UNIVERSITY OF LATVIA

# Multiproxy analytical comparison of industrially produced humic production

Karina Upska[1] Maris Klavins[2] Arturs Viksna[1]
[1]Faculty of Chemistry, University of Latvia, Riga, Latvia, karina.upska@lu.lv, arturs.viksna@lu.lv
[2]Faculty of Geography and Earth Sciences, University of Latvia, Riga, Latvia, maris.klavins@lu.lv

## Abstract:

Humic substances nowadays are not only topic of basic research, but also they are a industrially in amounts of tons produced substances, at first for application in agriculture. Considering diversity of functions there is a high potential of application of humic substances also for other aims, such as food additives, applications in cosmetics etc. The aim of the study is to compare properties of industrially produced humic substances by they origin (vermicompost, manure, sapropel, peat, coal, leonardite, water etc.). As known humic substances in the study were used potassium humates of it's nature and efectivity. Were used thirty-five industrially prouced humic substances of known origin (7 groups).The methods used for characterisation include element analysis, TOC (total organic carbon) and spectroscopic characterisation.

## Conclusion:

Research shows that humic substances of soil, peat, sapropel originates is most effective in fertilizer use. Firstly, organic material consists a highest nitrogen and carbon amounts in comparison to other samples. Secondly, they contain more than 50% humic acid fraction. Thirdly, the organic structures are less degraded and more stable than product of coal or lignite originates.

The study also showed that humic substances from compost, peat, and sapropel are closest in their structure and properties to natural humic substances from the soil. However, peat and sapropel products are more environmentally friendly and natural, since the composts, widely available on the market, are produced from municipal waste or manure (animal origin).

From the point of view of fertilizer, sapropel attracts attention not only to the similarity of humic substances with natural, and its rich composition. Sapropel contains a wide range of trace elements, vitamins, proteins, amino acids and enzymes, and all of them are of natural origin.

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

## Research results:

Large quantities of humic substances are produced in many countries around the world and their use in various areas of the economy is developing. However, it should be noted that the structure and properties of humic substances depend on their origin. Humic substances released from the soil and compost contain the highest amount of nitrogen and carbon, so they are useful to produce fertilizer production.  In some cases, high levels of contamination, such as high ash content, have been found in industrially produced humic products, reducing the quality of the product, or even limiting their intended use. The high ash content was found in product *EP*, isolated from lignite, can be explained, that product has got a high impurities content - silicates and heavy metals. The decrease of H/C atom ratio in the humic substances means the dehydrogenation of the sample (hydrogen removal from an organic compound), which could increase side reactions in soil. The obtained data from analyses are in the same range, thus all samples are stable. The increase of O/C atom ratio means the decarboxylation of organic material, too high values indicate degradation of sample. Product *BP*, *EP* and *GP* have got two times higher O/C values  in comparison to others. Can be concluded that humic substances of coal, lignite and water originates are more decomposed, thus partly have lost functional properties.

As the organic carbon is an important factor in fertility (affects plant growth), it was determined in humic products. The high total organic carbon content was found in product *EP* of lignin originates and smallest value in product *GP* of water originate. By the way, using this method was found humic and fulvic acid mass percentage in samples. Knowing these properties, efficiency of product can be predicted. Humic acid have got more strong and productive functions (accumulation, regulatory, protecting, physiological functions) in soil than fulvic acid. Humic substances isolated from soil and compost partially consist of 100% humic acid, that claims about benefit of fertilizer product. However, product of coal originates consist 79% of fulvic acid, that shows low quality product.

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

By UV-Vis spectra have been discovered absorption ratio of humic substances at specific wavelengths (E2/E3 and E4/E6). Were relatively determined which type of product has a higher aromaticity and molecular weight, which affects the product quality. Humic substances of sapropel originates show the smallest E2/E3, that indicate a high aromatic group content. Due to these properties, substitution and attachment reactions can occur faster in the soil. Lignite and coal originate humic substances show the highest E2/E3 values, which indicate a low aromatic group content. It may be noted that the highest E4/E6 ratio has also product of sapropel, therefore has a smaller molecular mass. That formed before peat, and where the humification / polymerization process is still unfinished. Therefore, properties of product of sapropel originates could be more effective.

**Table 1**

Elemental composition of humic products

| **Product** | **Origin** | **N, %** | **C, %** | **Ash, %** | **H/C** | **O/C** | **TOC, mg/g** | **$W_{FA, TOC}$, %** | **$W_{HA, TOC}$, %** |
|---|---|---|---|---|---|---|---|---|---|
| A | peat | 3,62 | 44,92 | 5,86 | 1,32 | 0,78 | 37,4 | 54,5 | 55,5 |
| B | coal | 0,41 | 33,25 | 4,53 | 1,15 | 1,43 | 34,0 | 79,1 | 20,9 |
| C | sapropel | 3,80 | 45,48 | 9,78 | 1,21 | 0,76 | 52,8 | 43,5 | 56,5 |
| D | soil | 3,82 | 51,12 | 9,78 | 1,14 | 0,59 | 46,9 | 7,9 | 92,1 |
| E | lignite | 0,44 | 34,36 | 35,23 | 1,12 | 1,35 | 63,7 | 60,2 | 39,8 |
| F | compost | 3,94 | 50,00 | 8,65 | 1,14 | 0,62 | 45,9 | 10,9 | 89,1 |
| G | water | 1,46 | 34,57 | 1,38 | 1,24 | 1,31 | 27,7 | 24,8 | 75,2 |

***N – nitrogen content, plays an important role in plant growth, protein, nucleic acid, chlorophyll and other organic substances synthesis, determines the potential soil fertility.**

***C – carbon content, the main organic element in the structure of humic substances, determines the quality of product.**

***Ash –indicates contamination of samples with inorganic substances (silicates. metals, non-metals).**

***H/C – hydrogen and carbpn atom ratio, represents the aromaticity index.**

***O/C – oxygen and carbon atom ratio, represents the number of oxygen-containing groups in the organic structure. High values indicate degradation of humic material.**

