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Venue: ARISTOTLE UNIVERSITY RESEARCH DISSEMINATION CENTER (KEDEA)





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# Qualitative analysis of municipal solid waste landfill leachate from Vojvodina, Serbia, and identification of endocrine disruptors

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#### **Abstract**

Numerous xenobiotic organic components can have a highly detrimental effect on human health and the environment. Endocrine disruptors, a group of chemicals that affect the endocrine system, are a serious cause for concern. The effects of this group of substances often manifest after a certain period of time. The risk arising from the broad use of these substances and the necessity of educating both natural and legal persons have been recognized on the national level. The first step in this direction was the adoption and implementation of the appropriate national legislation, namely the Law on Chemicals ("Official Gazette of RS", Nos. 36/2009, 88/2010, 92/2011, 93/2012,and 25/2015); Law on Biocide Products ("Official Gazette of RS", Nos. 36/2009, 88/2010, 92/2011, and 25/2015); The Lists of Substances of Very High Concern ("Official Gazette of RS", Nos. 94/2013, 101/2016, and 22/2018), which also includes endocrine disruptors; and Candidate List of Substances of Very High Concern ("Official Gazette of RS", Nos. 58/2016 and 22/2018). The national legislation was adopted based on the experience of other countries, primarily the European Union, and appropriate legislation, namely REACH Regulation (Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals), Authorisation List (included in Annex XIV, REACH ("Authorisation List")) and Candidate List of substances of very high concern for Authorisation (published in accordance with Article 59(10) of the REACH Regulation).

For the purpose of detection and identification of endocrine disruptors, qualitative analysis of leachate from non-sanitary ( $L_1$ ) and sanitary ( $L_2$ ) solid waste municipal landfill from the region of Vojvodina, Serbia, was carried out. In addition, semi-quantitative screening analyses of collected samples were performed using QP2010-Ultra GC-MS. The results are shown in Table 1,2, 3, and 4, and represent the basis for designing the treatment of solid waste municipal landfill leachate and removal of endocrine disruptors by applying economically cost-effective yet experimental methods of phytoremediation using plants such as *Potamogetonillinoensis*, *Potamogetoncrispus* and *Raphanussativus* (Trueman and Erber, 2013).

Table 1. Values of physical and chemical parameters of leachate from the site L1 Table 2. Values of physical and chemical parameters of

Leachate from the site L<sub>2</sub>

Parameter	Unit	Value
Temperature of leachate	[°C]	7.3
рН	[-]	7.31
Conductivity	[μS cm <sup>-1</sup> ]	10 560
COD	[mg l <sup>-1</sup> ]	3545
BOD <sub>5</sub>	[mg l <sup>-1</sup> ]	1040
BOD <sub>5</sub> /COD	[mg l <sup>-1</sup> ]	0.293
Ammonia nitrogen	[mg l <sup>-1</sup> ]	166
Sulphate	[mg l <sup>-1</sup> ]	188.0
Total Phosphorus	[mg l <sup>-1</sup> ]	26.256
Ortho-phosphate	[mg l <sup>-1</sup> ]	1.964
Turbidity	[NTU]	87.1
Total suspended solids	[mg l <sup>-1</sup> ]	7.4

Parameter	Unit	Value
Temperature of leachate	[°C]	6.2
pН	[-]	8.51
Conductivity	[μS cm <sup>-1</sup> ]	16 230
COD	[mg l <sup>-1</sup> ]	4380
BOD <sub>5</sub>	[mg l <sup>-1</sup> ]	180
BOD <sub>5</sub> /COD	[mg l <sup>-1</sup> ]	0.04
Ammonia nitrogen	[mg l <sup>-1</sup> ]	38.15
Sulphate	[mg l <sup>-1</sup> ]	102.7
Total Phosphorus	[mg l <sup>-1</sup> ]	66.256
Ortho-phosphate	[mg l <sup>-1</sup> ]	2.561
Turbidity	[NTU]	17.8
Total suspended solids	[mg l <sup>-1</sup> ]	4.29

