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Detection of volatile organic compounds in upland peat by means of proton-transfer-reaction mass spectrometry

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Abstract

This research represents the results of the detection of volatile organic compounds (VOCs) in the sphagnum moss and peat from two upland bogs located in Germany. Proton-transfer-reaction mass spectrometry (PTR-MS), used for the research, is a high-sensitive method, which permit to detect low concentrations of VOCs in ambient air. Along with natural VOCs of peat plants (generally sphagnum moss), the results of the study showed the presence of anthropogenic VOCs emissions like butanol, toluene, and benzene. This fact testifies about the capability of peat moss to accumulate these compounds. Possible sources of these VOCs in the peat samples can be agricultural machines and the traffic of the nearest roads.

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Keywords: sphagnum moss; upland peat; volatile organic compounds.

1. Introduction

Organic material like sphagnum moss and peat, composed by decomposed mosses, can comprise a significant fraction of particulate aerosol mass and gases[1,2,10,11]. Sphagnum moss is a perennial plant spread in wet territories, mostly in bogs (peatlands). Sphagnum moss has empty cells helping it to retain water and different chemical compounds. Thus, peat can be considered like a buffer for atmospheric aerosols.

Peatlands cover great territories of all continents, participating in carbon and nitrogen cycles[3]. They play a

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significant role in climate balance, serving as a reservoir for CO_2. Upland (ombrotrophic) peat bogs have also a property to keep the history of the chemical composition of the atmosphere[9,13,16,17,18], since the stored organic material is preserved from oxidation and maintained for a long time period.

Volatile organic compounds (VOCs) represents a large group of carbon compounds (except carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate) participating in biological processes and atmospheric photochemical reactions. The sources of VOCs can have both biogenic and anthropogenic origin. The natural or biogenic sources are mainly forests (trees), shrubs, herbs, orchards, oceans (algae) and some other ecosystems. The anthropogenic sources include motor vehicles, chemical manufacturing facilities, refineries, factories, consumer, cooking, heating, farming and commercial products. Anthropogenic VOCs contribute directly to the total burden of organic aerosols and a fraction of VOCs that are actually emitted through anthropogenic activities does not capture the whole human influence on the organic aerosol budget, as it ignores any possible enhancement, through anthropogenically emitted compounds of organic aerosols formation from true biogenic precursors[6,8].

VOCs of the anthropogenic origin are toxic for human and environment. First of all, they participate in the processes of smog formation. This is the reason why they are indirect primary pollutants that are regulated in the developed countries[4].

VOCs in peat are not sufficiently studied. The research of Rinnan et. al.[14] studied cyclic, aliphatic hydrocarbon, aromatic and carbonyl compounds, but this research did not provided quantitative concentrations of VOCs in peat. The present research proposes the study of quantitative concentrations of VOCs in upland peat from two bogs in Germany.

2. Methods

Two bogs located in the central part of Germany were used for the peat sampling and further investigations: Strohner Maarchen, Eifel region and Rotes Moor, Hassian Rhoen (Fig. 1). The first bog is located in agricultural and touristic region near the bottom of former volcano Eifel, the second one – in mountain region (Rhön Mountains).

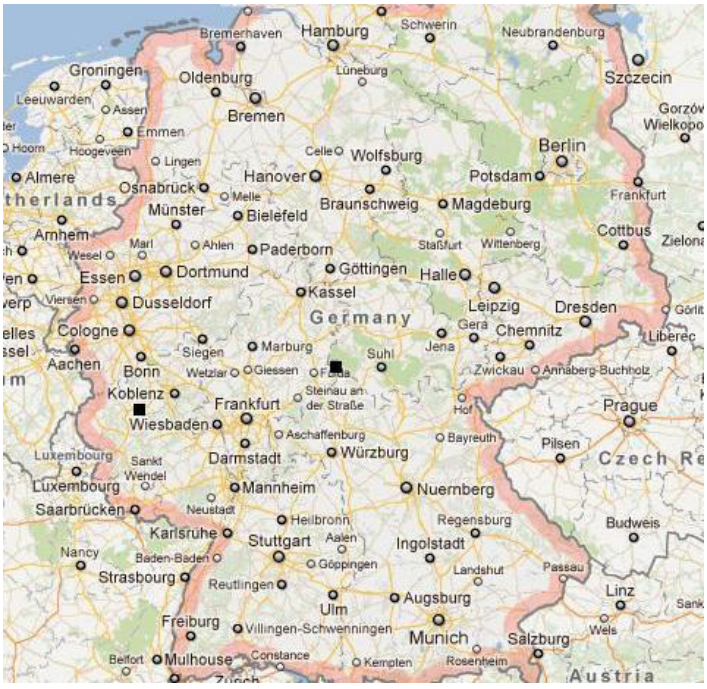

Fig. 1. The scheme of the location of the studied bogs (■)

The samples were collected by the method of open test pit to the depth of 30 cm (the stratum of active biological processes). The peat monoliths were placed into aluminium containers which were hermetically closed to avoid gas losses. Then the samples were transported to a laboratory of the Institute of Atmosphere and Environment of the Goethe University in Frankfurt am Main and studied using the highly-sensitive proton-transfer-reaction mass spectrometry (PTR-MS, Ionicon), which has been developed for the purpose of on-line trace gas monitoring[7,15].

