<td>r.Kara-Kol</td>
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<td>-</td>
<td>-</td>
<td>15,8 °C</td>
<td>8,05</td>
<td>470 nZv/hour</td>
<td>320 nZv/hour</td>
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<tr>
<td>Settlement Ak-Terek</td>
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<td>-</td>
<td>-</td>
<td>17,5 °C</td>
<td>8,24</td>
<td></td>
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</tr>
</tbody>
</table>

Soil. The top- soil of region is presented according to data with bright-brown soils, for which the weak humus is characteristic, that varies from 0,8 to 2,0 % with gradual decrease to a bottom.

The bright-brown soil is a carbonate from the surface and for the carbonate cutout is typical the uniform distribution of CO2 with some tendency of increasing from above to downwards. The maximum of carbonates accumulation is observed on depth of 40-50 cm. Bright-brown soils have alkaline reaction. On the average pH is equal to 8,0-8,5 on all top- soil [10, 11].

The content of general nitrogen in the soil is 0,1 to 0,25%, gross phosphorus -0,2-0,3 %. These soils rich in potassium, which amount to 2,0-2,5 %.

In a province of Kadji-Sai and contiguous territories the soil and the bulk dirt are characterized by the various content of uranium - 0,1·10-6 g/g to 35,0·10-6 g/g. The analysis has shown 20 samples of soil and dirt, that on tailing dump on the top horizon of a bulk dirt (0,20 cm) the content of uranium varies from 1,1 to 2,6·10-6 g/g, on the depth it arises- up to 3,0·10-6 g/g. The large concentration of uranium has an average zone of tailing dump where the content of uranium in the top horizon of a dirt is equal to 4,2·10-6 g/g, and in the bottom horizon, on depth of 40-60 cm -
The average level of a scale-background in technogenium subregion is shown in table 2.

Table 2. The level of a scale-background in technogenium uranium subregion of Kadji-Sai

<table>
<thead>
<tr>
<th>Places of selection</th>
<th>On a surface of soil</th>
<th>Surfaces of soil at height 1 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel of the river in area of a waste-deposite</td>
<td>150-200 nZv/hour</td>
<td>150-200-220 nZv/hour</td>
</tr>
<tr>
<td>Sedimentation № 3</td>
<td>200 nZv/hour</td>
<td>150 nZv/hour</td>
</tr>
<tr>
<td>Factory till processings of coal slags</td>
<td>200 nZv/hour</td>
<td>150 - 200 - 220 nZv/hour</td>
</tr>
<tr>
<td>Uppermost of waste-deposite of industrial zone</td>
<td>220-240 nZv/hour</td>
<td>200 nZv/hour</td>
</tr>
<tr>
<td>Above of waste-deposit, in area of a site with a high scale-background, industrial zone</td>
<td>1,4 mcZv/hour</td>
<td>220 nZv/hour</td>
</tr>
<tr>
<td>Inhabited zone</td>
<td>200 nZv/hour</td>
<td>150 nZv/hour</td>
</tr>
</tbody>
</table>

In a soil of the "Khan-Sarai" dude ranch situated on horizon lower of tailing dump, the average content of uranium in a soil is appeared to be above, than on tailing dump (6,3·10-6 g/g). It is established, that on territory of the dude ranch on depth of 20-40 cm the content of the concentration of uranium is high and is equal to 17,0-20,0·10-6 g/g. To our opinion, the radionuclides of tailing dump with subsoil and subterranean waters migrate downwards to the lake and are accumulated in a soils of the dude ranch.

According to the data of other researchers [8], it is pointed out the content of uranium in bright-brown soils of southern coast of Issyk-Kul (from 1,5·10-6 to 3,3·10-6 g/g). Mountain breeds serve the source of uranium in the soils of the hollow of Issyk-Kul. The influence of mountain breeds on a level of the content of uranium in the soils is defined by carrying of products of destruction breeds enriched with uranium, and by their direct participation in the process of soil formation, especially of low-powered soils of the hollow.

The radioactive elements are founded due to the analysis of soil tests on revealing the content of radionuclides: torium and radium. Their quantitative contents with their coordinate characteristics are presented in table 3. As evidently from the table the contents of torium and radium do not exceed natural norms.

The table 3
### The contents of thorium and radium in the soil

<table>
<thead>
<tr>
<th>Coordinates</th>
<th>Torium (mg/g)</th>
<th>Radium (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breadth</td>
<td>Longitude</td>
<td></td>
</tr>
<tr>
<td>42,646066</td>
<td>77,237182</td>
<td>0,061</td>
</tr>
<tr>
<td>42,643341</td>
<td>77,235671</td>
<td>0,072</td>
</tr>
<tr>
<td>42,594729</td>
<td>76,876809</td>
<td>-</td>
</tr>
<tr>
<td>42,59557</td>
<td>76,877175</td>
<td>0,018</td>
</tr>
</tbody>
</table>

Water. As aforesaid, the geochemical province Kadji-Sai is located near to a resort zone of the lake Issyk-Kul, and the content of uranium in the water has the important ecological value. According to the data of the different authors [3, 8, 12, 13] the amount of uranium in waters of the rivers Ton, Ак-Суу and the hollow Issyk-Kul are equal to 5,6·10⁻⁶ g/l. Seasonally and places of selection of the river Djergalan the content of uranium varies from 2,8·10⁻⁶ to 1·10⁻⁵ g/l, i.e. key waters of well and rivers of the hollow Issyk-Kul contain 10. However, in some cases 100 times more uranium, than water of areas of black terrestrial and not black terrestrial zones.

Vegetation: The vegetative cover is rarefied, the projection covering varies from 5 to 10 % and only on separate sites - to 50 %. Herbarium of 58 kinds of plants is revealed and collected on the territory of the province belonging to 47 sorts and 20 families [3].

Basically, the vegetative cover uranium tailing dump is presented in two formations: in the uppermost of southern part – different grass-estragon with domination of wormwood estragon (Artemisia dracunculus). The vegetative cover of tailing dump as inspection shown, are in a stage of formation. The vegetation regard to "a pure zone" is presented by flora of a building "Khan-Sarai" dude ranch which located on 1,5 kms from Kadji-Sai. This vegetation is a little cultivated.

It is necessary to note, that from the grassy plants the Lucerne (Medicago) and Melilotus from family bean is worth to be marked, which have low concentration of uranium at high factors of discrimination - 210,0-630,0. From the rest of different grasses it is necessary to specify on Marrubium alternidens, which accumulates in stalk to weight a lot of uranium, i.e. almost as much, how many it contained in ground. Thus Kto enrich by its uranium has reached the large sizes - 301,5. The rather high contents of uranium had Echium vulgare - 0,52·10⁻⁶ g/g at low Kdisk - 12,1.

On most uranium tailing dump 10 kinds of plant of a deserted type are revealed: Ulmus pinnato-ramosa, Elaeagnus songorica, Caragana Turfanica, Peganum harmala, Akantholimon alatavicum, Natraria sibirica, Clematis songorica. The contents of
uranium in the listed plants was small and changed 0,02-0,31·10^{-6} g/g, at Kto enrich from 1,0 to 15,5 and Kdisk - from 17,8 to 240,0.

Our data will be coordinated to the data of other researchers. So in 1968 the group of scientists of GEOHI of RAS, carried out extensive researches of the contents of uranium in breeds, soils, plants, animals and fishes of the hollow Issyk-Kul. They mark, that the plants of this area are rich by uranium and contain it 1,25·10^{-5} % - 2,1·10^{-4} % on dry substance or in 1,5-240 times more, than plant of Kursk reserve. By results of our researches, the percentage of uranium, in plants of a province of Kadji-Sai makes from 0,17 to 4,0·10^{-4} %. Hence, there are bases to speak, that the majority of plants of the region Kadji-Sai have the rather raised contents of uranium in comparison with clarc of Kursk reserve. The intermountain hollow of Issyk-Kul represents uranium biogeochemical province, within the limits of which all components of an environment are enriched by uranium: mountain breeds, ground, lake, river and underground waters, lake deposits and alive organisms.

As now the hollow of Issyk-Kul is biosphere territory and on coast of lake the sanatoriums, known resort of Cholpon-Ata and tourist bases are located, among the population there was a concern of perspective radioactive pollution "pearls of Kyrgyzstan". An average radio-activity, on the data of sintelation-spectrometer and the scale - background (DKS-96) not high, is possible to consider as radigeochemical background (which for uranium - radium is defined by values between 35 and 55 bk/kg).

The conclusion. Thus, the results of the executed researches allow to make the following conclusions - above a level of a background in the hollow are allocated with the raised radioactivity of anomaly of three types:

1. Natural anomaly of a radioactivities connected to layers, seldom acting from under friable adjournment, radioactive brown coals Jur age;
2. Technogenium anomaly, in hundreds time exceeding the background dated to fenced concrete wall dumps grey fine granular of substance.
3. Technogenium anomaly (their activity in tens time is higher than a background) in the cascade from four sedimentation with an equal flat surface lowered downwards on a valley from a minefield.

Inhabit of plants in environment with the raised concentration of uranium not only is accompanied by change of its bioefficiency, but also causes morphological variability. In area of the lake Issyk-Kul most infringement pigmentation of blossom at various kinds of plants frequently is shown. At a plant of Astragalus, borodinii the morphological variability directed to the party of splitting of a sheet plate is observed. Peganum garmala and Potentilla argentea - instead of usual 5 petals was 6-7 and their partial bifurcation. At the same time for other plants, their intensive development (Karagana, Scutellaria, Perovskia, Harmala) is observed.
In the whole results of the done research work show, that in researched territory the general level of external radiation is within the limits of norm, except for some technogenium territories.

**Literature**

SOLIDIFICATION/STABILIZATION OF TANNERY SLUDGE

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TUBITAK MRC, Gebze 41470, Kocaeli/Turkey

ABSTRACT

The objective of this study is to treat sludge derived from the treatment system of a leather tanning industry in order to produce a waste form that meets the requirements for final land disposal in Turkey. The article also discusses the results of the tests used to study and verify the treatment.

INTRODUCTION

Hazardous wastes destined for land disposal are required to be treated in order to reduce the risks posed by the wastes after land disposal. Biological, physical, and chemical technologies may be used in conjunction with one another to reduce the contamination to a safe and acceptable level [1]. Stabilisation/solidification (S/S) is known as one of the major technologies for treating and disposing of hazardous wastes [2, 3]. In this study, the applicability of S/S technology to leather tanning industry sludge which is subject to land disposal restrictions due to its high content of halogenated organic compounds, chloride, fluoride and total organic carbon concentrations, was investigated and the effects of S/S on the sludge were characterized. Chemical and contaminant release properties of the S/S waste were evaluated to determine if the S/S treatment technology reduced the amount of hazardous contaminants leached in standard leaching tests.

EXPERIMENTAL SECTION

The treatment sludge collected at different dates from a tannery wastewater treatment facility was solidified by mixing with additives, e.g., gypsum, lime, activated carbon and zeolite, in different proportions, Table 1. Leaching of raw sludge and the treated sludge was performed according to DIN 38414 - S4 [4]. The eluates were analyzed regarding to the criteria given in the Turkish Regulation of Hazardous Waste Control, TRHWC. Standard methods were used in these analyses [5].
RESULTS AND DISCUSSION

The properties of the raw sludge (S) eluate are given in Table 2. It is seen that the concentration of halogenated organic compounds, chloride, fluoride and total organic carbon in the eluate of raw sludge are higher than the required limits in TRHWC. The effectiveness of the solidification process was evaluated by the leaching test to define the amount of the toxic material in the eluate. It is observed that the concentration of TOC, fluoride and chloride increased with CaO addition to the sludge, Table 2. However, the concentration of TOC, fluoride and chloride in the sludge treated with CaO is decreasing with the increasing CaO/sludge ratio compared to the values found for raw sludge. On the other hand, the values for TOC and fluoride are still above the restricted limits in TRHWC. The concentration of chloride decreased in the sludge treated with CaO/sludge ratio equal to 2/8 and 3/8, respectively, and these values are acceptable for TRHWC. The addition of activated carbon to CaO to treat sludge resulted in the reduction in TOC and AOX contents.

Table 1. Ratio of the mixtures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO/sludge</th>
<th>Sample</th>
<th>CaO+activated carbon/sludge</th>
<th>Sample</th>
<th>CaSO₄/sludge</th>
<th>Sample</th>
<th>Zeolite/sluide</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-1</td>
<td>1:8</td>
<td>S2-1</td>
<td>2:5:1:4</td>
<td>S3-1</td>
<td>1:5</td>
<td>S4-1</td>
<td>1:2</td>
</tr>
<tr>
<td>S1-2</td>
<td>2:8</td>
<td>S2-2</td>
<td>4:5:1:4</td>
<td>S3-2</td>
<td>1:2</td>
<td>S4-2</td>
<td>1:1</td>
</tr>
<tr>
<td>S1-3</td>
<td>3:8</td>
<td>S2-3</td>
<td>33:20:1:4</td>
<td>S4-3</td>
<td>3:2</td>
<td>S4-4</td>
<td>2:1</td>
</tr>
</tbody>
</table>

Table 2. The properties of eluate derived from raw sludge and treated sludge.