***TOC – total organic carbon, an important fertility factor.**

***$W_{FA}$- mass percentage of fulvic acid.**

***$W_{HA}$- mass percentage of humic acid.**

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

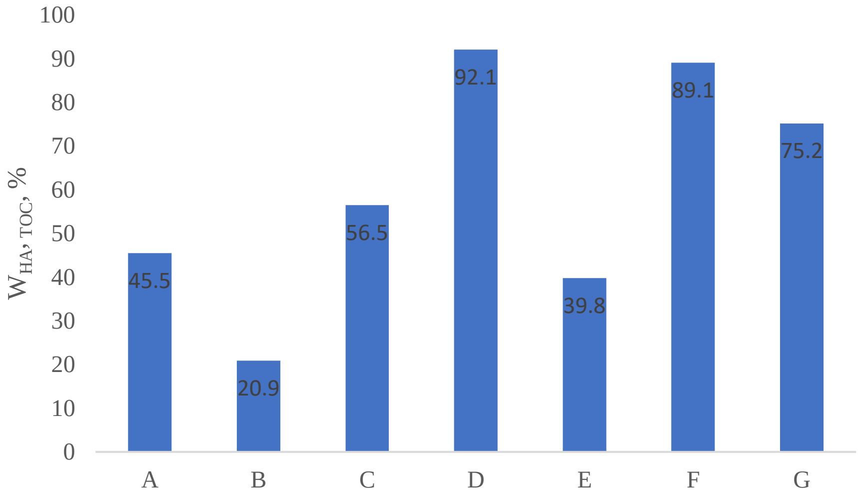



**Fig. 1.** Mass percentage of humic acid in humic products

**Table 2**

The absorption ratios of humic substances in UV-Vis spectra

| Product | Origin | E2/E3 | E4/E6 |
|---|---|---|---|
| AP | peat | 2,40 | 11,27 |
| BP | coal | 3,01 | 5,08 |
| CP | sapropel | 2,16 | 16,35 |
| DP | soil | 2,39 | 5,00 |
| EP | lignite | 3,19 | 5,11 |
| FP | compost | 2,39 | 5,00 |
| GP | water | 2,68 | 4,94 |

***E2/E3 – absorption at 250 nm and 365 nm reflects the degree of aromaticity, degradation of phenols and quinone groups in the humate structure, the lower the values, the higher the degree of aromaticity**

***E4/E6 - absorbance at 465 nm and 665 nm, indicating molecular weight, condensation and maintenance of humic substances in time environment.**

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

It has also indicated the impurity or low quality of organic matters in some products. EEM spectra provides information on the relative intensity of fluorescence of humic substances at various excitation-emission wavelengths. They make it possible to distinguish between the presence of selective and sensitive dissolved organic substances - humic acid, fulvic acid, proteins (tryptophan and tyrosine) in the sample, as well as its relative amount compared to the other fractions.

Figure 2 shows the EEM spectra of the product *AP*, where the peak **α** - 470/550 (Ex / Em, nm) characterizes the fraction of humic acid, peak **β** (350 / 520) – fulvic acid and peak **γ** – protein fraction. The spectra is typical for humic substances. Was observed, that peat (*AP*) and soil (*DP*) originates EMM spectra are similar, indicating the equivalence of product compositions. Figure 4 shows sapropel originates (*CP*) product contains more fulvic acid fraction in comparison to other samples.