Table 3. Values of microbiological parameters of leachate from landfill sites  $L_1$  and  $L_2$ 

Parameter	Method	Unit	$L_1$	L <sub>2</sub>	Limit value <sup>1</sup>	Limit value <sup>2</sup>
Number of aerobic heterotrophs	Kohl	UCF/1mL	32.227.273	302.272	-	-
Total Coliform Bacteria	Membrane filtration	UCF/100mL	20.000.000	200	10.000	10.000
Fecal Coliform Bacteria	Membrane filtration	UCF/100mL	9.000.000	100	2.000	2.000
Detection and enumeration of intestinal enterococci	Membrane filtration	UCF/100mL	8.000.000	200	400	200

<sup>&</sup>lt;sup>1</sup>Regulation on emission limit values for pollutants in waters and deadlines for their reaching ("Official Gazette of the RS" No. 67/11, 48/12 and 01/16), article 13, Table 4; Annex II, Chapter III Urban wastewaters

<sup>&</sup>lt;sup>2</sup>Bathing Water Directive (CD 76/160/EEC), Table 10; Directive concerning the quality of Bathing Water COM (2002) 581, Annex I, Table 11

On the basis of microbiological examination, the sample of leachate from the landfill site  $L_1$ does not correspond to limit values stipulated by corresponding national and EU regulations. *Escherichia coli* (37°C, 44°C) represents a type of microorganisms identified in the sample  $L_1$  and  $L_2$ , and the presence of another type of microorganisms - *Klebsiellapneumoniae* (37°C, 44°C) was identified only in the sample  $L_2$ .

Table 4. Organic analysis of the sample of leachate from landfill sites L<sub>1</sub>and L<sub>2</sub>