<table>
<thead>
<tr>
<th>Parameter, mg/l</th>
<th>S</th>
<th>S1-1</th>
<th>S1-2</th>
<th>S1-3</th>
<th>S3-1</th>
<th>S3-2</th>
<th>S3-3</th>
<th>TRHWC / Appendix – 11 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.92</td>
<td>12.39</td>
<td>12.51</td>
<td>12.61</td>
<td></td>
<td></td>
<td></td>
<td>4 – 13</td>
</tr>
<tr>
<td>TOC</td>
<td>666</td>
<td>3126</td>
<td>2695</td>
<td>2572</td>
<td>800</td>
<td>400</td>
<td>275</td>
<td>40 – 200</td>
</tr>
<tr>
<td>Arsenic</td>
<td>&lt;0.003</td>
<td>0.01</td>
<td>0.005</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.11</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td></td>
<td></td>
<td>0.4 – 2</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td></td>
<td></td>
<td></td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>Chromium +6</td>
<td>0.15</td>
<td>0.04</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td></td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>Copper</td>
<td>0.030</td>
<td>2.265</td>
<td>0.123</td>
<td>0.406</td>
<td></td>
<td></td>
<td></td>
<td>2 – 10</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.0760</td>
<td>2.01</td>
<td>1.32</td>
<td>1.52</td>
<td></td>
<td></td>
<td></td>
<td>0.4 – 2</td>
</tr>
</tbody>
</table>

Σ ≤ 5
The concentration of TOC considerably decreased to 207 and then to 33 mg/l in the eluate of the sludge treated with 1:5 and 1:2 of CaSO₄ : sludge ratio, respectively, as seen in Table 3. However, the second treatment provided the required values by the TRHWC. It is observed that flouride and chloride contents in the treated sludge eluate decreased dramatically to the acceptable values for the land disposal. However, sulphate content increased. A slight decrease in the AOX content, which is not enough for land disposing, is observed.

**Table 3. The properties of the eluate derived from sludge treated with CaSO₄.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>mg/l</th>
<th>S3-1</th>
<th>S3-2</th>
<th>S4-1</th>
<th>S4-2</th>
<th>S4-3</th>
<th>S4-4</th>
<th>TRHWC / Appendix –</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td></td>
<td>207</td>
<td>33</td>
<td>315</td>
<td>219</td>
<td>175</td>
<td>110</td>
<td>Hazardous waste</td>
</tr>
<tr>
<td>Floride</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>4.4</td>
<td>4.5</td>
<td>3.8</td>
<td>3.7</td>
<td></td>
<td>Inert waste</td>
</tr>
<tr>
<td>Chloride</td>
<td>517</td>
<td>571</td>
<td>771</td>
<td>685</td>
<td>613</td>
<td>485</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphate</td>
<td>2010</td>
<td>1982</td>
<td>371</td>
<td>220</td>
<td>199</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AOX</td>
<td>1.11</td>
<td>0.07</td>
<td>0.84</td>
<td>0.66</td>
<td>0.37</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sludge treatment with zeolite resulted in reduction in each parameter as seen in Table 3. As the zeolite concentration was increased the concentration of the parameters decreased. The concentration of the parameters obtained by the treatment
of sludge with zeolite: sludge ratio as 3:2 and 2:1 were acceptable by TRHWC for land disposing.

CONCLUSIONS

This study describes the application of S/S technology as an alternative treatment technology to the sludge derived from the treatment system of a leather tanning industry and therefore, to convert the waste into solid and non-hazardous waste form suitable for landfill disposal in Turkey. Although the treatment of sludge with additives resulted in lower concentrations of the examined parameters required in the TRHWC, the best result was obtained during the treatment of sludge with zeolite. In general, the lower concentrations of hazardous substances were obtained with increasing content of the additive. As was mentioned by E.F. Barth [6], solidification processes may not necessarily decrease leachability but refers to a purposeful chemical reaction that has occurred to make waste constituents less leachable. On the other hand, even lower content of zeolite worked quite well to decrease the concentrations of the contaminant release parameters during zeolite treatment.

REFERENCES

4. DIN 38414-4: 10.84 Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Schlamm und Sedimente (Gruppe S); Bestimmung der Eluierbarkeit mit Wasser (S 4).
TESTING WASTE HAZARDOUSNESS FOR ACCEPTANCE TO LANDFILLING. ROMANIAN PROCEDURES AND CRITERIA – A CASE STUDY

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ABSTRACT
A study of testing the hazardousness of the red mud resulted from production of alumina (aluminium oxide - Al₂O₃), deposited within the tailing pond owned by the production company is presented. The testing was based on procedures required by Romanian standards and the hazardousness was established by criteria contained in Romanian regulations. The testing has identified red mud as a hazardous waste, despite the classification of non-hazardous given in the frame of the European List of Waste.

INTRODUCTION
Aluminium is a material with a large range of application in different fields: transportation, construction, electricity and mechanical sector, packaging industry, household appliances. The aluminium industry is the largest and the youngest of the non-ferrous metal industries, while aluminium smelting begun only about a century ago. Primary aluminium is produced from bauxite that is converted into alumina (aluminium oxide - Al₂O₃). 100 tones of bauxite produce 40-50 tons of alumina from which it results 20-25 tons of aluminium.

Obtaining alumina from bauxite is based on the well known Bayer process. To extract alumina from bauxite ore the process uses caustic soda – Na OH - and lime – CaO added in digesters, at high temperature and pressure. The resulted slurry contains dissolved sodium aluminate and a mixture of metal oxides called red mud that is removed in thickeners. The aluminate solution is cooled and seeded with alumina to crystallize hydrate alumina. Crystals are washed and then calcinated in rotary kilns. Aluminium oxide (alumina) is the raw material used for aluminium production by electrolysis.

The red mud resulted as waste during extraction of alumina from bauxite is generally alkaline and contains 3 to 12 kg of NaOH per tone of alumina produced. It is a current practice to deposit red mud near the production site in specially designed and sealed tailing ponds. The excess water separated at the tailing pond surface is returned to the process.
The generation of red mud is a main environmental issue of the aluminium industry in Romania because of the large generated quantity (1.3-1.5 ton per each ton of alumina produced), the need for transport by pipes and the disposal in engineered tailing ponds.

In order to assure a careful handling and disposal of the red mud a definition of its hazardousness was necessary while the European List of Waste transposed within the Romanian legislation (Governmental Decision no 856/2002 - for keeping records on waste management and approval of the waste list) does not identify it as a hazardous waste (code 01 03 09).

**EXPERIMENTAL SECTION**

The Romanian Legislation referring to waste acceptance for landfilling is represented by the Ministerial Order no. 95/2005 (transposing Council Decision 2003/33/CE) which nominates:
- criteria for waste acceptance to landfill
- preliminary procedures for testing the waste acceptance for landfilling
- methods for sampling and analyses of samples
- the national lists of wastes accepted in each category of the 3 landfill categories: for inert waste, for non-hazardous waste and for hazardous waste (as established within the Governmental Decision no. 349/2005 regarding waste landfilling).

The criteria for waste acceptance for landfilling are based on the characteristics of waste resulted from:
- the origin of waste, respectively the technological process generating waste and the chemical composition of waste
- the leaching behavior of waste.

Conditions related to the composition of waste are included within the Governmental Decision no. 856/2002 that approved the list of waste including the hazardous waste. These conditions consist of concentration limits (expressed as percentage) for toxic, hazardous, corrosive, irritant, mutagenic and other harmful elements.

The leaching behavior of waste is important because the release of soluble constituents upon contact with water is regarded as a main mechanism which generates a potential risk to the environment during the disposal of waste. For testing waste capacity to generate such a risk methods described within Romanian standards SR ENV 12920:2002 and International standards adopted as Romanian Standards - SR EN 12457-1:2003 and SR EN 12457-2:2003 are used. These standards contain compliance tests that provide information on leaching of granular wastes and sludges having a particle size below 4 mm, under specified experimental conditions, particularly to a liquid to solid ratio of 2 l and 10 l to one kg dry matter. Applying
these tests procedure produces an eluate/leachate that shall subsequently be analyzed according to appropriate methods.

Criteria related to the leaching behavior of waste are stipulates within the Ministerial Order no. 95/2005 and they consist of limit values (by waste categories - hazardous, non-hazardous and inert) for main toxic and hazardous substances that could be dissolved from waste:

- heavy metals, sulfate, chlorine, fluorine
- organic carbon components (expressed as dissolved organic carbon – DOC).

The first step of testing the red mud hazardousness was the physical and chemical characterization. Knowing the composition of raw materials entering in the alumina production process the content of heavy metals has been determined by atomic absorption spectroscopy (AAS) within the following types of samples: crude red mud from transport pipe, crude red mud from tailing pond surface and red mud from the tailing pond at 40 cm depth.

Values obtained by AAS have been judged considering the provisions of the Governmental Decision 856/2002.

The second step of testing consisted of leaching the same red mud samples. As standardized, the leaching conditions have been the following:

- leaching agent: distilled water (pH = 6)
- rapport of solid (waste) / liquid (leaching agent) = 1/10, respectively 1/2
- leaching time = 24 hours
- agitation during leaching
- ambient temperature.

The eluate /leachate content of heavy metals (Cu, Cd, Cr, Mn, Ni, Fe, Pb) has been determined and the values obtained by AAS analysis have been compared with the limit values stipulated in the Ministerial Order no. 95/2005.
RESULTS AND DISCUSSION

Metal contents of different samples of red mud are presented in table no 1.

Table 1. Metal content in analysed red mud samples (% of dry matter)

<table>
<thead>
<tr>
<th>Metals</th>
<th>Crude red mud from transport pipe (% of dry matter)</th>
<th>Crude red mud from pond surface (% of dry matter)</th>
<th>Red mud from the pond at 40 cm depth (% of dry matter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.0760</td>
<td>0.0039</td>
<td>0.0057</td>
</tr>
<tr>
<td>Cd</td>
<td>absent</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0043</td>
<td>0.0022</td>
<td>0.0034</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0260</td>
<td>0.0142</td>
<td>0.0184</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0149</td>
<td>0.0283</td>
<td>0.0118</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0006</td>
<td>0.0010</td>
<td>0.0004</td>
</tr>
<tr>
<td>Fe</td>
<td>20.1160</td>
<td>11.7400</td>
<td>13.8355</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0311</td>
<td>0.0295</td>
<td>0.0273</td>
</tr>
</tbody>
</table>

By comparing the values in Table no. 1 with the conditions specified within Governmental Decision 856/2002 it was concluded that the red mud could be considered non-hazardous because the total concentration of Cu, Cd, Zn, Cr, Ni and Pb does not exceed 1% of dry matter.

The content of heavy metals within the leachates / eluates resulted from leaching of the red mud samples in solid to liquid ratios of 2 l/kg and 10 l/kg are presented in tables no. 2, 3 and 4, together with the leaching limit values mentioned by the Ministerial Order 95/2005.

By analyzing data from Tables no 2, 3 and 4 it resulted that the red mud should be considered a hazardous waste because the total Chromium concentration in leachates exceeds the limit value for depositing as non-hazardous waste, especially at a liquid to solid ratio of 2 l/kg.

The variation of concentration obtained in case of the tested samples could be explained by the different origin and characteristics of the raw material used in the industrial process.
Table 2: Heavy metals in leachate obtained by leaching crude red mud from transport pipe at a liquid to solid ratio of 2 l/kg and 10 l/kg

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Concentration (mg/kg of dry matter)</th>
<th>Limit values in Ministerial Order 95/2005 (mg/kg of dry matter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 l/kg</td>
<td>10 l/kg</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1050</td>
<td>0.0840</td>
</tr>
<tr>
<td>Cd</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>Zn</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>Cr total</td>
<td>11.2092</td>
<td>9.0332</td>
</tr>
<tr>
<td>Ni</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1464</td>
<td>0.3690</td>
</tr>
</tbody>
</table>

Table 3: Heavy metals in leachate obtained by leaching crude red mud from tailing pond surface at a liquid to solid ratio of 2 l/kg and 10 l/kg

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Concentration (mg/kg of dry matter)</th>
<th>Limit values in Ministerial Order 95/2005 (mg/kg of dry matter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 l/kg</td>
<td>10 l/kg</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0758</td>
<td>0.0160</td>
</tr>
<tr>
<td>Cd</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>Zn</td>
<td>absent</td>
<td>absent</td>
</tr>
<tr>
<td>Cr total</td>
<td>3.1024</td>
<td>2.0752</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0024</td>
<td>absent</td>
</tr>
<tr>
<td>Pb</td>
<td>0.2204</td>
<td>0.0243</td>
</tr>
</tbody>
</table>

Table 4: Heavy metals in leachate obtained by leaching red mud from the tailing pond at 40 cm depth at a liquid to solid ratio of 10 l/kg

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Concentration (mg/kg of dry matter)</th>
<th>Limit values in Ministerial Order 95/2005 (mg/kg of dry matter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 l/kg</td>
<td>10 l/kg</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0952</td>
<td>0.1740</td>
</tr>
</tbody>
</table>
In order to identify the influence of the deposited red mud on the ground water quality, water samples extracted from the monitoring wells (W 1-8) have been analyzed too, by determining their pH, alkalinity and heavy metal contents. Table no 5 presents the data obtained by analyzing ground water samples, water returned from the tailing pond to the factory and clarified (by settlement) water extracted from the red mud transport pipe.