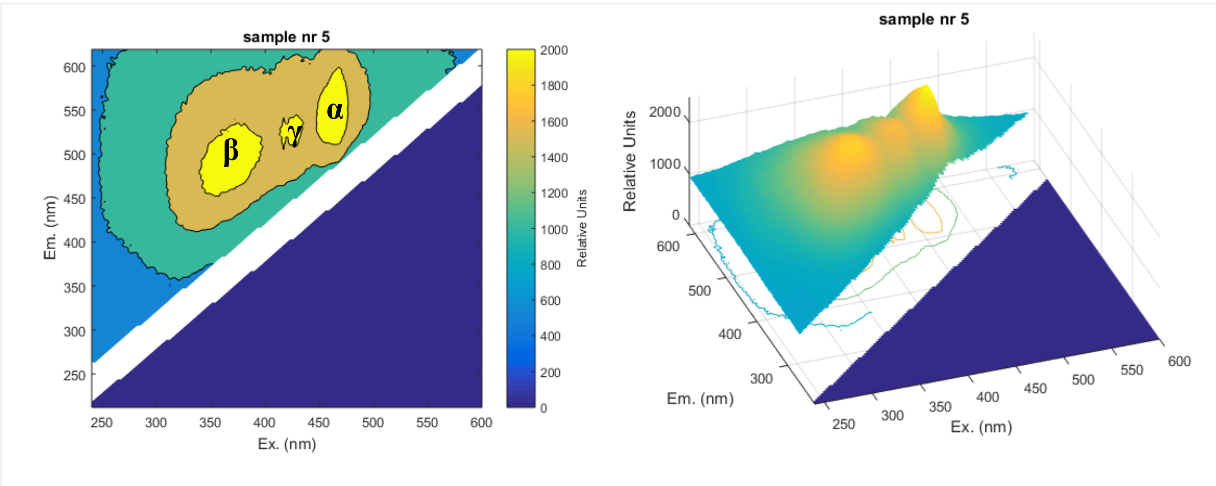



**Fig. 2**. *AP* product (peat originates) 2D (left) and 3D (right) EEM spectras

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

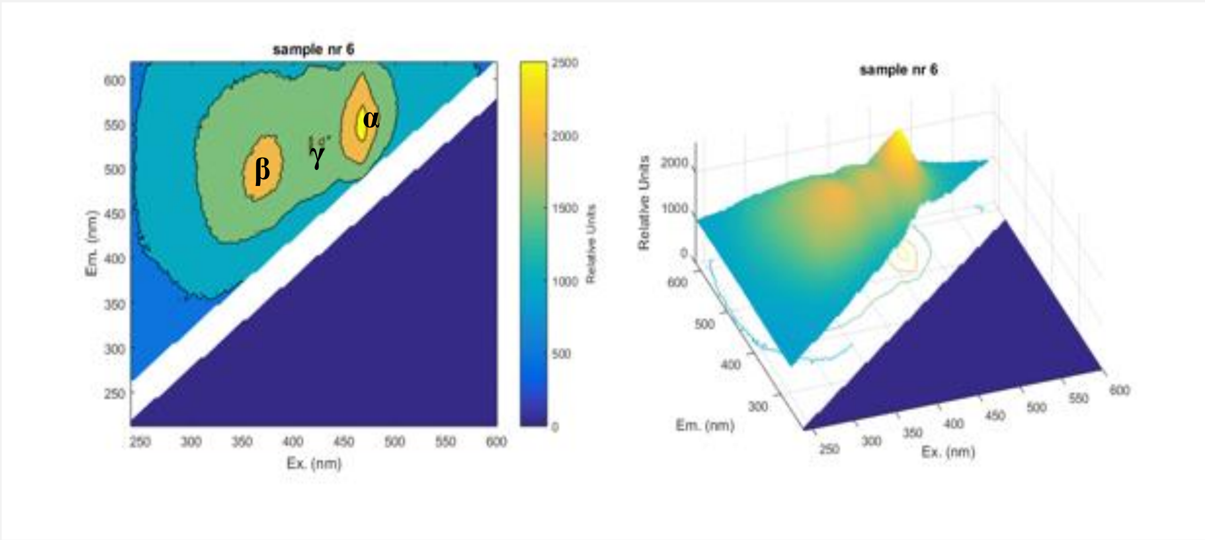



**Fig. 3**. *DP* product (soil originates) 2D (left) and 3D (right) EEM spectras

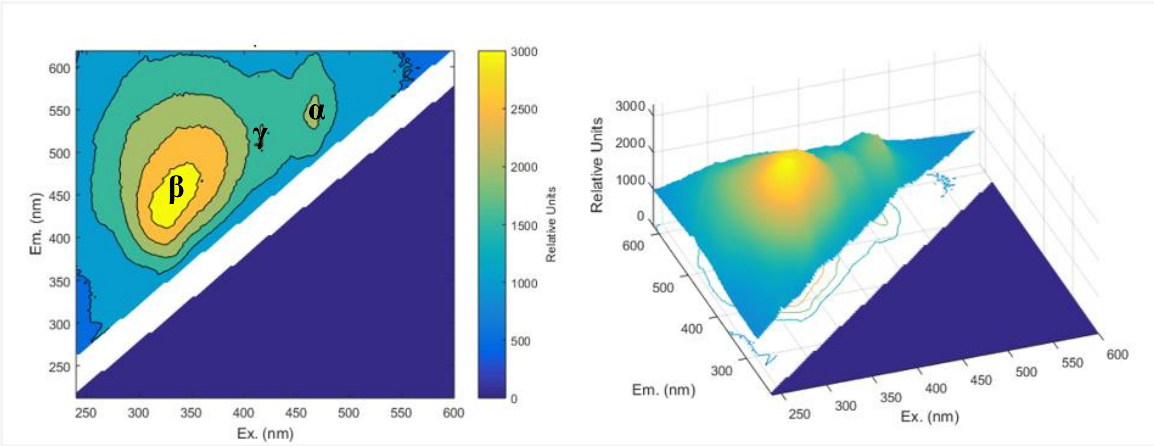



**Fig. 4**. *CP* product (sapropel originates) 2D (left) and 3D (right) EEM spectras

In some cases, the HS product does not respond to the labeled name. For example, in figure 3 you can see high quality (left side) *D* product, which contain 3 main organic fractions (humic acid, fulvic acid and protein) for humic substances. However, the product *B* lacks such properties. The manufacturer states that the HS product consists of 80-90% humic acid, but figure 3 (right side) shows a relatively high fulvic acid peak β (350/520) and almost no detectable humic acid peak α (470/550).

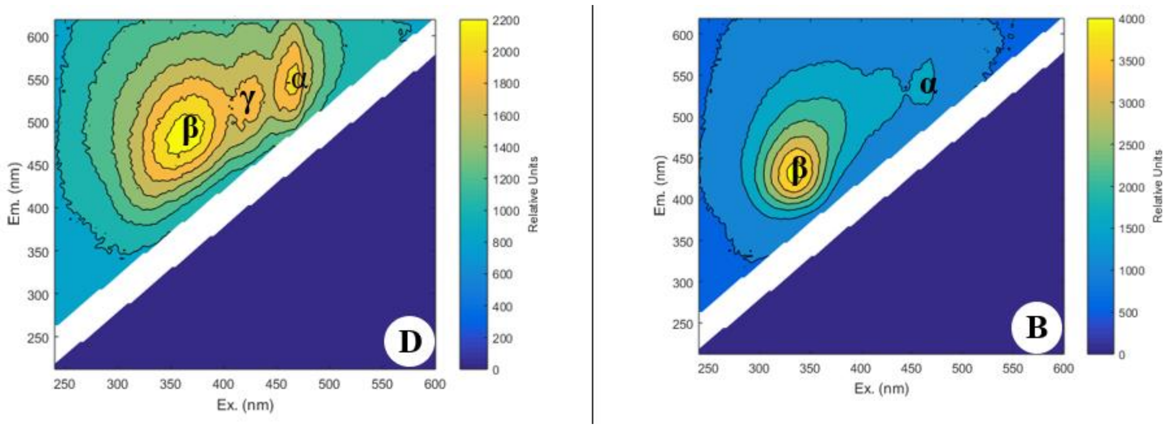



**Fig. 4.** 2D EEM spectra: high quality (left) – *DP* humate product (soil originates) and low quality (right) – *BP* humate product (coal originates)

Appendix 1

**Table 3**

Characteristic of humic substances samples for this study

| **Sample** | **Origin** | **Sample** | **Origin** |
|---|---|---|---|
| A | Coal | T | Water |
| B | Coal | U | Coal |
| C | Coal | V | Peat |
| D | Coal | W | Coal |
| E | Peat | X | Water |
| F | Coal | Y | Water |
| G | Peat | Z | Water |
| H | Sapropel | AA | Water |
| J | Peat | AB | Water |
| K | Peat | AC | Lignite |
| L | Peat | AD | Coal |
| M | Sapropel | AE | Water |
| N | Peat | AF | Water |

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

| | | | |
|---|---|---|---|
| O | Soil | AG | Leaf compost |
| P | Peat | AH | Vermicompost |
| Q | Leonardite | AJ | Manure |
| R | Peat | AK | peat |
| S | Peat | | |