Compound	Retention time [s]	CAS number	Molecular formula	Molecular weight [g mol <sup>-1</sup> ]	GHS Classification		
$L_1$							
7-Hexadecenal, (Z)-	10.068	56797-40-1	$C_{16}H_{30}O$	238.41	/		
Guanosine	11.57	118-00-3	$C_{10}H_{13}N_5O_5$	283.24	Signal: Danger		
Phenol	17.468	108-95-2	$C_6H_6O$	94.11	Signal: Danger		
Phenol, 4-methyl-	25.145	106-44-5	C7H8O	108.14	Signal: Danger		
Triisopropylphosphate	35.017	513-02-0	$C_9H_{21}O_4P$	224.23	Signal: Warning		
Indole	40.948	120-72-9	C <sub>8</sub> H <sub>7</sub> N	117.15	Signal: Danger		
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	50.005	126-86-3	$C_{14}H_{26}O_2$	226.36	Signal: Danger		
2,6-Dimethylphenyl isocyanate	53.973	28556-81-2	C <sub>9</sub> H <sub>9</sub> NO	147.17	Signal: Danger		
Methyl (4S,5R)-2,2,5-trimethyl-1,3-dioxolane-4-carboxylate	56.063	38410-80-9	C8H14O4	174.19	Signal: Warning		
Tributyl phosphate	56.628	126-73-8	C <sub>12</sub> H <sub>27</sub> O <sub>4</sub> P	228.31	Signal: Warning		
4-Oxo-4-(para-tolyl)-butyric acid	59.698	4619-20-9	$C_{11}H_{12}O_3$	192.21	Signal: Danger		
s-Trioxane, 2,4,6-triethyl-	68.275	2396-42-1	C <sub>9</sub> H <sub>18</sub> O <sub>3</sub>	174.24	Signal: Warning		
Phthalic acid, monoethyl ester	76.093	2306-33-4	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	194.18	Potential effect on thyroid gland activity in pregnant women		
Propyphenazone	80.12	479-92-5	$C_{14}H_{18}N_2O$	230.31	Signal: Warning		
Phenol, 4,4'-(1-methylethylidene)bis-	90.153	80-05-7	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>	228.29	Signal: Danger		
Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-	131.478	995-82-4	C <sub>12</sub> H <sub>36</sub> O <sub>5</sub> Si <sub>6</sub>	428.92	/		
$L_2$							
Dodecanoic acid, 3-hydroxy-	11.188	1883-13-2	$C_{12}H_{24}O_3$	216.32	Signal: Warning		
Trans-2-undecenoic acid	11.47	15790-94-0	$C_{11}H_{20}O_2$	184.28	Signal: Warning		
Nonanal	27.243	124-19-6	C <sub>9</sub> H <sub>18</sub> O	142.24	Signal: Warning		
Undecanal	27.28	112-44-7	C <sub>11</sub> H <sub>22</sub> O	170.29	Signal: Warning		
Pentadecanoic acid	27. 33	1002-84-2	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	242.40	Signal: Warning		
2-Undecanone, 6,10-dimethyl-	55.363	1604-34-8	C <sub>13</sub> H <sub>26</sub> O	198.35	Signal: Warning		
Octanoic acid, 7-oxo-	55.465	14112-98-2	C8H14O3	158.19	Signal: Warning		
Benzenesulfonamide	57.803	98-10-2	C <sub>6</sub> H <sub>7</sub> NO <sub>2</sub> S	157.19	Signal: Warning		
7-Hexadecenal, (Z)-	58.188	56797-40-1	C <sub>16</sub> H <sub>30</sub> O	238.41	/		
Gabapentin	58.76	60142-96-3	C <sub>9</sub> H <sub>17</sub> NO <sub>2</sub>	171.24	Signal: Danger		
1-Hexadecanol	59.648	36653-82-4	C <sub>16</sub> H <sub>34</sub> O	242.44	Signal: Warning		
1,2-Epoxy-5,9-cyclododecadiene	64.145	943-93-1	C <sub>12</sub> H <sub>18</sub> O	178.27	Signal: Warning		
Glycine, N-[(4-methylphenyl)sulfonyl]-	67.105	1080-44-0	C9H11NO4S	229.25	Signal: Warning		
Cyclopentadecanone	67.213	502-72-7	C <sub>15</sub> H <sub>28</sub> O	224.38	Signal: Warning		
Benzenesulfonamide, N-butyl-	70.905	3622-84-2	$C_{10}H_{15}NO_2S$	213.30	Signal: Warning		
Propyphenazone	80.083	479-92-5	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O	230.31	Signal: Warning		
Card-20(22)-enolide, 3,5,14,19-tetrahydroxy-, (3.beta.,5.beta.)-	85.58	560-54-3	C <sub>23</sub> H <sub>34</sub> O <sub>6</sub>	406.51	Signal: Danger		
Di-n-octyl phthalate	106.145	117-84-0	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	390.56	Signal: Danger		
9-Octadecenamide	114.68	301-02-0	C <sub>18</sub> H <sub>35</sub> NO	281.48	Signal: Warning		
Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-	135.38	995-82-4	C <sub>12</sub> H <sub>36</sub> O <sub>5</sub> Si <sub>6</sub>	428.92	/		

By performing organic analyses of leachate samples from landfill sites  $L_1$  and  $L_2$ , the presence of 39 substances was detected in the sample  $L_1$  and 55 substances were detected in the sample  $L_2$ . Table 4 shows detected xenobiotic organic compounds with GHS classification, namely the proven hazardous effects on the environment and human health. 7-Hexadecenal, (Z)- and Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl- were detected in both samples. One endocrine disruptor, Phenol, 4,4'-(1-methylethylidene)bis- (Bisphenol A), was detected in the sample  $L_1$ . Identification of endocrine disruptor Bisphenol A, a compound

that is proven toxic to reproduction, is a very important basis for realisation of future research related to the treatment of landfill leachate.

Keywords: Landfill leachate, Municipal solid waste landfill, Xenobiotic, Endocrine disruptors

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### References

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