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Chemical Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
</tr>
<tr>
<td>W 8</td>
<td>6.9</td>
</tr>
<tr>
<td>W 2</td>
<td>8.8</td>
</tr>
<tr>
<td>W 3</td>
<td>8.5</td>
</tr>
<tr>
<td>W 6</td>
<td>8.6</td>
</tr>
<tr>
<td>W 1</td>
<td>10.1</td>
</tr>
<tr>
<td>W 4</td>
<td>10.4</td>
</tr>
<tr>
<td>Water returned from pond</td>
<td>11.6</td>
</tr>
<tr>
<td>Clarified water from pipe</td>
<td>11.8</td>
</tr>
</tbody>
</table>

From Table no. 5 it results that the quality of the ground water has been modified by infiltration from the red mud tailing pond as follows:
- the metal content is higher in the nearest monitoring wells – W 1, W 4 – and is decreasing with the increase of distance from the monitoring wells to the tailing pond, the less polluted well being the most distant one – W 8.
- pH and alkalinity of well’s water show the same influence patterns, being higher near the pond and lower in the most distant well.
CONCLUSIONS

1. The testing of the hazardousness for acceptance to a specific waste deposit type of the red mud generated by the Romanian industry producing alumina, by using Romanian procedures and criteria, has identified this waste as a hazardous one, despite the classification given in the frame of the European List of Waste.

2. The actual disposal practices have generated negative influences on the ground water quality, expressed by increased metal content and modified pH and alkalinity.

3. As a consequence special technical arrangements for the existing tailing pond have to be considered together with a careful handling and disposal of the red mud, as well as a new program for emissions monitoring.

REFERENCES

1. SR ENV 12920:2002 Characterization of waste - Methodology for determining leaching behaviors of a waste in specified conditions:

2. SR EN 12457-1:2003 Characterization of waste - Leaching – Compliance test for leaching of granular waste materials and sludges - Part 1: One stage batch test at a liquid to solid ratio of 2 l / kg for materials with high granular solid content and particle size below 4 mm (with or without size reduction).

3. SR EN 12457-2:2003 Characterization of waste - Leaching – Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l / kg and particle size below 4 mm (with or without size reduction).
USING ISOTOPIC ANALYSIS TO INVESTIGATE AND MONITOR ORGANIC CONTAMINANTS IN THE ENVIRONMENT

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ABSTRACT

Understanding the sources, partition and degradation of contaminants in the environment is essential to effective assessment, monitoring, remediation, and policy decisions. Compound specific isotopic analysis of organic contaminants and microbial cellular components can provide greater resolution of contaminant sources and fates than can be achieved with concentration analysis alone. This abstract discusses the basis of the application of stable isotopic analysis to contaminated systems and the types of information that may be obtained from this approach.

INTRODUCTION

The recent developments in compound specific stable isotopic analysis have provided new tools for the investigation, assessment and monitoring of organic contaminants in the environment. Using concentration based approaches alone, it is often difficult or impossible to differentiate between potential sources of contaminants to an environmental system, particularly when there may be both natural and anthropogenic sources of a compound. Differentiating between anthropogenic sources and natural backgrounds is essential for determining remediation targets for contaminated areas. For such remediation to be most effective, it needs to target the primary sources of a contaminant to an environmental system. And assessing the extent to which natural or engineered remediation schemes are removing contaminants requires analytical tools that can directly identify and assess the degradation of the contaminants.
APPROACH

Compound specific isotopic analysis directly measures variations in the ratios of isotopes in a sample. The isotopic ratios most applicable to organic contaminants in the environment are $\delta^{13}$C, $\delta^2$H, $\Delta^{14}$C, and to a slightly lesser extent, $\delta^{37}$Cl, $\delta^{18}$O, $\delta^{15}$N. In this delta notation the isotopic ratio is being expressed as the ratio of the heavy isotope over the light as compared to an internationally accepted standard as illustrated for $\delta^{13}$C in equation 1.

$$\delta^{13}\text{C} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000$$  (1)

where $R = ^{13}\text{C} / ^{12}\text{C}$. Gas Chromatography – Isotope Ratio Mass Spectrometry (GC-IRMS) can determine this ratio for any organic compound that can be analyzed by traditional GC methods.

The isotopic composition of an organic compound may behave in two ways in the environment. In some cases, the isotopic composition is conserved in the environment. In such cases, if two sources of a compound have distinct isotopic compositions, this isotopic distinction will be retained in the environment and can be applied to differentiate between contaminant sources. The alternative possibility is that the isotopic composition of a compound may be fractionated as it undergoes environmental processes. In such cases, the extent of fractionation can provide information about the processes that are affecting the compound and the extent to which they are occurring.

A particularly powerful recent development is the use of compound specific $^{14}$C analysis. Because the majority of anthropogenic contaminants are produced from petroleum based feed-stocks, which are millions of years old, they contain no $^{14}$C ($\Delta^{14}\text{C} = -1000\%o$). In contrast, natural organic matter that has been recently photosynthesized has modern levels of $^{14}$C ($\Delta^{14}\text{C} = 100 +/- 50 \%o$). This extreme isotopic distinction between natural and anthropogenic contaminants can be highly effective in differentiating sources and identifying fates of organic contaminants in the environment. This report will illustrate the applications of these approaches using several case studies.

SOURCE DIFFERENTIATION

Differentiation of compound sources in the environment via compound specific stable isotopic analysis has two requirements: i) there must be an isotopic
distinction between the two sources that is greater than the precisions at which isotopic ratios can be measured; and ii) the isotopic composition of a compound must be conserved as the compound moves through the environment. When these criteria are met, compound specific isotopic analysis has been applied to differentiate sources of contaminants ranging from volatile organic compounds such as solvents to larger molecular weight compounds such as PCBs and PAHs e.g. (Walker et al., 2005).

**DEGRADATION STUDIES**

In cases when the isotopic composition of a compound is changed, or fractionated, during a process, information can be gained about the nature of the process occurring and the extent to which it has occurred. This approach can differentiate between microbial degradation pathways (Hirschorn et al., 2004), or determine the extent of degradation in an environmental system (Sherwood Lollar et al., 2001).

**14C STUDIES**

Compound specific 14C analysis is the most recent development in isotopic analysis. This involves collecting sufficient mass of a contaminant for 14C analysis by accelerator mass spectrometry (AMS). This approach is particularly powerful as a method to determine whether a compound has a natural or anthropogenic source. Recently it was used to demonstrate a natural source for methoxy polybrominated diphenyl ethers found in a North Atlantic True’s beaked whale (Teuten et al., 2005). This approach has also been applied to differentiation wood combustion from diesel combustion inputs to the atmosphere in Sweden and Japan (Kanke et al., 2004; Mandalakis et al., 2004).

Compound specific 14C analysis can also be used to study the degradation of contaminants. My recent work has shown that the extent to which an organic contaminant is being metabolized by a microbe can be determined using a comparison of microbial cellular components and potential carbon sources. These studies demonstrated that, in one case, no significant degradation of a 30 year old oil spill was occurring (Slater et al., 2005), whereas at a recent spill bacteria were significantly metabolizing the contaminant carbon (Slater et al., in press).
SUMMARY

Effective environmental remediation and protection requires accurate understanding of the sources and processing of organic contaminants in the environment. While concentration based approaches have provided a great deal of information on these issues, greater understanding is often required. Compound specific isotope analysis is an effective way to generate such understanding and to monitor the behaviour and impact of organic contaminants in the environment. Further discussion of the compound specific isotope approach can be found in Slater, G.F. (2003) and Schmidt et al. (2004) (Schmidt et al., 2004; Slater, 2003).

REFERENCES


MODELING A DIFFUSIVE TRACER TEST FOR DETERMINING NAPL RESIDUAL SATURATION IN THE UNSATURATED ZONE

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²School of Civil Engineering and Geosciences, University of Newcastle upon Tyne, UK
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ABSTRACT

A new method is introduced for the determination of NAPL residual saturation in the unsaturated zone and tested in a large-scale lysimeter experiment with a heterogeneous NAPL distribution. This method uses gas tracers with different affinities for the NAPL phase, which are transported by diffusion through the soil volume of interest, and monitors the gas concentration with time. Code R-UNSAT is modified and used in this study to simulate the diffusion of the gas tracers in the lysimeter. Since the model was able to forward predict the experimental results, it was then used to perform several sensitivity analyses related to the heterogeneity of the NAPL saturation in the lysimeter. Several scenarios were investigated. Results indicated that the method predicts the NAPL residual saturation within a narrow volume around the point of injection. The monitoring of tracer concentrations at some distance from the injection point in combination with modeling allows for an estimate of the NAPL residual saturation in between the two points.

INTRODUCTION

Non-aqueous phase liquids (NAPLs) are common subsurface contaminants. Being in the subsurface it is difficult to observe the spatial distribution and the quantity of the contamination – a crucial knowledge for the remediation of the site. Several techniques have been developed such as soil core extraction, gas phase monitoring, etc [1,2]. These techniques are costly, difficult to apply, and the results do not account for the heterogeneity of the NAPL residual saturation. The use of
diffusive tracers has been proposed as an in-situ method that can compliment the gas concentration monitoring providing residual saturation data at different points [3]. This method is based on the comparison of the gas-phase concentrations of a conservative and a non-conservative tracer that will partition into the NAPL phase and its spreading will be retarded. The objectives of this presentation are: (a) to present the diffusive tracer method and (b) to evaluate the applicability of this method through the use of a validated model.

APPLICATION OF THE DIFFUSIVE TRACER METHOD IN A LARGE SCALE LYSIMETER

A large scale, cylindrical field lysimeter with a diameter of 120 cm and a 250 cm depth was used as the experimental system, see Figure 1 [4]. The lysimeter was filled with coarse alluvial sand. At depths between 1.0 and 1.2 m, a zone of the same sand contaminated with an artificial fuel mixture was embedded with a residual NAPL saturation Sn of approximately 3.5% of the total porosity. Sn as determined by NAPL extraction from sand was 2.4% immediately after source emplacement. At point A in Figure 1 the tracer mixture was injected and the gas concentration of these tracers was monitored over time at all three points (A, B, and C). The tracer mixture included different concentration of sulfurhexafluoride (SF6), dichlorodifluoromethane (CFC-12), and trichlorofluoromethane (CFC-11). Gas concentrations were measured with a Gas Chromatograph equipped with an ECD detector.

![Experimental setup for the lysimeter study](image)

Figure 1 Experimental setup for the lysimeter study [4]. A: the injection point, B and C: monitoring points
MODELING APPROACH

Each tracer breakthrough curve is simulated separately. The reaction-diffusion equation under transient conditions is adopted here, which has the following form for a single component:

\[ A \frac{\partial C_g}{\partial t} - \nabla \cdot (D \nabla C_g) = 0 \]  

(1)

where \( A = \theta_g + (\theta_w / H) + (K_n \theta_n / H) \) with \( \theta_g \) and \( \theta_w \) being the gas and water fractions of the unsaturated zone, respectively, \( H \) is Henry’s law constant (dimensionless, \( C_g/C_w \)), \( K_n \) is the NAPL partitioning distribution coefficient, and \( \theta_n \) is the NAPL fraction of the unsaturated zone. \( C_g \) is the gas phase tracer concentration, \( t \) is the time, and \( D = D_{ge} + (D_{we} / H) \) where \( D_{ge} \) and \( D_{we} \) are the gas and aqueous phase effective diffusion coefficients, respectively. The gas phase diffusion coefficient is calculated from \( D_{ge} = D_g \theta_g \tau_{fg} \) where \( D_g \) is the molecular diffusion coefficient and \( \tau_{fg} \) is the gas phase tortuosity factor. Values for \( \tau_{fg} \) are calculated from Millington and Quirk’s equation \( \tau_{fg} = \theta_g^{7/3} / (\theta_g + \theta_w)^2 \) [5]. The aqueous phase effective diffusion coefficient and the tortuosity factor are calculated in an analogous manner. \( K_n \) values were determined through batch experiments in previous work [4].

Code R-UNSAT [6] is modified and used in this study, to simulate experimental data from the lysimeter. Modeling of the lysimeter experiment was done in cylindrical coordinates to simulate the actual lysimeter shape (see Figure 1). It was assumed that diffusion into the ambient air through the topsoil surface was sufficiently rapid to justify the \( C_g=0 \) condition at the upper boundary. The bottom and the walls were impermeable and thus, were assigned the conditions \( dC_g/dz=0 \) and \( dC_g/dr=0 \), respectively.

RESULTS

Figure 2 presents the experimental data for the tracer breakthrough curves along with the model predictions for one of the monitoring probes (C). The simulation curves are forward predictions of the experimental data and follow similar trends as the experimental data. Even better agreement of experimental data and predictions was obtained for the tracer breakthrough curves of the other two probes.

The model is then used to perform several sensitivity analyses. A set of scenarios tested is presented in Figure 3. The tracers are injected in probe A as in the experimental case. The parameter that varies among scenarios is a second zone that
moves vertically in the lysimeter. The heterogeneity of the NAPL residual saturation does not have an impact on the predicted NAPL residual saturation, which are derived from the tracer concentrations at the injection point (at probe A). The NAPL residual saturation can also be derived from the breakthrough curves monitored at some distance from the injection point (at point B and C). The NAPL saturation derived from breakthrough curves appears to represent the NAPL saturation in between the two probes, and is not affected by changes in the NAPL content outside of this volume. These results are presented in Table 1. More results will be presented in the workshop.