Appendix 2

**Table 4**

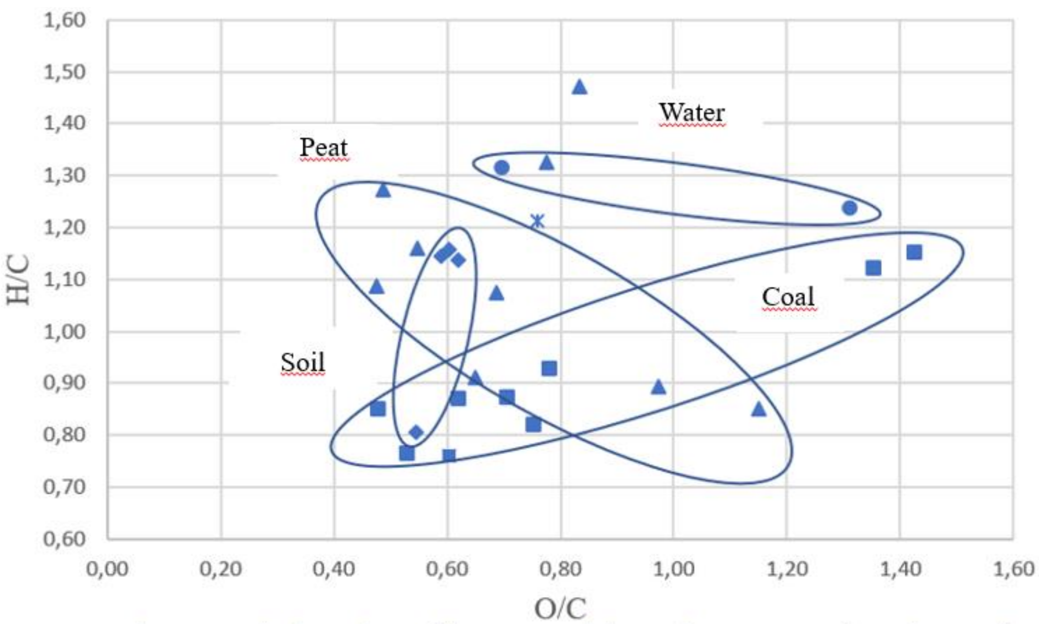
Elemental composition of humic substances

| **Sample** | **N, %** | **C, %** | **H, %** | **O, %** | **Ash, %** | **H/C** | **O/C** |
|---|---|---|---|---|---|---|---|
| A | 1,20 | 49,03 | 3,59 | 46,18 | 13,69 | 0,87 | 0,71 |
| B | 1,01 | 47,74 | 3,28 | 47,97 | 18,69 | 0,82 | 0,75 |
| C | 0,96 | 46,71 | 3,64 | 48,69 | 20,49 | 0,93 | 0,78 |
| D | 1,50 | 52,67 | 3,35 | 42,48 | 5,77 | 0,76 | 0,61 |
| F | 0,89 | 41,78 | 3,13 | 54,20 | 30,68 | 0,89 | 0,97 |
| Q | 3,31 | 50,89 | 3,71 | 42,09 | 2,71 | 0,87 | 0,62 |
| E | 3,62 | 44,92 | 4,99 | 46,47 | 5,86 | 1,32 | 0,78 |
| G | 2,31 | 48,71 | 4,39 | 44,59 | 8,17 | 1,07 | 0,69 |
| H | 3,82 | 43,01 | 5,31 | 47,86 | 9,27 | 1,47 | 0,84 |
| J | 3,05 | 53,06 | 5,16 | 38,73 | 1,38 | 1,16 | 0,55 |

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| K | 1,43 | 55,67 | 3,57 | 39,33 | 8,65 | 0,76 | 0,53 |
| L | 1,51 | 57,09 | 5,20 | 36,20 | 0,39 | 1,09 | 0,48 |
| N | 2,54 | 55,46 | 5,92 | 36,08 | 0,89 | 1,27 | 0,49 |
| P | 1,06 | 50,89 | 3,89 | 44,16 | 1,76 | 0,91 | 0,65 |
| R | 1,05 | 57,86 | 4,13 | 36,96 | 1,43 | 0,85 | 0,48 |
| M | 3,80 | 45,48 | 4,62 | 46,10 | 9,78 | 1,21 | 0,76 |
| O | 3,80 | 53,54 | 3,61 | 39,05 | 1,37 | 0,80 | 0,55 |
| V | 1,98 | 50,81 | 4,86 | 42,35 | 0,19 | 1,14 | 0,63 |
| U | 3,23 | 31,71 | 4,03 | 61,03 | 0,79 | 1,51 | 1,44 |
| W | 4,69 | 39,29 | 4,88 | 51,14 | 10,85 | 1,48 | 0,98 |
| T | 0,60 | 48,71 | 4,01 | 46,68 | 25,85 | 0,98 | 0,72 |
| AC | 0,44 | 34,36 | 3,23 | 61,97 | 35,23 | 1,12 | 1,35 |
| AE | 2,12 | 48,00 | 5,30 | 44,58 | 9,27 | 1,32 | 0,70 |
| AF | 1,46 | 34,57 | 3,59 | 60,38 | 1,38 | 1,24 | 1,31 |
| AG | 3,94 | 50,00 | 4,77 | 41,29 | 8,65 | 1,14 | 0,62 |
| AH | 3,69 | 50,64 | 4,91 | 40,76 | 0,39 | 1,16 | 0,60 |
| AJ | 3,82 | 51,12 | 4,91 | 40,15 | 9,78 | 1,14 | 0,59 |
| AD | 0,41 | 33,25 | 3,21 | 63,13 | 4,53 | 1,15 | 1,43 |

Appendix 3




Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

**Fig. 5.** Van Krevelen graph, humic acid composition elements H / C depending on O / C Ratio (Peat (▲), Coal (□), Soil (◊), Sapropel (×), Water (●))