![Figure 2](image_url)

**Figure 2** Breakthrough curves at Point C for the 3 tracers. Experimental (markers) and modeling (lines) results.

![Figure 3](image_url)

**Figure 3** Five of the scenarios tested with the validated model
Table 1 Results for the NAPL residual saturation resulted for each scenario

<table>
<thead>
<tr>
<th>Scenarios in Figure 3</th>
<th>i</th>
<th>ii</th>
<th>iii</th>
<th>iv</th>
<th>v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone Depth (cm)</td>
<td>100-120</td>
<td>100-120 &amp; 40-60</td>
<td>80-120</td>
<td>100-140 &amp; 175-195</td>
<td>100-120</td>
</tr>
<tr>
<td>A, SF6/CFC-11</td>
<td>-</td>
<td>-</td>
<td>3,1</td>
<td>3</td>
<td>3,2</td>
</tr>
<tr>
<td>A, CFC-12/CFC-11</td>
<td>0,5</td>
<td>0,5</td>
<td>2,5</td>
<td>0,5</td>
<td>0,1</td>
</tr>
<tr>
<td>B, SF6/CFC-11</td>
<td>2,6</td>
<td>2,6</td>
<td>2,8</td>
<td>2,4</td>
<td>2,9</td>
</tr>
<tr>
<td>B, CFC-12/CFC-11</td>
<td>2,5</td>
<td>2,5</td>
<td>2,7</td>
<td>2,4</td>
<td>3,0</td>
</tr>
<tr>
<td>C, SF6/CFC-11</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
</tr>
<tr>
<td>C, CFC-12/CFC-11</td>
<td>2,5</td>
<td>2,5</td>
<td>2,7</td>
<td>2,4</td>
<td>3,0</td>
</tr>
<tr>
<td>Sn</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
<td>2,8</td>
</tr>
</tbody>
</table>

A: injection point 0, 110; B: sampling point 0, 80; C: sampling point 30, 110 (cm)

CONCLUSIONS

The conclusions of the present work are:

1) The model is able to forward predict the experimental data.

2) The experimental data and the model show that the tracer curves at the injection point provide a correct value for the local NAPL residual saturation.

3) Heterogeneity of the NAPL present in the area does not affect the measurement of the residual saturation at the point of injection or the monitoring point.

4) A combination of diffusive partitioning tracer methods with soil gas monitoring and numerical modelling may provide a promising concept for the investigation of NAPL residual in the vadose zone.

More conclusions will be presented in the workshop.

ACKNOWLEDGEMENTS

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REFERENCES


BIOREMEDIATION OF OIL-CONTAMINATED SEDIMENTS

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\textsuperscript{2}Dept. of Sanitary and Environmental Engineering, Rio de Janeiro State University UERJ

ABSTRACT

This paper presents the results of a full-scale remediation of an oily-leachate pond downstream a landfill in Estonia. The relatively simplified full-scale technology for treatment of the contaminated pond water and aged oily sediment proved to be appropriate to meet the legal requirements. The results confirm the high potential for application of biodegradation processes to treat hazardous compounds such as TPH and PAH.

INTRODUCTION

An environmentally sound and cost-effective method for remediation of oily waste, leachate and contaminated underlying sediment material was carried out in Laguja landfill in Estonia (Kriipsalu et al., 2005) in cooperation with the Company EcoPro Ltd. The purpose was to remediate a 9 800 m\textsuperscript{2} pond of leachate and oily waste where leachate is drained from the upstream landfill and oily waste started to be disposed about 25 year ago and stopped 10 years before the remediation action was implemented. The pond contained approximately 6 000 m\textsuperscript{3} of oil plus leachate and 3 500 m\textsuperscript{3} of contaminated bottom sediments. Most of the oil was found in an underlying soft water-rich heterogeneous layer of sediments as well as in a 30-cm-thick bottom layer of weathered and dense sediments. The integrated remediation plan carried out on top of the closed landfill consisted of the following phases: (i) removal and treatment of the oily leachate; (ii) removal and bioremediation of the oily-contaminated sediments; (iii) filling two smaller emptied pond sections with inert demolition waste; (iv) landfill profiling and capping; (v) construction of a wetland for further treatment of leachate.

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METHODOLOGY

The landfill and the pond area are shown in Figure 1. After the pond was divided into three parts, the water was pumped out and treated on-site in an oil separator, a series of sedimentation basins, and a two-section activated carbon filter (Figure 2). The results obtained during the first year of treatment are shown in Table 2. COD, PAHs and P after treatment were still above the target concentrations required for infiltration according to Estonian regulation (Table 2).

![Figure 1](image_url)

**Figure 1.** The Laguja landfill area and the pond: 1a, 1b and 1c pond sections; 2 embankment; 3 landfill; 4 leachate-oil treatment area; 5 infiltration area; 6 composting area for treatment of sediments; P6, P7 and P8 groundwater monitoring wells (Source: Kriipsalu et al., 2005).

The residues of floating oil were removed in the oil separator, which had a volume of 1.5m$^3$. The two settling basins (200m$^3$ each) were lined with a 0.5-mm-thick geomembrane. Between the two basins, two activated carbon filters were installed. With a retention time of 15 minutes, the capacity of the two 330-liter up-flow oil filters was 1.2m$^3$ h$^{-1}$. They were used alternately, and the depleted activated carbon was replaced after 200–250 m$^3$ had been pumped through the filter. A third settling pond and an additional infiltration field project were added at the beginning of the second year of the remediation. The multi-stage treatment was mostly efficient, and the final infiltration of the treated water apparently did not influence the quality of
groundwater during the period investigated (three years). However, depending on the site, more complex treatment measures might be needed. The analyses were carried out according to standard methods (Table 1).

Table 1. Treatment of pond water/leachate (Source: Kriipsalu et al, 2005).

<table>
<thead>
<tr>
<th></th>
<th>Pond water before treatment</th>
<th>Effluent after treatment</th>
<th>Target values for infiltration*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPH</td>
<td>mg L⁻¹</td>
<td>26.3–(44 000)**</td>
<td>0.25–0.30</td>
</tr>
<tr>
<td>PAH</td>
<td>µg L⁻¹</td>
<td>0.22–0.9</td>
<td>0.022–0.35</td>
</tr>
<tr>
<td>DS</td>
<td>mg L⁻¹</td>
<td>168–1240</td>
<td>18–32</td>
</tr>
<tr>
<td>BOD₇</td>
<td>mg O L⁻¹</td>
<td>53–390</td>
<td>5–7</td>
</tr>
<tr>
<td>N₉tot</td>
<td>mg L⁻¹</td>
<td>48–83</td>
<td>16–26</td>
</tr>
<tr>
<td>P₉tot</td>
<td>mg L⁻¹</td>
<td>4.2–10</td>
<td>0.63–2.3</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>6–8.25</td>
<td>8.40–8.80</td>
</tr>
<tr>
<td>Monophenols***</td>
<td>mg L⁻¹</td>
<td>&lt; 2.0</td>
<td>0.01–0.03</td>
</tr>
<tr>
<td>COD Cr</td>
<td>mg O L⁻¹</td>
<td>1 100–1 800</td>
<td>380–570</td>
</tr>
<tr>
<td>SO₄</td>
<td>mg L⁻¹</td>
<td>117–141</td>
<td>10–34</td>
</tr>
<tr>
<td>Cr</td>
<td>mg L⁻¹</td>
<td>55–100</td>
<td>0.3–0.05</td>
</tr>
<tr>
<td>Pb</td>
<td>mg L⁻¹</td>
<td>27–100</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>As</td>
<td>mg L⁻¹</td>
<td>3–4</td>
<td>0.001</td>
</tr>
<tr>
<td>Hg</td>
<td>mg L⁻¹</td>
<td>0.10–0.20</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>mg L⁻¹</td>
<td>&lt; 100</td>
<td>0.05– 0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>mg L⁻¹</td>
<td>&lt; 100</td>
<td>0.1–0.05</td>
</tr>
</tbody>
</table>

* RT I 1999, 15, 237; ** Extreme values obtained from samples taken from bottom layers; *** Total concentration of cresols and dimethyl phenols

Bottom sediment in laboratory-scale treatment: A laboratory test was carried out to evaluate the effect of different amendments and bulking materials on hydrocarbons decay during composting. Different performances of four different mixtures in lab-scale indicated that the structure of the material and the mixing and frequency procedure may affect the results. The content in the sediments (DS) of TPH was 170 000 mg kg⁻¹, phenols 12.93 mg kg⁻¹, PAHs 759 mg kg⁻¹, and PCB <50 µg kg⁻¹. The following mixtures were tested:
- **Mixture I**: sediments and peat [TPH 11 000 mg kg\(^{-1}\) (DS); pH 7.54; total organic carbon (TOC) 31% (DS); and moisture content 68%].
- **Mixture II**: 108 kg of sludge and 23 kg of shredded straw [TPH 110 000 mg kg\(^{-1}\) (DS); pH 6.79; TOC 45% (DS); and moisture content 80%].
- **Mixture III**: 45.7 kg of sludge, 59 kg of horse manure mixed with bedding peat, and 94 kg of bark: [TPH 85 000 mg kg\(^{-1}\) (DS), pH 6.54; TOC 41% (DS); and moisture content 57%].
- **Mixture IV**: 51.7 kg of oily sludge and 156 kg of bark [TPH 53 000 mg kg\(^{-1}\) (DS), pH 6.61; TOC 49% (DS); and moisture content 49%].

Moisture was first added according to field capacity, and was checked and adjusted during every remixing event. In Mixtures I and II stable levels of moisture 60-70% was retained. In coarse Mixtures III and IV, containing bark, the moisture content was lower: 50-60%. These mixtures had a tendency to dry faster than the others. Since N appeared to be a limiting nutrient, N-rich waste can be used for moistening the compost. During the initial seven-month period, the four mixtures were mechanically remixed monthly. Each time, composite samples from each mix were analyzed for TPH, dry matter, and water content. After seven month, the frequency of remixing and sampling was reduced. After three months of composting, the TPH content had been reduced up to 45% in Mixture I, 26% in Mixture II, 60% in Mixture III, and 30% in Mixture IV. After 21 months, the reduction values were 79%, 86%, 91%, and 92%, respectively. The target value 5 000 mg kg\(^{-1}\) (DS) was achieved only in Mixtures I [2300 mg kg\(^{-1}\) (DS)] and IV [4 240 mg kg\(^{-1}\) (DS)]. The initial hydrocarbon content of Mixtures II and III were significantly higher than commonly recommended for efficient bioremediation and concentrations of TPH above 50 000 mg kg\(^{-1}\), should be avoided (von Fahnestock et al., 1998). This value, considered acceptable in ventilated biopiles seems to be too high for passive static pile remediation. Due to the fact that contaminated sediments had been on site for many years since the disposal of oily waste was interrupted 10 years before the remediation action, it was expected that lighter fractions of hydrocarbons had already volatilized or being biodegraded by the time the treatment started. Only weathered oil was likely to be found on site for treatment, as confirmed by the C-numbers found from raw sludge. Carbon Number Distribution revealed, that 100 mg/kg was exceeded in fractions C\(_{14}\)–C\(_{35}\). Concentrations exceeding 1 000 mg kg\(^{-1}\) was recorded in fractions
C_{17-18}, C_{21-22}, and C_{25}, being remarkably high also in C_{16}, C_{19}, C_{24}, and C_{26-29} (Vill et al., 2003). Namkoong et al. (2002) recorded only 2% of volatilization loss of TPH, compared to the initial concentration, whereas normal alkanes lost by volatilization were mainly compounds of C_{10} to C_{16}. Other authors also agree that bio-degradation was the dominant component of the remediation process in treatment of sediments (Del'Arco et al., 2001). The C:N:P ratio was adjusted by selecting amendments. Phosphorous was found in excess (8-26 times) in all mixtures, which, otherwise fitted in recommended 300:10:1 ratio (Peramaki and Blomker, 1997). A typical initial increase in temperature - a key indicator of microbial activities (Jorgensen et al. 2000, Semple et al., 2001, Liang et al., 2003) - occurred particularly in Mixtures II and III. This rise can be attributed to the adding of easily degradable additives such as straw and horse manure, which probably had a ‘kick-start’ effect on the degradation. Based on the lab-scale treatment, it was advisable to mix contaminated sediment with a water-retaining material (e.g. peat, shredded straw), but also coarse material to achieve porosity. Nitrogen was a limiting nutrient, thus it had to be added together with adjustment of moisture. Difficulties in homogenisation of the composting mass indicate that mixing of mass should be frequent during the first 2–3 months. Oily sediments tended to form balls, which were mechanically disintegrated only after the second or third remixing.