Appendix 4

**Table 5**

Content of inorganic elements in humic substances - I
(aluminum, arsenic, boron, barium, beryllium, calcium, cadmium, cobalt)

| Sample | Al, µg/g | As, µg/g | B, µg/g | Ba, µg/g | Be, µg/g | Ca, µg/g | Cd, µg/g | Co, µg/g |
|---|---|---|---|---|---|---|---|---|
| A | 16360 | 18 | 14 | 42 | <0,02 | 309 | 0,46 | 3,9 |
| B | 31550 | 23 | 11 | 42 | <0,02 | 197 | 0,38 | 4,1 |
| C | 31390 | 27 | 12 | 51 | 0,02 | 322 | 0,52 | 4,4 |
| D | 3461 | <2 | 31 | 61 | <0,02 | 1806 | <0,15 | 2,3 |
| E | 1492 | 1,3 | 14 | 2,6 | <0,04 | 10384 | <0,17 | 0,8 |
| F | 33440 | 26,5 | 24 | 49 | 4,01 | 9176 | <0,17 | 12 |
| G | 762 | 0,7 | 10 | <0,4 | <0,04 | 1709 | <0,17 | 0,7 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| H | 392 | 1,7 | 6 | 1,9 | <0,04 | 822 | <0,17 | 0,3 |
| J | 11090 | 5,5 | 27 | <0,4 | <0,04 | 162 | <0,17 | 6,3 |
| K | 7140 | 2,2 | 65 | 4,3 | <0,04 | 1777 | <0,17 | 2,2 |
| L | 148 | <1,6 | 9 | <0,4 | <0,02 | <6 | 0,15 | 2,5 |
| M | 158 | <1,6 | 3 | <0,4 | <0,02 | 10 | <0,14 | 1,3 |
| N | 3850 | 3 | <6 | 21,9 | 0,03 | 229 | <0,15 | 2,4 |
| O | 16 | 3,1 | 23 | 0,4 | <0,02 | <6 | 0,49 | 8,1 |
| Q | 69 | 3,3 | 7 | 4,5 | <0,02 | 511 | 0,14 | 1,0 |
| R | 2270 | <1,6 | 24 | 40 | <0,02 | 3155 | 0,29 | 0,6 |
| U | 882 | <1,4 | 108 | 19 | <0,04 | 19848 | <0,18 | 0,6 |
| V | 40 | 1,4 | 80 | <0,6 | <0,04 | <0,5 | <0,18 | <0,2 |
| W | 17 | <1,6 | 343 | <0,4 | <0,02 | <6 | 28,50 | 0,3 |
| X | 175 | <1,6 | 47 | 5,9 | 0,06 | 2280 | 0,63 | 2,6 |
| AA | 86 | <4,8 | 227 | <1,2 | <0,06 | <20 | <0,42 | 0,5 |
| AC | 10 | <1,6 | 997 | 0,9 | <0,02 | 1099 | <0,14 | 571 |
| AD | <1 | <1,4 | 462 | <0,6 | <0,04 | 150 | <0,18 | 214 |
| AE | 260 | 3,5 | 61 | 159 | 0,05 | 10 | <0,18 | 3,4 |
| AF | 10790 | 2,7 | 23 | 153 | 0,16 | 109 | <0,18 | 3,1 |
| AG | 1310 | 1,4 | <9 | 7,3 | <0,04 | 215 | <0,18 | 2,8 |
| AH | 729 | 1,6 | <9 | 5,3 | <0,04 | <0,5 | <0,18 | 1,8 |
| AJ | 1190 | 1,5 | <9 | 111 | <0,04 | <0,5 | <0,18 | 5,9 |

Appendix 5

**Table 6**

Content of inorganic elements in humic substances - II
(chromium, copper, iron, potassium, magnesium, manganese, molybdenum, sodium, nickel)

| **Sample** | **Cr, µg/g** | **Cu, µg/g** | **Fe, µg/g** | **K, µg/g** | **Mg, µg/g** | **Mn, µg/g** | **Mo, µg/g** | **Na, µg/g** | **Ni, µg/g** |
|---|---|---|---|---|---|---|---|---|---|
| A | 34 | 17 | 8570 | 10000 | 439 | 6,3 | 9,4 | 1080 | 17 |
| B | 51 | 31 | 7440 | 2670 | 448 | 7,3 | <0,3 | 78 | 21 |
| C | 44 | 21 | 7350 | 3810 | 562 | 9,0 | <0,3 | 69 | 20 |
| D | 6,4 | 2,7 | 3500 | 8500 | 210 | 18 | 0,4 | 203 | 7,1 |
| E | 6,9 | 2,5 | 8400 | 12050 | 1390 | 88 | <0,3 | 189 | 3,6 |

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| F | 51 | 38 | 11630 | 3020 | 1270 | 22 | <0,3 | 25160 | 45 |
| G | 5,2 | 5,1 | 1230 | 404 | 136 | 6,9 | 1,4 | 28200 | 1,8 |
| H | 5,8 | 3,3 | 3510 | 120 | 54 | 3,9 | 2,1 | 2810 | 3,8 |
| J | 14 | 54 | 4990 | 3630 | 1500 | 19 | 31 | 2730 | 11 |
| K | 3,8 | 5,4 | 3340 | 6470 | 422 | 2,7 | 2,3 | 14500 | 19 |
| L | 4,6 | 10 | 91 | 876 | <0,5 | 4,3 | <0,4 | 261 | 4,0 |
| M | 2,0 | 7,6 | 94 | 753 | <0,5 | 2,8 | <0,4 | 189 | 1,6 |
| N | 21 | 665 | 3890 | 3540 | 20 | 8,0 | 0,5 | 33 | 19 |
| O | 26 | 295 | 915 | 658 | <0,5 | 2,3 | 4,9 | 187 | 12 |
| Q | 4,7 | 21 | 2950 | 4030 | <0,5 | <0,1 | 24 | 151 | 17 |
| R | 52 | 18 | 1570 | 60 | 22 | 5,4 | 54 | 2140 | 34 |
| U | 0,6 | 0,9 | 792 | 27220 | 6750 | 37 | 0,8 | 21500 | 0,6 |
| V | <0,6 | <0,6 | 59 | 706 | 57 | <0,1 | 0,2 | 478 | <0,3 |
| W | 7,2 | 1,4 | 121 | 296 | <0,5 | 1,4 | 8,1 | 28970 | 5,5 |
| X | 4,9 | 110 | 1710 | 287 | 336 | 14 | 51 | 12820 | 17 |
| AA | 2,5 | 17 | 35 | 105 | <1,5 | <0,3 | 5,8 | 1150 | 1,7 |
| AC | <0,4 | 729 | 66 | 102200 | 131 | 673 | 19 | 43570 | 2,0 |
| AD | <0,6 | 298 | 9 | 40610 | 16 | 240 | 19 | 16410 | <0,3 |
| AE | 0,8 | 30 | 2320 | 726 | 1 | 3,1 | 2,1 | 4700 | 5,3 |
| AF | 12 | 31 | 7860 | 3150 | 1200 | 37 | 0,6 | 3920 | 6,6 |
| AG | 1,1 | 25 | 1040 | 2660 | 126 | 4,6 | 16 | 16 | 2,5 |
| AH | 0,7 | 21 | 489 | 1450 | 28 | 1,5 | 7,8 | <11 | 0,5 |
| AJ | 20 | 201 | 1000 | 1470 | 27 | 0,6 | 7,7 | <11 | 2,9 |

Appendix 6

**Table 7**

Content of inorganic elements in humic substances - III
(phosphorus, lead, sulfur, selenium, silicon, strontium, tungsten, zinc)

| Sample | P, µg/g | Pb, µg/g | S, µg/g | Se, µg/g | Si, µg/g | Sr, µg/g | V, µg/g | Zn, µg/g |
|---|---|---|---|---|---|---|---|---|
| A | 91 | 3,7 | 4020 | <3 | 158 | 26 | 26 | 6,0 |
| B | 107 | <1 | 3760 | <3 | 115 | 25 | 45 | 13 |
| C | 108 | <1 | 3520 | <3 | 80 | 28 | 42 | 12 |
| D | 16 | 4,2 | 4660 | <3 | 300 | 24 | 5,6 | 4,4 |

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| E | 227 | 0,9 | 1460 | <3 | 860 | 18 | <0.7 | <0,1 |
| F | 133 | 2,5 | 3640 | <3 | 210 | 68 | <0.7 | <0,1 |
| G | 297 | 3,4 | 2730 | <3 | 697 | 7,1 | <0.7 | <0,1 |
| H | 333 | 3,7 | 2880 | <3 | 371 | 3,3 | <0.7 | <0,1 |
| J | 518 | 4,7 | 13520 | 5 | 438 | 5,3 | <0.7 | <0,1 |
| K | 46 | 2,3 | 2750 | <3 | 477 | 18 | <0.7 | <0,1 |
| L | 526 | <0.9 | 4630 | <2 | 204 | 0,3 | <0.7 | 6,8 |
| M | 263 | <0.9 | 4730 | <2 | 93 | 0,4 | 0,9 | 7,6 |
| N | 2070 | 37,9 | 2040 | <3 | 168 | 2,2 | 12 | 26 |
| O | 1970 | 16,2 | 3560 | 8 | 55 | 0,5 | 1,6 | 90 |
| Q | 256 | 3,3 | 5570 | 2 | 24 | 12 | 1,3 | 146 |
| R | 30 | 1,7 | 5710 | <2 | 268 | 39 | 1,4 | 5,2 |
| U | <2 | 1,0 | 11370 | <2 | 117 | 196 | 1,7 | 1 |
| V | <2 | <1 | 1470 | <2 | 46 | 2 | 0,5 | <0,1 |
| W | 790 | 2,0 | 72100 | <2 | 83 | 0,5 | <0.7 | 11 |
| X | 723 | 3,2 | 10780 | 9 | 784 | 7,1 | 9,4 | 50 |
| AA | 721 | 1,9 | 8350 | <6 | 1939 | <0.3 | 0,8 | 13 |
| AC | 561 | <0.9 | 52850 | <2 | 172 | 7,8 | <0.7 | 862 |
| AD | 38 | <1 | 28500 | <2 | 32 | 2,2 | <0,5 | 284 |
| AE | 7 | 4,3 | 10520 | <2 | 229 | 2,2 | 5,8 | 5,6 |
| AF | 189 | 6,1 | 5130 | <2 | 33 | 7,5 | 17 | 14 |
| AG | 641 | 2,4 | 5690 | 2 | 37 | 1,3 | 5,2 | 13 |
| AH | 294 | <1 | 5260 | <2 | 40 | <0,1 | 3,6 | 6,5 |
| AJ | 477 | 80 | 4570 | 3 | 81 | 1,4 | 3,5 | 25 |

**Table 8**

Amount of humic acid and fulvic acid in humic substances

| Paraugs | TOC, mg/g | $W_{FA, TOC}$, % | $W_{HA, TOC}$, % | Paraugs | TOC, mg/g | $W_{FA, TOC}$, % | $W_{HA, TOC}$, % |
|---|---|---|---|---|---|---|---|
| A | 152,0 | 73,0 | 27,0 | S | 98,6 | 67,9 | 32,1 |
| B | 188,2 | 46,1 | 53,9 | T | 43,6 | 75,6 | 24,4 |
| C | 169,6 | 77,0 | 23,0 | U | 31,1 | 89,3 | 10,7 |
| D | 105,3 | 78,9 | 21,1 | V | 50,3 | 95,4 | 4,6 |
| E | 37,4 | 54,5 | 45,5 | W | 31,1 | 92,9 | 7,1 |
| F | 201,2 | 41,6 | 58,4 | X | 40,9 | 57,0 | 43,0 |
| G | 213,8 | 36,0 | 64,0 | Y | 69,2 | 94,9 | 5,1 |
| H | 26,0 | 36,9 | 63,1 | Z | 113,6 | 58,2 | 41,8 |
| J | 167,5 | 41,8 | 58,2 | AA | 57,1 | 69,6 | 30,4 |
| K | 132,4 | 50,4 | 49,6 | AB | 108,5 | 58,8 | 41,2 |
| L | 136,4 | 83,1 | 16,9 | AC | 63,7 | 60,2 | 39,8 |
| M | 125,8 | 43,5 | 56,5 | AD | 34,0 | 79,1 | 20,9 |
| N | 118,3 | 22,7 | 77,3 | AE | 44,3 | 34,5 | 65,5 |
| O | 146,4 | 44,6 | 55,4 | AF | 27,7 | 24,8 | 75,2 |
| P | 108,0 | 81,8 | 18,2 | AG | 45,9 | 10,9 | 89,1 |
| R | 119,2 | 31,5 | 68,5 | AH | 55,1 | 7,4 | 92,6 |
| Q | 120,8 | 32,7 | 67,3 | AJ | 46,9 | 7,9 | 92,1 |