**Bottom sediment in field scale treatment:** Before constructing embankments, about 1 m of sediments was removed, mixed with sawdust, and stockpiled on site for bio-treatment. As there is usually no clear boundary between the semi-liquid upper and the more solid lower layers of oily sediments, large amounts of water-absorbing material are needed. Since the soil or peat underneath the layer of sediments is also contaminated and needs treatment, it is not recommended to restrict excavating to the heavily contaminated sediments only. Co-composting of sediments along with the underlying peat was considered a desirable strategy. In this way the need for addition of extra bulking material could be reduced, by a large degree. The excavated mixture of bottom sediments and underlying peat was treated at a nearby composting area, prepared on top of an old landfill section (Figure 1). The site was leveled using fine inert demolition waste and was lined with 0.25m of compacted clay. The selection of the top of the old landfill to install the treatment area was based on environmental safety reasons, since a 0.25m of clay should be considered insufficient in any other surface. All activities were carried out within the catchment’s area, so any leachate
eventually drains back to the pond that is under remediation. If the pond is developed into a constructed wetland, the closed loop is guaranteed. To promote the composting process, sawdust was added to the mixture for adsorbing liquids, and the material was stockpiled. The stockpiles were not regularly mixed as indicated by the lab-scale experiment, but only occasionally. The initial TPH content (DS) of the windrows, in material collected in October 2002, was 9 447–30 342 mg/kg, and the concentration of PAHs was 27–122 mg kg⁻¹. After eight months, oil content in the stockpiles had fallen to 3 897–7 014 mg kg⁻¹ and PAH had fallen to 14–115 mg kg⁻¹. After 22 months, the TPH content was 5 100 mg kg⁻¹ and it was possible to use the material for covering the closed landfill. In the second stockpile the oil decay is not sufficient and in this case, the process goes on until it is considered acceptable for covering the landfill. After the sediment had been excavated for treatment, the pond section 1a was totally, and section 1c partly filled with demolition waste (Figure 1). Pond 1b was transformed into a constructed wetland for leachate treatment (Kriipsalu et al., 2005).

CONCLUSIONS
The selected strategy assumes some risks, as for instance, when using a thin layer of compacted clay to prepare the bottom for treatment of contaminated sediments. At the same time, by keeping all procedures inside the original contaminated drainage basin and by using the top of the landfill for treatment, the risk of spreading contamination was reduced. Monitored natural attenuation was selected as a low-cost follow-up measure. Compared to requirements on water treatment, the treatment of sediments is much less prescribed. In addition to parameters frequently used, such as C:N:P ratio, temperature, TPH, PAHs, moisture, the monitoring program could include the analysis of potential inhibitors for the process. Due to the mass heterogeneity, representative sampling is one of the most difficult targets, particularly in a full-scale composting pile. Sawdust and peat showed to be good water absorbers but are not efficient structure-improving materials for composting. For that purpose, bark or wood chips could be recommended.

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PLANTS WITH POTENTIAL FOR PHYTOREMEDICATION OF OIL-
CONTAMINATED SOIL BASED ON GERMINATION AND BIOMASS 
GROWTH

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ABSTRACT

This study investigated the germination rate and root and aerial biomass production by six species (Ricinus communis, Helianthus annus, Glicine max, Acacia holosericea, Brachiaria brizantha, Tibouchina granulose) growing in a in vitro cell culture chamber in sand soil contaminated by crude-oil at 0.05%; 0.5%; 2%; 4%; 6% (w/w). It was observed that depending on the specie and the oil concentration, germination can be postponed, anticipated, reduced or even increased; root and/or aerial biomass growth can also be reduced or increased. A. holosericea was the only specie that showed no significant effect of the presence of the oil for the variable or oil concentrations studied. All other species were to some extent affected in at least one of the variables and concentrations. The results support the hypothesis that there is more than one type of interaction oil-soil-plant and therefore, the selection of the specie to be used must be based on its behavior under the conditions found in the specific site to be cleaned-up. Low costs and short time required (less than one month), makes germination rate and initial biomass growth useful variables for screening and selection of adequate specie for remediation of contaminated site on a case-by-case basis.

INTRODUCTION

One of the first requirements for implementing a phytoremediation scheme in a contaminated area is that plant germination and biomass growth shall not be significantly affected by the presence of the contaminant. According to Kulakow et al. (2000), species with better development in contaminated soils can be considered potentially useful for remediation projects. However, tolerance - although essential for
establishment of the plant in the contaminated site - is not always followed by phytoremediation capacity. Phytotoxicity can be defined as any change in the normal development of cultivated or native species, due to toxic effects caused by the presence of chemical compounds. The adverse effects of crude oil and in particular some target groups of petroleum hydrocarbons on plant development result from a number of physical and/or chemical interactions with the plant system, from reduction of phyto-transpiration and carbon fixation processes to plant death (Pedrozo et al., 2002). Regarding chemical effects, heavy oils usually have less toxic effects than light oils, which apparently have easier penetration into the plant, preventing leaves growth and sprouts regeneration (Pezeshki et al., 2000). According to Henner et al. (1999) the phytotoxicity of sites contaminated with petroleum (crude oil) or by-products is mostly caused by volatile compounds. It has also been demonstrated that petroleum hydrocarbons toxicity to microorganisms, animals and aquatic plants is enhanced by the action of radiation (Ankley et al., 1994; Ren et al., 1994). Some experiments report the reduction of germination rate in the presence of PAHs in recently-contaminated soils or in solution (Smith et al., 2005; Chaîneau et al., 1997; Henner et al., 1999; Smreczak and Maliszewska-Kordybach, 2003). Chaîneau et al. (1997) found a connection between low germination rate and plant growth in soils recently contaminated by petroleum hydrocarbons. The decrease in germination rate might be explained by the absorption of oil into the seeds, which in turn would change metabolic reactions, causing embryo death (Baker, 1970). The absence of germination inhibition during tests with PAHs of high molecular weight suggests these compounds pose no phytotoxicity, at least during germination, possibly, because these compounds have low water solubility and can be strongly adsorbed to the organic matter. Li et al. (1997) and Smith et al. (2006) observed no effect on germination, but a growth reduction in oleaginous and grass species, which suggests that germination rate alone, is not sufficient to evaluate the phytoremediation potential. Reduction of biomass growth in the presence of contaminants has been observed by Chaîneau et al. (1997); Gallegos Martinez et al. (2000); Reis (1996) and Merkl et al. (2004) among others.

The objective of this investigation was to assess the toxicity effects of different concentrations of crude oil-contaminated sand germination rate and biomass growth during plantlet establishment. For that, six plant species were studied, including native and exotic bushes and crops in tropical climate in a controlled environment.
METHODOLOGY

Six species including three oleaginous species biodiesel producers: Helianthus annus (sunflower) variety Embrapa 2000, Glicine max (soy beans) variety M-Soy 5826 and Ricinus communis (castor beans) variety Guarani. The other three species were: Brachiaria brizantha (brachiaria) variety Marangatu, Acacia holosericea (candelabra wattle) and Tibouchina granulose (“quaresmeira” Brazilian native specie from Atlantic Rainforest). Crude oil from Alagoas basin, Alagoas state, Brazil (Table 1) was added to a fine sand soil (0.20-0.05 mm), previously sterilized at 120°C (1 atm) during one hour. Sterilized sand was mixed at the concentrations of 0% (control), 0.05%; 0.5%; 2%; 4% and 6% (dry weight). Transparent HDPE boxes (19 x 11 x 5.5 cm) previously disinfected where filled with 400g of sand each. Four repetitions with 50 seeds resulted in 24 experimental units and a total of 200 seeds for each specie. Seeds of R. communis, B. brizantha and A. holosericea were scarified with the purpose of promoting germination. The boxes were kept in shelves in a culture room (24- 25°C, humidity of 98% and photoperiod of 8-12h). During five weeks dead seeds, seeds with fungi and shoots were counted. Shoots were washed, roots were separated from the aerial part dried up at 60°C for 24hs and weighted. Four biomass measurements were taken: root (early and late germination) and aerial (early and late germination). Since most data didn’t follow normal distribution, the Kruskal-Wallis (a nonparametric alternative to the one-way analysis of variance) was performed to test the equality of medians. For those variables where H0 was rejected (at $\alpha = 0.05$), Mann-Whitney was performed for each treatment (oil concentration) compared to the control.

Table 1. Characteristics of the crude oils used.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Relative density (g ml$^{-1}$)</th>
<th>°API</th>
<th>Class</th>
<th>TPHs mg g$^{-1}$</th>
<th>BTEXT mg g$^{-1}$</th>
<th>PAHs mg g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>0.824</td>
<td>40.2°</td>
<td>light</td>
<td>727.366</td>
<td>31.467</td>
<td>2.688</td>
</tr>
</tbody>
</table>

°API = [(141.5/especific gravity) – 131.5]; BTEXT = benzene, toluene, ethylbenzene, xylene, trimethylbenzene
RESULTS

Germination rates for six species in different concentrations of oil are presented in Figure 1.

Figure 1. Boxplots of total germination rate (Gtot) as %, in oil-contaminated sand at 0%, 0.05%, 0.5%, 2%, 4% and 6% of crude oil. (a) *A. holosericea Ah*; (b) *B. brizantha Bb*; (c) *H. annus Ha*; (d) *R. communis Rc*; (e) *G. max Gm*; (f) *T. granulose Tg*. 

\[ \text{Boxplots of GtotAh by Conc_SC} \]
\[ \text{Boxplots of GtotBb by ConcSC} \]
\[ \text{Boxplots of GtotGm by ConcSC} \]
\[ \text{Boxplots of GtotRc by Conc_SC} \]
\[ \text{Boxplots of GtotHa by Conc_SC} \]
\[ \text{Boxplots of GtotTb by Conc_SC} \]
Sunflower (at 6% of oil) and quaresmeira (at 4% and 6% of oil) showed a significant decrease of the total germination rate. When the total germination rate was split into two stages - early germination (seeds that germinated during the first days of the germination period) and late germination (seeds that germinated during the last days) - braquiaria showed a significant decrease of early germination at 6% compensated by an increase in the late germination; castor beans did not have late germination from 0.5% to 6%. In both cases, the total germination was not significantly affected. Figure 2 shows the germination index obtained through equation 1:

\[
\text{Germination Index} = \frac{\text{Average germination rate at } X}{\text{Average germination rate at the control (X=0)}}
\]

where X is the oil concentration in %.

*Acacia holosericea, Glicine max* and *Braquiaria brizantha* indexes remained closer to 1 as the oil concentration increased. *Helianthus annus, Tibouchina granulose* and *Ricinus communis* indexes showed an accentuated decrease, particularly at 6%, although for *R. communis* this reduction was not statistically significant. Regarding root biomass, two opposite responses were observed: (i) an increase in early germinated sunflowers (0.5-4% of oil) and soybeans (0.05-0.5% of oil) and (ii) a decrease for late germinated soybeans (0.05-0.5%, 6%). Regarding aerial biomass, it was observed a decrease for early germinated brachiaria (0.5-6% of oil) and late germinated sunflower (0.05% of oil).

**Figure 2.** Germination indexes for each specie and oil concentration. Ah = candelabra wattle; Ha = sunflower; Tb = quaresmeira; Bb = braquiaria; Rc = castor bean; Gm = soybean.

**CONCLUSIONS**

Depending on: (i) concentration, (ii) oil characteristics; (iii) age of the contamination; (iv) plant specie and (v) the experimental/environmental conditions,
plants can respond differently to the presence of the oil in the soil, including: no effect, total inhibition of germination, anticipation, postponing or increasing in germination rate and/or in biomass. Based on the present study, and taking into consideration the criteria: (1°) absence of any effect of the oil in the tested concentrations; (2°) no significant decrease of total germination; 3°) no significant decrease of root and/or aerial biomass. The species were ranked as following: 1st) candelabra wattle; 2nd) castor beans; 3rd) braquiaria and soybean; 4th) sunflower and quaresmeira.

Having in mind that tolerance to grow in a contaminated soil does not obligatorily mean phytoremediation capacity, additional investigation is needed with focus on rizodegradation, phytoextraction, phytodegradation and phytovolatilization processes.

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EMISSION OF PLATINUM GROUP ELEMENTS FROM AUTOMOBILE CATALYST ATTRITION IN THE URBAN ENVIRONMENT

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ABSTRACT

The increasing use of automobile catalysts leads to the emission of the platinum-group elements (PGEs), mainly platinum, rhodium and palladium into the environment. To account for PGEs accumulation, road dust and soil samples were analysed and characterized in detail through an annual survey in Ioannina city (NW Greece). Validation of the analytical results was performed by recovery experiments with a certified reference material (BCR-723). The determination of PGEs was achieved with electrothermal atomic absorption spectrometry (ET-AAS). Sample preparation involved complete microwave-assisted acid digestion of the matrix with \( \text{HNO}_3 \)-HF mixtures in high-pressure Teflon bombs. Concentrations of Pt, Pd, Rh in soils and road dusts taken from areas of variable traffic flows and driving conditions show that high concentrations of PGEs are associated with high traffic densities. Samples taken from streets of lower traffic flows were found to contain the lower concentrations. The concentrations ranges of Pt, Pd and Rh in road dust samples were from 29.0–356.4 ng/g, 4.4-12.8 ng/g and 14-39.7 ng/g, respectively. In soil, the concentrations were ranging from 35-113.2 ng/g, 4.9-14.0 ng/g and 10.0-25.4 ng/g, for Pt, Pd and Rh, respectively. These values correlated well with the levels of lead which were also high ranging from 20.5-48.4 \( \mu \text{g/g} \) and 16.1-42.3 \( \mu \text{g/g} \) for road dust and soil samples.

INTRODUCTION

Platinum group elements (PGEs) play a decisive role in the performance of exhaust systems, world-wide applied in vehicles and in some household utensils, to reduce the emission of gaseous pollutants such as carbon monoxide, nitrogen oxides and hydrocarbons [1]. However, the hot exhaust gases flowing through the converter cause abrasion / ablation of these units, leading to the emission of the PGEs to the environment. Thus, these novel anthropogenic metals have an increasing impact on
nature due to the increasing number of cars equipped with catalytic converters [2]. Moreover, several PGEs and their complex salts (e.g. Pd- and Pt-chlorides) have been reported as potential health risks to humans, causing asthma, allergy and other serious health problems [3]. Several methods have been proposed for the digestion of the samples including microwave digestion [4, 5] and nitric acid and HF [6] involving graphite furnace atomic absorption spectrometry (GFAAS) [5].

In this study, the subsequent determination of Platinum Group Elements (PGEs) in road dust and urban soil is presented. The method is based on a three step process: microwave-assisted digestion from the solid matrix, preconcentration and finally detection by electrothermal atomic absorption spectrometry (ETAAS).

EXPERIMENTAL

Solutions

For the decomposition of the samples, nitric and hydrofluoric acids (analytical grade) were used. Stock solution of 1000 mg l-1 of the Pt, Pd and Rh, were prepared by diluting the appropriate amount in water and stored in the refrigerator at 4 ºC, protected from the light. Working solution of HNO₃ was prepared by diluting 63.5 ml 16 M HNO₃ in 1000 ml of double distilled water.

Instrumentation

A Shimadzu AA-6800 flame atomic absorption spectrophotometer with hollow cathode lamps operating at 10 mA, 14 mA and 12 mA for Pd, Pt and Rh respectively were used throughout measurements which were made at 244.8 nm, 266.0 and 343.5 nm, respectively. The non flame procedures were performed in a Shimadzu GFA-6500. A pH meter, WTW 552 Model glass-electrode was employed to measure pH values. The output signals were collected and processed in the continuous peak height mode.

Sampling

The samples (road dust, urban soil and grass) were collected from the cities of Ioannina and Preveza in the region of Epirus in northwestern Greece (Fig. 1). The sampling strategy was designed to ensure representative coverage of major urban highways, major intersections and residential roads. The samples were collected from one square metre by using a plastic hand brush and dust pan. The weight of sample
collected from each square metre varied from site to site. However, the requirement of a representative minimum sub sample of 10 g for analysis was obtained for all sites.

![Sampling Area](image)

**Figure 1.** Sampling Area: 1) Preveza Tolls, 2) University avenue, 3) Front Lake Road, 4) Traffic lights-Entrance to National road (Ioannina-Hgoumenitsa), 5) National road (Ioannina- Preveza), 6) City Center (Traffic lights).

**Sample Pre-treatment**

The road dust and soil samples were air dried and then sieved to produce a 2 mm fraction, and screened to produce < 63 mm material. A representative minimum subsample of 10 g was submitted in a sealed secure container for analysis. After air drying in a clean room the samples were put in an oven for 4 h at 85 °C. Approximately 0.2 g of the sample was placed in PTFE pressure vessels with 2 ml nitric acid and 3 ml hydrofluoric acid and introduced in an oven—assisted sample digestion system.

**Experimental Procedure**

Approximately 0.2 g of the sample was placed in PTFE pressure vessels with 2 ml nitric acid and 3 ml hydrofluoric acid. The vessels were closed and 6 samples were heated at the same time in the microwave oven using the optimized microwave programme (Table 1). After the digestion programme, the vessels were cooled to room temperature and approximately 0.5 g of H$_3$BO$_3$ was added. The samples were
then filtrated and evaporated until dryness. Then the samples were dissolved with 1 ml HNO$_3$ 1 M and measured with graphite furnace atomic absorption spectrometry.

**Table 1:** Optimized digestion programme for the determination of PGEs in road dust and soil samples.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Power (Watt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>270</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>450</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>630</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>450</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

The contents of platinum, palladium and rhodium in various environmental materials, such as road dust, soil and plant samples evaluated by atomic absorption spectrometry are presented in figures 2, 3 and 4 for road dust samples respectively and figures 5, 6 and 7 for soil samples. It is obvious that, the highest pollution is determined in the national road Ioannina - Preveza. The results are influenced by the weather conditions including rain level and wind speed. The PGEs levels are higher during summer and are continuously decreasing during the winter.

![Figure 2: Platinum content in road dust starting from 05-2005 until 04-2006](attachment:image.png)
Figure 3: Palladium content in road dust starting from 05-2005 until 04-2006

Figure 4: Rhodium content in road dust starting from 05-2005 until 04-2006

Figure 5: Platinum content in soil samples starting from 05-2005 until 04-2006
CONCLUSIONS

The determination of Pt, Pd and Rh in various environmental compartments has gained increasing attention due to the increasing number of catalytic automobiles. Thus, the demand for accurate, simple and reliable procedures for the determination of PGEs in road dust, soil and plants will continuously rise in the future.
ACKNOWLEDGEMENTS

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In case of industrial pollution of Mercury by plant Radical in Kiev only working cooperation of Governmental, Municipal, Industrial, Mass-media and NGO in decision of most dangerous environmental problem in Kiev can give good results

Picture 1: Most dangerous enterprises on Kiev territory.

During its work starting in 1954, the public company RADIKAL, as a result of imperfect technological processes of production of chlorine, caustic soda (via the mercury method), pesticides, copper oxychloride and other chemical substances resulted in significant pollution of soil and ground water on the territory of the facility. The fact of pollution was confirmed by the findings of the chemical analyses
conducted in 1990 by the State Geological Party “NorthUkrGeology” on the instruction of the State EcoSafety Administration of the town of Kyiv. The fact of soil contamination with mercury became known in December 2000. But according to the head of the project department of the joint enterprise “Evrokhim”—the department that was working on the problem of demercurization of this facility—the total loss of mercury (between 1954 and 1996) comprises 200 tons. RADIKAL is not active since 07.15.1996.

October 24, 2001 Ukrainian officials dismissed Russian media reports about a disastrous mercury spill at a chemical plant in the capital Kiev but said the plant was dangerous because of outdated equipment, news reports said Tuesday.

Ecology and Natural Resources Minister Serhiy Kurykin said there were "no grounds for panic or extraordinary actions" over reports on tons of mercury spilled at the Radikal plant, according to the Kievskie Vedomosti daily.
Ukraine's Emergency Situations Ministry denied the alarming reports once they appeared on Russian television last week, saying that plant workers were engaged in ordinary operations to collect mercury in tanks.

However, Oleksiy Pasiuk, an expert at Ukraine's Ecological Center, said there was recently a mercury spill within the now-closed plant. Pasiuk could not specify the amount of mercury spilled but said there was no danger of it contaminating underground water sources, only of vapors.

"There is no sense to say that the mercury spill was catastrophic, but it can become so if the situation at that plant is not improved," Pasiuk said, adding that the plant had even more dangerous materials stored improperly. "The authorities must take radical measures at the plant."

Kurykin said the plant was in poor condition and could cause an ecological disaster due to mercury spilled during 47 years of Radikal's work and outdated tanks containing dangerous acids, Kievskie Vedomosti reported. Kurykin said no safety measures were taken in the process of the plant's closure several years ago, and a large amount of mercury had gotten into the soils around the plant.

Industrial pollution of soil on territories of facilities from toxic waste is rather typical for Ukraine. Thus, it was not accidental when in November 2000 a law was passed about “The Utilization of Toxic Waste.” This case can be compared to others in size and type of pollution as well as in inadequate reaction of the industrial enterprise.

Mercury got in soil on the territory of the plant RADIKAL that later went bankrupt. The depth of mercury contamination varied between 3 and 10 meters. The main source of contamination was the department producing caustic soda and chlorine, where electrolyzers with mercury cathodes were located. Even now they contain 109.7 tons of mercury and 44 tons of collected mercury-containing sludge. In addition, 24.9 tons of mercury is stored in metal containers in the storage facility #80. The analyses found that the main contaminants of soil on the territory of the facility were hazardous chemical elements of the I category that aggregate to: 10-200 mg/kg of mercury (whereas ambient air standard is 2 mg/kg), 30-200 mg/kg of lead (whereas ambient air standard is 30 mg/kg), 5-30 mg/kg of cadmium (whereas ambient air standard is 4 mg/kg), etc.

Soil contamination directly affected the quality of ground water under the plant. Pollution was discovered in 10 observation and public safety wells in the area of 12
ha. Ambient air standard for mercury was exceeded 20 times on average in ground water. The most dangerous problem for the public company RADIKAL as well as for the city of Kyiv, remains the problem of soil contamination, pollution of ground water, and plant departments with mercury and salts of heavy metals.

As a result of bankruptcy, the plant limited its control and maintenance of the mercury remains in the first department to a minimum. The law of “The Utilization of Toxic Waste” listed public company RADIKAL as one the most hazardous facilities. RADIKAL is one of the main polluters of the environment in Kyiv, and thus the environmental status of the plant is under the constant control of the Ministry of EcoSafety of Ukraine State EcoSafety Administration in Kyiv conducted an examination of the plant to determine threats of environmental pollution. The examination found that the environmental state of the plant is not improving, despite the fact that the plant departments are not functioning. At the request of the State EcoSafety Administration of Kyiv, public company RADIKAL developed a 14,8 mln UAH program to demercurize the production area. Financing of the program has not been resolved till today. The first task of the program includes removing mercury from electrolyzers and delivering 44 tons of sludge to the plant “Merkurii” in the town of Horlivka. The cost of the project is 550,000 UAH.

In 2005 year the representations of environmental NGOs suggest to Major of Kiev city to organize on Kiev can opening a small river Darnitsa and to create a recreation park „Green quiet”. The main response person-superior of ecology and transport questions of Dniprovskiy municipal region of Kiev Viktor Linnik confirms that this decision will be supported by local administration as most convenient and environmentally friendship.
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4. In Kiev can be open the river Darnitsa and park “Green quite”
COMPARISON OF ACCELERATED SOLVENT EXTRACTION (ASE) AND SOXHLET EXTRACTION FOR LOW LEVEL ANALYSIS PCBs and PAHs in CONTAMINATED SOIL SAMPLES

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ABSTRACT

The performance of accelerated solvent extraction in the analysis of persistent organic pollutants (POPs) in soil samples was investigated and compared with those of soxhlet extraction with respect to yield, extraction time, reproducibility and solvent consumption. Artificial contaminated soil samples (PAHs and PCBs separately) were extracted by ASE and soxhlet. The results show that ASE gives essentially equivalent data to soxhlet extraction. However, extractions made with ASE are performed in less time and with less solvent than by the classical soxhlet extraction technique.

1. INTRODUCTION

Soxhlet extraction is the most commonly used robust liquid-solid extraction technique in the world. This technique brings a pure organic solvent into contact with the solid material to be extracted by distillation and refluxing. The main drawback of this technique, however, is the refluxing with cold solvent which is time consuming i.e., extraction times lasting many hours (up to 24). Furthermore, the solvent consumption is considerable, demanding the evaporation of a large amount of solvent before further clean up [1]. Organic solvents required to extract solid samples can comprise the largest source of waste in the environmental analysis laboratory. Typical solvent volumes can range from 150 mL to over 300 mL per sample analysis procedure [2]. For routine analysis capacity (10 sample per week), 72 to 144 liter contaminated toxic liquid waste is produced from laboratory.

The aim of any extraction technique in analytical chemistry is to effectively remove the analyte from its matrix, rapidly, with minimal solvent usage and quantitatively. Too much interference such as oil, colour, suspended matter are also unwanted circumstances for extraction because of the problems encounter in sample clean up steps. The choice of extraction technique is frequently decided upon based
on initial capital cost, operating costs, simplicity of operation, amount of organic solvent required and sample throughput [3].

Accelerated solvent extraction (ASE) is an extraction technique that uses limited amount of organic solvent in the recovery semi volatile organics mainly from solid matrices. ASE operates at high pressures and temperatures above the boiling point of the organic solvent. The use of higher temperature increases the ability of solvent to solubilize the analyte, decreases the viscosity of liquid solvents, thus allowing better penetration of the solvent into the matrix and promotes “wetting” of the matrix particles so as to achieve contaminant recovery. The use of higher pressure facilitates the extraction of analyte from samples by improving the solvent accessibility to the analytes that are trapped in the matrix pores. Detailed comparison of the Soxhlet and ASE techniques is made and given in Table 1 in addition to the literature [4].

Table 1. Comparison of Soxhlet and ASE extraction technique

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ASE</th>
<th>Soxhlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction time</td>
<td>15-45 min</td>
<td>20-24 h</td>
</tr>
<tr>
<td>Solvent consumption</td>
<td>20-60 ml</td>
<td>150- 300 ml</td>
</tr>
<tr>
<td>Capital investment</td>
<td>High (about 50,000 USD)</td>
<td>Low (about 50 USD)</td>
</tr>
<tr>
<td>Additional requirements</td>
<td>Nitrogen (Technical grade), electricity</td>
<td>Isolated vacuum chamber, water recirculation, electricity</td>
</tr>
<tr>
<td>Automatic/manual Detection limit</td>
<td>Automatic ppm-ppb</td>
<td>Manual ppm-ppb</td>
</tr>
<tr>
<td>Conditions employed</td>
<td>Harsh</td>
<td>Harsh</td>
</tr>
<tr>
<td>Concentrating the extract</td>
<td>Small solvent volume requires minimal concentration of analyte</td>
<td>Large solvent volume requires considerable concentration of the analyte</td>
</tr>
<tr>
<td>Labor intensive</td>
<td>Concern</td>
<td>Major concern</td>
</tr>
<tr>
<td>Analyte loss</td>
<td>Since concentration step is shorter or not required, less analyte loss</td>
<td>Since concentration step is required and longer, the analyte loss is higher</td>
</tr>
<tr>
<td>Approximate cost</td>
<td>2-4 Euro/sample*</td>
<td>10-20 Euro/sample*</td>
</tr>
</tbody>
</table>

* Excluding human source for handling
Persistent organic pollutants (POPs) are amongst the most dangerous substances released by humans into the environment. They possess toxic characteristics and are likely to cause significant adverse effects on health of exposed wildlife and humans, such as allergy, damaged nervous system and immunity, congenital diseases, cancer [5]. While the PCBs were major industrial products whose use continues, although production is banned, the PCDDs/PCDFs and PAHs were never intentionally produced and are unwanted by products of industrial process [1-4].