Appendix 8

**Table 6**

Absorption ratios of humic substances in UV-Vis spectra and ΔlogK

| Paraugs | E2/E3 | E4/E6 | E270/400 | E280/664 | logK |
|---|---|---|---|---|---|
| A | 2,36 | 6,80 | 2,88 | 34,04 | 0,81 |
| B | 2,21 | 7,50 | 2,79 | 31,78 | 0,59 |
| C | 2,21 | 7,51 | 2,79 | 31,82 | 0,59 |
| D | 2,07 | 5,57 | 2,57 | 20,84 | 0,52 |
| E | 2,40 | 11,27 | 3,13 | 64,45 | 0,69 |
| F | 2,17 | 8,93 | 2,73 | 36,02 | 0,55 |
| G | 2,03 | 11,03 | 2,52 | 43,34 | 0,55 |
| H | 2,88 | 13,15 | 3,57 | 88,12 | 0,68 |
| J | 2,14 | 12,83 | 2,70 | 55,41 | 0,51 |
| K | 2,02 | 7,36 | 2,56 | 30,23 | 0,61 |
| L | 2,05 | 7,99 | 2,54 | 31,66 | 0,54 |
| M | 2,16 | 16,35 | 2,65 | 65,89 | 0,48 |
| O | 2,00 | 3,64 | 2,40 | 13,05 | 0,56 |
| P | 2,40 | 6,55 | 2,83 | 36,88 | 0,87 |
| Q | 2,32 | 5,29 | 2,79 | 24,36 | 0,74 |
| R | 2,16 | 4,93 | 2,57 | 21,03 | 0,70 |
| N | 2,78 | 6,82 | 3,00 | 43,45 | 0,90 |
| AC | 3,19 | 5,11 | 4,52 | 46,69 | 0,78 |
| AD | 3,01 | 5,08 | 4,17 | 41,05 | 0,79 |
| AE | 2,90 | 6,30 | 3,82 | 46,27 | 0,91 |
| AF | 2,68 | 4,94 | 3,39 | 32,71 | 0,81 |
| AG | 2,49 | 6,54 | 3,13 | 42,60 | 0,92 |
| AH | 2,50 | 6,31 | 3,16 | 40,20 | 0,88 |
| AJ | 2,39 | 5,00 | 3,09 | 27,93 | 0,77 |