In this paper, our first results relevant to extractions of POPs from contaminated soil samples by both ASE and soxhlet are presented. As opposite to literature, lower PAH and PCB concentrations have been studied for these experiments. ASE and Soxhlet extractions gave results similar in respect of recovery. On the other hand, ASE is faster than the conventional Soxhlet extraction and reduces the solvent consumption.

2. EXPERIMENTAL SECTION

All PCBs and PAHs used as internal, recovery and calibration standards were supplied by from Wellington Laboratories. The solvents used in the extractions were HPLC grade and obtained from Merck.

For PAH and PCB extractions, soil samples were collected and combusted at 550°C for 24 h. After conditioning in dessicator at the room temperature, 7 grams of samples weighted certified standards spiked to the samples.

PAH and PCB samples are extracted with DCM and Hexane respectively ASE for 20 minutes and Soxhlet apparatus for 24 hours. ASE programme was applied as given in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>DCM (for PAH) and Hexane (for PCB)</td>
</tr>
<tr>
<td>Temperature</td>
<td>175–200 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>1500 psi</td>
</tr>
<tr>
<td>Static Time</td>
<td>5–15 min</td>
</tr>
<tr>
<td>Flush Volume</td>
<td>60–70%</td>
</tr>
<tr>
<td>Purge Time</td>
<td>60–100 s</td>
</tr>
<tr>
<td>Number of Static Cycles</td>
<td>2 or 3</td>
</tr>
</tbody>
</table>
Soxhlet apparatus was arranged 4-6 cycle per hour and all the glassware used in the system was cleaned with automated washing machine. After extractions, samples were cleaned according to EPA 3630 silica gel clean up method.

Shimadzu HPLC equipped with UV detector was used as an analytical device for PAH analysis. 254 nm wavelength was selected for detector gain and Phenomenex PAH column was used for PAH analysis. All the other analytical conditions were arranged suitable to EPA 8310 PAH method. 30 µl PAH Mix (each analyte concentration was 10 ng/µl) was added to the soil matrix and the final sample volume has been reduced near to dryness and then solvent was changed to acetonitrile (ACN). The final volume of the ACN was 1 ml.

Thermo Finnigan GC equipped with Phenomenex PCB capillary column was used for PCB analysis. EPA 8082 protocol was applied for PCB analysis also. PCB 206 was used as an internal standard for recovery control and spiked to the samples prior to the extraction. 1 µl PCB Mix (each analyte concentration was 10 ng/µl) was added to the soil matrix and the final sample volume has been reduced to 100 µl.

3. RESULTS AND DISCUSSION

Calculated PCBs and PAHs results are given in Table 3 and Table 4 respectively. According to the results, recovery values of soxhlet system are a little bit higher than ASE results. Because of ppb levels of PCB and PAH congeners in the soil samples, lower recovery values were obtained both of extraction systems compared to the literature. As we did experiments with very low concentration levels of PAHs and PCBs, values of PAH and PCB congeners obtained isn’t very close to real values.

Table 3. PCB concentrations calculated

<table>
<thead>
<tr>
<th>PCBs</th>
<th>ASE, ppb</th>
<th>Soxhlet, ppb</th>
<th>Certified value ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 18 (225 Trichlorobiphenyl)</td>
<td>70,08</td>
<td>83,82</td>
<td>100</td>
</tr>
<tr>
<td>PCB 31 (245 Trichlorobiphenyl)</td>
<td>60,20</td>
<td>71,29</td>
<td>100</td>
</tr>
<tr>
<td>PCB 29 (244 Trichlorobiphenyl)</td>
<td>84,99</td>
<td>85,87</td>
<td>100</td>
</tr>
<tr>
<td>PCB 44 (2235 Tetrachlorobiphenyl)</td>
<td>88,46</td>
<td>112,85</td>
<td>100</td>
</tr>
<tr>
<td>PCB 101 (22455 Pentachlorobiphenyl)</td>
<td>68,41</td>
<td>105,26</td>
<td>100</td>
</tr>
<tr>
<td>PCB 149 (223456 Hexachlorobiphenyl)</td>
<td>90,76</td>
<td>87,90</td>
<td>100</td>
</tr>
<tr>
<td>PCB 118 (23445 Pentachlorobiphenyl)</td>
<td>108,90</td>
<td>80,27</td>
<td>100</td>
</tr>
<tr>
<td>PCB 180 (2234455 Heptachlorobiphenyl)</td>
<td>108,21</td>
<td>123,16</td>
<td>100</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

The results obtained by ASE were compared with those obtained with Soxhlet extraction. Both ASE and Soxhlet systems offer high efficiencies when operating at their optimal conditions and in addition, compared to Soxhlet extraction, ASE extraction procedures are significantly less time and less solvent consuming. But Soxhlet extraction serves much more reliable and repeatable experimental results. In literature, mix of solvents (i.e. acetone and hexane or acetone and dichloromethane) has been used to increase the recoveries of PCBs, PAHs and also PCDD/PCDF [6,7,8].

<table>
<thead>
<tr>
<th>PAHs</th>
<th>ASE, ppb</th>
<th>Soxhlet, ppb</th>
<th>Certified value, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtalene</td>
<td>226</td>
<td>217</td>
<td>300</td>
</tr>
<tr>
<td>Acenaphtalene</td>
<td>267</td>
<td>316</td>
<td>300</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>239</td>
<td>260</td>
<td>300</td>
</tr>
<tr>
<td>Fluorene</td>
<td>360</td>
<td>323</td>
<td>300</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>266</td>
<td>324</td>
<td>300</td>
</tr>
<tr>
<td>Anthracene</td>
<td>276</td>
<td>257</td>
<td>300</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>370</td>
<td>309</td>
<td>300</td>
</tr>
<tr>
<td>Pyrene</td>
<td>347</td>
<td>237</td>
<td>300</td>
</tr>
<tr>
<td>Benz(a)anthracene</td>
<td>276</td>
<td>338</td>
<td>300</td>
</tr>
<tr>
<td>Chrycene</td>
<td>210</td>
<td>327</td>
<td>300</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>279</td>
<td>358</td>
<td>300</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>373</td>
<td>309</td>
<td>300</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>440</td>
<td>323</td>
<td>300</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>395</td>
<td>355</td>
<td>300</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>209</td>
<td>350</td>
<td>300</td>
</tr>
<tr>
<td>Indeno(1,2,3-c,d)pyrene</td>
<td>344</td>
<td>319</td>
<td>300</td>
</tr>
<tr>
<td>Total</td>
<td>4877</td>
<td>4922</td>
<td>4800</td>
</tr>
</tbody>
</table>
REFERENCES

CHEMICALS AND WASTE MANAGEMENT IN THE REPUBLIC OF ARMENIA

Anahit Aleksandryan
Ministry of Nature Protection, Republic of Armenia

The Republic of Armenia recognizes the necessity of more efficient assessment/evaluation and regulation on chemicals for achievement of goals set forth in Article 23 of Johannesburg Plan of Implementation aimed at chemicals sound use throughout the entire life-cycle, sound disposal of hazardous wastes, minimizing the harm resulting from chemical production and use towards human health and the environment by application of scientifically justified transparent procedures, risk evaluation and reduction, and considering the precautionary requirements of Principle 15 of Rio de Janeiro Declaration on Environment and Development.

Nowadays, Armenia is on the way to develop more efficient structures and measures, the majority of which are already undertaken, e.g. such as ratification of international conventions, adoption of normative and legal documents aimed at implementation of conventions at the national level.

In order to protect human health and the environment against the harmful impact of chemicals and wastes, as well as for sound management of toxic substances and prevention of the illegal traffic of toxic and hazardous substances and waste the Republic of Armenia has ratified a number of International Conventions regulating the issues of sound chemicals and wastes management, including the following:
### Convention Status

<table>
<thead>
<tr>
<th>Convention Description</th>
<th>Signature</th>
<th>Ratification by the National Assembly</th>
<th>Registration at UN Secretariat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kyoto Protocol (Kyoto, 1997)</td>
<td></td>
<td>26 December 2002</td>
<td>25 April 2003</td>
</tr>
<tr>
<td>- Protocol on Pollutant Release and Transfer Registers (Kiev, 2003)</td>
<td></td>
<td>21 May 2003</td>
<td></td>
</tr>
</tbody>
</table>

To ensure implementation of country obligations under international agreements and in order to prevent the illicit traffic of chemicals and waste, the Republic of Armenia Government approved more than 20 regulating legal documents, including “The Republic of Armenia Law on Waste”, “National Profile to Assess the national Infrastructure for management of Chemicals and Waste in the Republic of Armenia”, “Republic of Armenia List of Hazardous Waste”, “Republic of Armenia: List of Prohibited Hazardous Waste”, etc.

Harmonized chemicals and waste management requires further improvement of legislative and institutional basis. Proceeding from this, as well as in order to facilitate development and implementation of the state policy in the area of waste management.
and to ensure environmentally sound waste handling, the “Waste Research Center”
was established within the structure of the Ministry of Nature Protection of the
Republic of Armenia.

In order to solve a number of priority ecological problems relevant to chemicals
and waste, the Republic of Armenia jointly with the International organizations
implemented and is performing now such Programmes as:

− “Programme on Strengthening the Integrated National Programme of
Chemicals and Waste Environmentally Sound Management in the
Republic of Armenia” (UNITAR, 2004-2006);
− “Establishment and operation of a National Cleaner Production Programme in
Armenia “ (UNIDO, 2006-2007);
− “Strengthening of Integrated Waste Management in Armenia” (UNDP CO,
2006).

Issues on regulation of chemicals are involved in documents dealing with the
national strategy of sustainable development and poverty reduction.

For sound chemicals and waste management an important aspect is the necessity to
develop a system of unified actions involving and linking all the aspects of chemical
life cycle, including production, import, export, storage, transportation, distribution,
use and disposal of chemicals and wastes, i.e. chemicals and wastes life-cycle
management.

Transition to sustainable development requires coordination of actions in all
spheres of the social life, as well as the appropriate re-orientation of various state
institutions: social, economic, educational, etc. On setting up the methodology and
technology basis for reforms an important part and great attention should be drawn to
development of mechanisms allowing to use in practice country wealth of research,
technical, cultural and endogenous potential.

In accordance with the principles of sustainable development there should be
supposed implementation of an entire complex of measures and actions aimed at
preservation of human life and health, solving demographic challenges, poverty
eradication, and alteration of consumption structure, as well as decreasing the
differentiation in incomes of general population.

Problems relevant to waste management remain to be of priority for Armenia.
The most urgent issues deal with disposal of existing stocks of hazardous industrial
waste, expired medicine, obsolete pesticides, chemicals, as well as POPs-containing waste (equipment and PCB-contaminated oils), which requires environmentally sound solution. Of no less urgency are issues related to management of household wastes. The potentialities of existing waste dumps are exhausted. Insufficient capacity for waste collection and disposal brought forth the emergence of uncontrolled dumps and, in this regard, the entire complex of ecological problems. The problem of waste management is aggravated by the fact that in Armenia there are neither waste processing/treatment entities, nor specially allotted sites for disposal of industrial, hazardous and household wastes.

We should express our appreciation of support and assistance rendered to Armenia by International organizations for implementation of such Programmes as:


In the course of Programme implementation the following priority trends were identified for integrated capacity building for chemicals and waste management in the Republic of Armenia:

- Harmonization of the National Legislative Basis for Integrated Chemicals and Waste Management and Development of the Harmonized Regulating System on Strengthening Aspects of Control on Import and Export of Chemicals and Waste;

- Strengthening the analytical capacity for sound chemicals and waste monitoring and environmentally sound risks management; strengthening of organizational systems for state control and carrying out inventory on existing stockpiles of hazardous wastes (obsolete pesticides, PCB-containing oils and equipment, expired medicine, etc.)

- Enhancing the skills of decision-makers for risk evaluation and risk management of first-priority chemicals and waste (PCB-containing oils and equipment, obsolete pesticides, contaminated areas, etc.), awareness raising in concern of hazards and risks of chemicals and waste

- Capacity building for Customs Service officials to ensure control on import/export of regulated chemicals and wastes;
Coordination of problems dealing with chemicals and wastes management in emergency situations and ensuring preparedness to accidents and incidents;

Strengthening national capacity for implementation of Stockholm Convention on Persistent Organic Pollutants (POPs) in the Republic of Armenia.

“Establishment and operation of a National Cleaner Production Programme in Armenia “ (UNIDO, 2006-2007)

Of high importance is application of the integrated precautionary environmental strategy in industrial processes, in ready-made produce, in the sphere of services provision in order to increase the efficiency and to decrease the impact to humans and the environment, i.e., - implementation of the Cleaner Production (CP) practices.

Due to CP specifics, CP realization positive results are obtained not only in the area of the environment, but in the sphere of economy as well. Main advantages of CP are as follows:

- Reduction of industrial waste alongside with the observance of environmental standards;
- Environmental risk reduction by means of limited/decreased use of hazardous chemicals, as well as limitation of their content in waste;
- Improvement of the working industrial environment;
- Economy of expenses for waste utilization (expenses for exploitation of the end-of-the-pipe technologies, fees, etc.);
- Economy of expenses for purchases of raw materials, which are definitely and irrevocably “lost” as waste (including energy and labour, contained in raw materials and, therefore in waste). About 10 times more means are saved in this case;
- Quality increase of obtained produce, etc.


With the aim to facilitate development of the policy for efficient approaches and to fulfill complex measures targeted at improvement of environmentally sound
management of wastes in Armenia jointly with the UNDP (Armenia) Office and due
to its financial support there was initiated implementation of “Strengthening waste
integrated management in Armenia” Project (UNDP CO, 2006).

Project implementation will facilitate improvement of the Data Base on issues
relevant to waste management, development of the entire complex of actions on
environmentally sound waste management, strategic planning, and formation of the
legislative basis.

Improvement and strengthening of regulating, information and methodic basis
would facilitate maintenance of relevant aspects of wastes environmentally sound
management in Armenia. The following should be performed for this purpose:

- Information collection and analysis in concern of wastes placement,
treatment/decontamination and utilization;
- Information collection and analysis in concern of existing/functioning
  waste disposal sites/facilities and mapping thereof;
- Information collection and analysis on wastes generating on the territory of
  the Republic of Armenia;
- Information review and analysis in respect of methodic approaches to
  wastes risk impact assessment;
- Compilation and publication of a Catalogue (Directory) on wastes
  generated at the territory of the Republic of Armenia.

Project main output will embrace improvement of information and methodic
maintenance of issues relevant waste management at the national level. To be precise,
preparation and publication of the “National Catalogue of wastes generating on the
territory of the Republic of Armenia” is supposed.

It should be mentioned that in Armenia there are no facilities for recycling of
secondary raw materials, while the previously existing system for recycling of some
categories of wastes used as second-hand materials (paper, glass, textile, etc.) is
broken, disrupted due to the lack of connections with the Republics of Former USSR.

Moreover, the Republic of Armenia has no entities or specially allotted sites
(polygons) for disposal of hazardous industrial wastes; as a result the problems of
waste disposal remain to be unsolved, in particular the problems of disposal of such hazardous wastes as expired medicine, obsolete agrochemicals and other chemicals.

In this respect the Government has already taken serious steps toward improvement of integrated waste management system.

Tangible results were achieved in improvement of legislative and regulatory framework. Framework Law on waste has been approved and number of regulations adopted:

- “Lists of regulated and non-regulated wastes, hazardous properties thereof, documents on the procedure of applications, notices and disposal/ removal” approved by the Ministry of Nature Protection Order No. 96 dated August 10, 1999; Agency act);
- Decision of the Government of the Republic of Armenia «On approval of the “Republic of Armenia List of hazardous wastes” (No.874-A dated May 20, 2004);
WASTE DISPOSAL PROBLEMS IN ARMENIA

Artak Khachatryan

Waste Research Center, Republic of Armenia

Environmentally sound management of wastes, reinforcement of organizational systems for state control and inventory taking of available stocks of hazardous wastes (obsolete pesticides, POPs-containing wastes, etc.), as well as assessment of their risks are of top-priority in the area of chemicals and waste management in Armenia.

The on-going growth in chemical manufacturing and other human activities result in releases of toxic pollutants. Many of these activities are essential to modern society, but can also pose a serious threat to human health and the environment.

Of special importance are wastes containing POPs, wastes composed of or contaminated with POPs. Such wastes should be disposed in a manner so that they do not exhibit the characteristics of persistent organic pollutants. Unfortunately, in Armenia, there is no plant for household wastes processing. Therefore, such wastes cumulate at the dumps.

Waste is disposed and collected at dumps, which are considered to be areas with visual (evident) pollution and, thus, present threat for human and environmental health.

Our studies performed in 2002-2003 revealed that at the territory of the Republic of Armenia there functioned 448 dumps of household wastes, excluding unorganized places of waste dumps (Table 1).

Table 1. Dumps of Household Wastes

<table>
<thead>
<tr>
<th>No.</th>
<th>regions of Armenia</th>
<th>Urban settlements</th>
<th>Dumps</th>
<th>Inappropriate Urban settlements</th>
<th>Rural settlements</th>
<th>Dumps</th>
<th>Inappropriate Rural settlements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aragatsotn</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>112</td>
<td>59</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>Ararat</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>90</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Armavir</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>91</td>
<td>34</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>Gegharkunik</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>88</td>
<td>46</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>Lori</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>116</td>
<td>50</td>
<td>43</td>
</tr>
<tr>
<td>6</td>
<td>Kotai</td>
<td>8</td>
<td>4</td>
<td>3</td>
<td>60</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>Shirak</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>104</td>
<td>55</td>
<td>54</td>
</tr>
<tr>
<td>8</td>
<td>Sinnik</td>
<td>7</td>
<td>7</td>
<td>6</td>
<td>131</td>
<td>117</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>Vajots Dzor</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>43</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>10</td>
<td>Tavush</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>57</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>11</td>
<td>Yerevan</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL:</td>
<td></td>
<td>53</td>
<td>46</td>
<td>43</td>
<td>892</td>
<td>448</td>
<td>347</td>
</tr>
</tbody>
</table>

According to data of the Ministry of Health in Armenia now there are 45 urban and 429 village waste dumps, which, in the majority, do not correspond to the sanitary
requirements: that is all urban and 368 village dumps. In 892 rural settlements, there were 448 dumps, of which 377 did not correspond to the requirements of sanitary hygienic safety. Territories of urban and village dumps are also polluted.

As a rule, waste dumps are located at a distance varying from some few to 15-20 km. Natural cavities serve as dumps. The dumps are not surrounded by fences; no preventive sanitary hygienic zones are indicated.

Despite the fact that special areas were allotted for dumps in rural inhabited locality, the wastes cumulated in different places. Very frequently, it occurred along the banks of the rivers and rivulets. The definite part of wastes from the dumps was then spread in the vicinity and on the roads to the dumps.

Thirteen dumps of rural settlements and towns were chosen for sampling. When choosing, the peculiarities of inhabited area were taken into consideration, as this latter conditioned the type of household wastes and the degree of pollution. Soil samples were taken from the territory of dumps and analyzed for certain Persistent Organic Pollutants (POPs): DDT, DDE, DDD, HCH, and Polychlorinated Biphenyls (PCBs). The analyses were performed by means of gas-chromatography method.

The revealed amounts of OCPs and PCBs might be both the source and the cause of pollution evident at the adjoining area and in (under)ground waters. All the waste dumpsites on the territory of the Republic of Armenia are polluted by PCBs.

In order to facilitate development and implementation of the State Policy and strategy in the area of waste management, as well as to secure environmentally sound/safe management of chemicals and waste within the structure of the Ministry of Nature Protection (Armenia) in 2005 there was established the “Waste Research Center”, which is engaged in issues relevant to waste inventory taking, classification thereof according to the hazard degree, carrying out research activity to study the unfavourable impact of waste (final) disposal sites towards the environment, working out normative acts (regulations/standards) in the area of waste management, as well as gathering and analysis of information on low-waste and waste-free technologies, entities at which wastes are generated, processed and used.
Table 2: PCBs in soils of waste dumps (2002-2003, mcg/kg)

<table>
<thead>
<tr>
<th>No.</th>
<th>Location of the dump site</th>
<th>PCB levels (mcg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ranchpar (village)</td>
<td>63.327</td>
</tr>
<tr>
<td>2.</td>
<td>Ararat (town)</td>
<td>59.404</td>
</tr>
<tr>
<td>3.</td>
<td>Vedi (town)</td>
<td>137.863</td>
</tr>
<tr>
<td>4.</td>
<td>Echmiadzin (town)</td>
<td>84.623</td>
</tr>
<tr>
<td>5.</td>
<td>Armavir (town)</td>
<td>369.877</td>
</tr>
<tr>
<td>6.</td>
<td>Bazarchai (village)</td>
<td>25.817</td>
</tr>
<tr>
<td>7.</td>
<td>Eghegnadzor (town)</td>
<td>79.362</td>
</tr>
<tr>
<td>8.</td>
<td>Kapan (town)</td>
<td>72.354</td>
</tr>
<tr>
<td>9.</td>
<td>Vanadzor (city)</td>
<td>163.643</td>
</tr>
<tr>
<td>10.</td>
<td>Gymri (city)</td>
<td>81.821</td>
</tr>
<tr>
<td>11.</td>
<td>Yerevan (capital city)</td>
<td>123.292</td>
</tr>
<tr>
<td>12.</td>
<td>Berd (town)</td>
<td>22.340</td>
</tr>
<tr>
<td>13.</td>
<td>Gavar (town)</td>
<td>29.384</td>
</tr>
</tbody>
</table>

The results of soil monitoring performed at waste dumps located in different regions of Armenia signify to presence of PCB residual amounts, which vary in the range of 22.3 - 369.9 mcg/kg (Table 2).

Figure 1: POPs residual amounts in soils of waste dumps, mcg/ kg
Besides, till 1990s there were more than 600 warehouses of chemical means of plant protection "Armselkhozkhimia" (“Armenian Agricultural Chemistry”), at which pesticides were stored and wherefrom these chemicals were distributed to facilities/farms. Data of monitoring on soils of the territories of former warehouses (premises) testify to the presence of residual amounts of Organochlorine Pesticides in soils of these territories.

Figure 2: POPs Residual amounts in soils of former pesticide warehouses, 2002, mcg/kg

On the average, the levels of organochlorine pesticides revealed in soils are not high. However, the problem is that monitoring was not held at all the contaminated sites. Therefore, it is necessary to perform a comprehensive inventory of POPs contaminated areas in order to have their appropriate ranking/rating.

Figure 3: Residual amounts of organochlorine pesticides in soils of regions of Armenia, mcg/kg
At present the state of contaminated territories (areas of enterprises of energy complex, waste dump sites, former pesticide storehouses) is of high importance for Armenia. Both organized and non-organized waste dump sites, which are scattered all over the territory of Armenia present themselves sources of environmental pollution by dioxins/ furans; this latter cannot but cause alarm and concern. Due to periodically occurring foci of low-temperature ignition and smoldering of wastes followed by generation of dioxins/ furans, these areas present hazard.

Owing to the fact that at present final disposal (burying) of hazardous wastes at the municipal dumps is the most prevalent mode for their disposal, these dump sites scattered all over the territory of Armenia can be considered anthropogenically emerged “hot spots”.

From contaminated areas POPs penetrate to different environmental media (ground and surface waters, air), plants, agricultural produce, and then by trophic chains POPs residues penetrate into human organism.

The disposal of the obsolete pesticides is one of the national prior problems and requires urgent solution. It should be mentioned that till now there is no waste treatment factory as well as specialized polygons for neutralized hazardous wastes in Armenia. Taking into consideration this fact, it is rational to use available national industrial capacities to treat, utilize and disposal the hazardous wastes in environmentally sound manner to protect the human health and environment from their adverse impact. The complexity of this issue solution lies in the fact that the problem of obsolete pesticides disposal is not regulated in Armenia yet as there isn’t specialized enterprise where the disposal of these types of wastes may be fulfilled by ecologically safe ways.

The problem of banned and obsolete pesticides became urgent already since late 1970s, when there arose the problem of elimination/withdrawal of banned and obsolete pesticides (mainly organochlorine ones) accumulated at the territory of Armenia. In early 1980s the special place was approved and allotted for pesticides burial near Bardzrashen village. At the territory of the organized burial place about 500 tons of obsolete pesticides were buried (finally disposed), of which the volume of banned organochlorine pesticides made 250 tons.

The complexity of the problem dealing with the obsolete pesticides burial is worsened by the fact that the site allotted for burial is located in the zone of active landslide processes, which can cause damage/crippling and a possible “breakthrough” of the contents (“innage”) and subsequent penetration of residues of buried obsolete pesticides, including organochlorine ones, into the environment resulting in environmental pollution.
In order to take measures on improvement of ecological situation in the vicinity of the burial a preliminary evaluation was performed on the costs of activity required for ensuring the ecological safety of the burial.

As a result of the activity performed by the Ministry of Nature Protection there was prepared and then approved the Decision of the Government of the Republic of Armenia “On approval of a list of measures ensuring safety of pesticides burial and assigning financial resources of state budget of the Republic of Armenia for FY 2004” (No. 526-A of April 22, 2004). Implementation of measures was entrusted to the Department of Emergency Situations at the Government of the Republic of Armenia, to which in accordance with the approved Decision 8 504.7 thousand AMD will be assigned at the expense of the reserve fund of the Government of the Republic of Armenia.

Coordination and control on implementation of measures is laid on the Ministry of Nature Protection of the Republic of Armenia.

The List of measures ensuring safety of pesticides burial embraces the following:

1. Study on the landslides at the territory neighbouring with the burial of obsolete pesticides;
2. Study aimed to examine the concrete construction of the burial of pesticides and determine its integrity;
3. Fencing of the burial of obsolete pesticides and reconstruction of drainage/water catchment system around it;
4. Study on contamination of soils and ground waters adjacent to the burial.

Solution of the problem on remediation of polluted areas and wastes dump sites is of prime significance and urgency for Armenia. The problem is more than serious due to the fact that its solution requires a continuous period of time and is complicated by the limited financial resources.
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