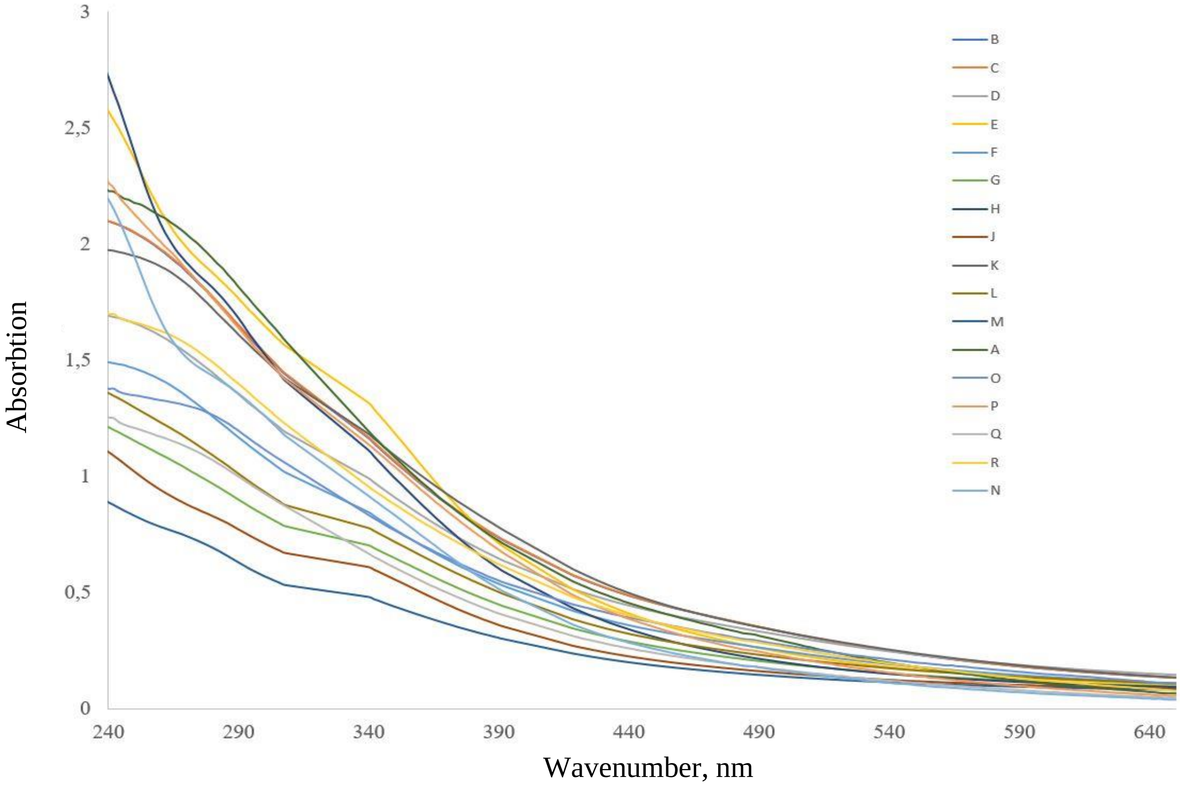



**Fig. 6.** UV-Vis spektra of humic substances

Appendix 9

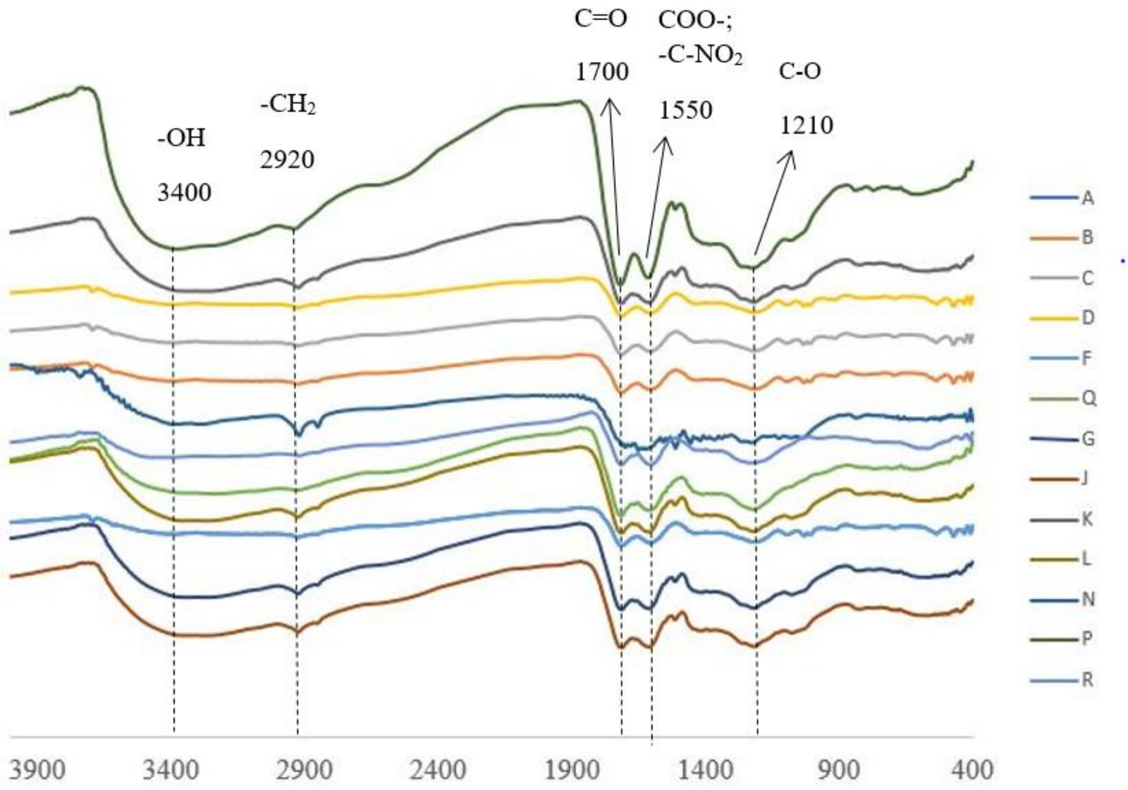



**Fig. 7.** Fourier transform infrared spektra of humic substances

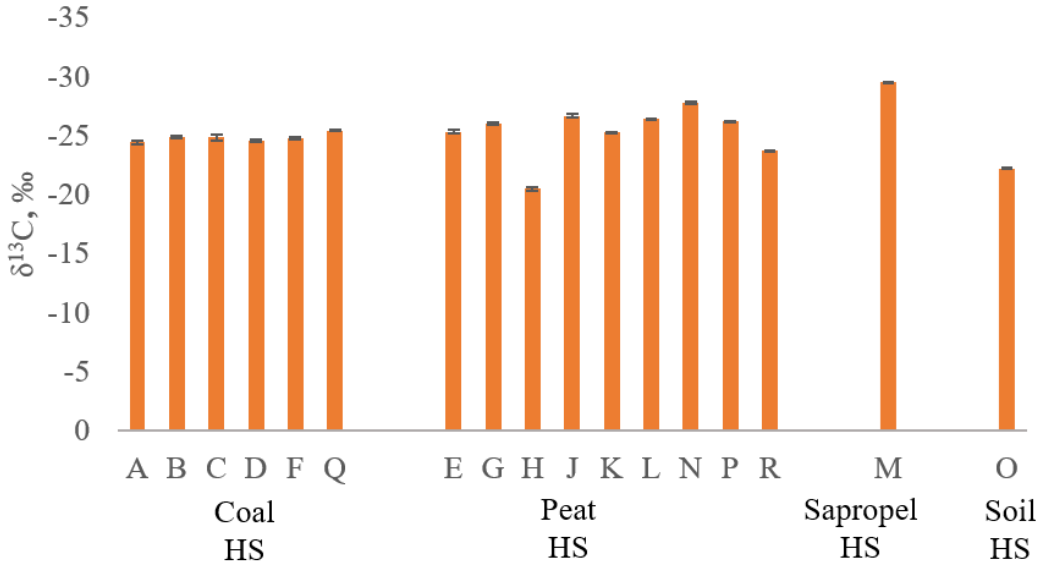



**Fig. 8.** $\delta^{13}$C isotopic ratios of humic substances samples

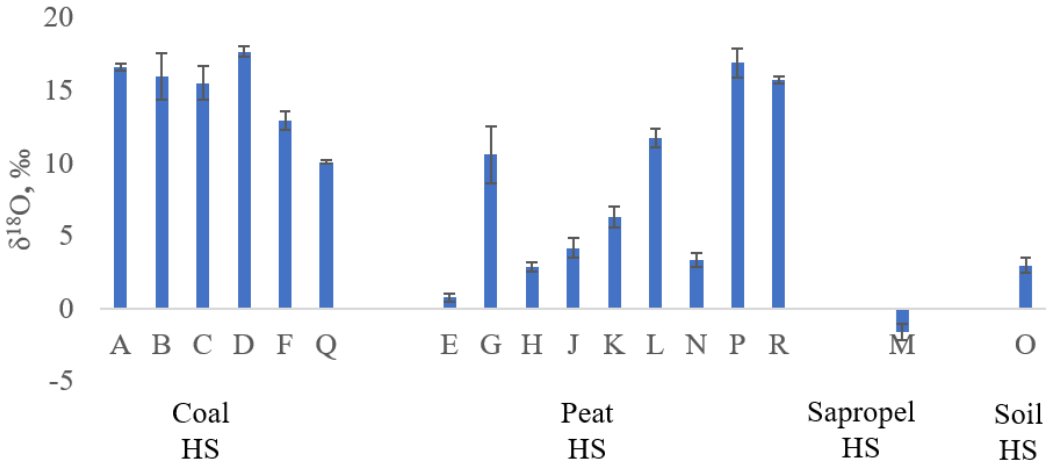



**Fig. 9.** $\delta^{18}$O isotopic ratios of humic substances samples

Report was prepared by Karina Upska, karina.upska@lu.lv, +371 20042387