In the PTR-MS method, a chemical ionization system, which is based on proton-transfer reactions, is applied. On-line measurements of trace compounds in air with concentrations as low as a few pptv are possible on the basis of proton transfer reactions. Online detection limit for VOCs is less than 5 pptv. The quantity measured with PTR-MS is usually the intensity of a protonated compound and for this compound the information about its mass is obtained. The PTR-MS system consists of three sections: an ion source, a drift tube, and an ion detection section. The method has a good reliability of results[5,7].

VOCs in our peat samples were measured in the gas phase emitted from the samples through holes made in the containers. One tube through one hole was connected to the charcoal filter that to supply the sample with the clean air in place of the gas emitted from the sample. Gas emissions from the second tube were measured by means of PTR-MS method.

Every sample was being scanned during 20 minutes. The scan results were displayed in the form of mass-spectrums of organic compounds. The method allows determining compounds with molar mass from 20 to 250 g/mol. The interpretation of spectrums was realized by means of the Software for PTR-MS method. VOCs concentrations have been recalculated with respect to the purified air, where VOCs concentrations were also determined.

The investigations of VOCs in natural peat ecosystems have some difficulties because of individual peculiarities of bogs in different climatic conditions. The amount and composition of VOCs in bogs depends on the bog type and botanical composition[14].

3. Results and discussion

The scan results for studied VOCs are shown in the Table 1. The column with the mean VOC concentrations in the peat samples contains the results of calculations counting the VOC concentrations in the ambient air (4th column). Isoprene and acetaldehyde are characteristic for natural plant organic emissions, and we can observe their high concentrations in both peat samples. But in the sample from Rotes Moor isoprene has two times higher concentration than in the sample of Strohner Maarchen, and acetaldehyde is two times higher in the sample of Strohner Maarchen than that from Rotes Moor. The concentrations of acetone in both samples are approximately at the same level as in the air, and for propene, butanol, benzene and toluene we observe higher concentrations in the Strohner Maarchen sample, than in Rotes Moor. Propene has three times higher contents in the peat of Strohner Maarchen. The concentrations of butanol, benzene and toluene in the Rotes Moor sample are approximately at the same level as in the ambient air.

Table 1. Concentrations of VOCs in the studied peat samples (mean for 20 minute monitoring).

Detected mass, g mol^{-1}	VOC name	Detection limit, ppb	Mean concentration in the purified air, ppb	Mean concentrations of VOCs, corrected with the purified air, ppb	
				Strohner Maarchen	Rotes Moor
1	2	3	4	5	6
43	propene	10^{-3}	0.076	0.221	0.073
45	acetaldehyde	10^{-3}	2.08	0.529	0.265
58	acetone	10^{-3}	0.223	<0.004	<0.001
69	isoprene	10^{-3}	0.062	0.111	0.202
74	butanol	10^{-3}	0.09	0.02	<0.001
78	benzene	10^{-3}	0.018	0.007	<0.001
92	toluene	10^{-3}	0.046	0.002	<0.001

The Figures 2 and 3 represent the whole measured mass spectrums of organic compounds emitted from the peat samples. Every mass-spectrum corresponds to one or several compounds. Terrestrial plants emit a wide variety of reactive organic compounds, including isoprene, terpenes and oxygenated compounds, which form an important contribution to the global budget of non-methane hydrocarbons[15].

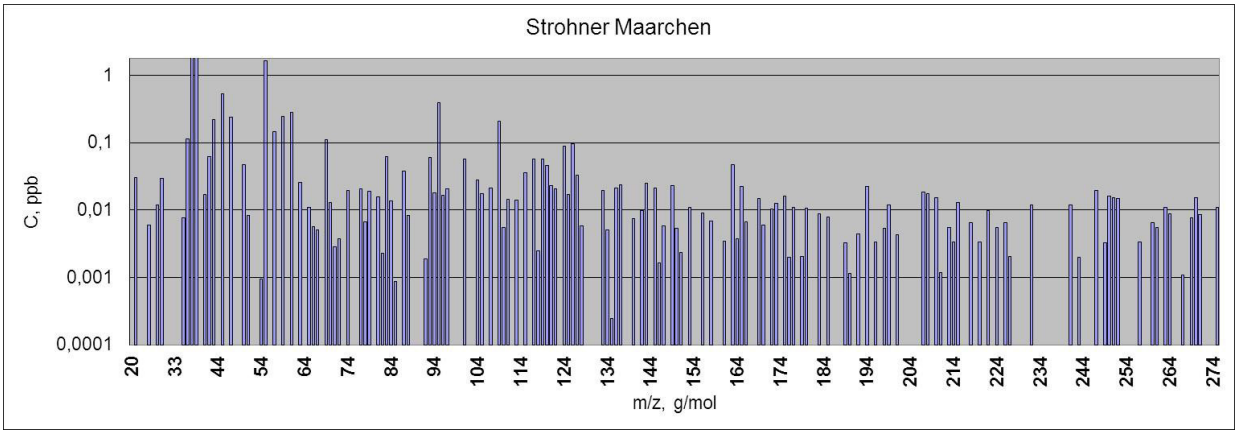

Fig. 2. Mass-spectrums of VOCs in the gas phase of the peat from Strohner Maarchen

Fig. 3. Mass-spectrums of VOCs in the gas phase of the peat from Rotes Moor

Alone with the organic substances of natural origin, emitted by bog plants in the Strohner Maarchen sample, we can observe the mass spectrums of the following organic compounds of anthropogenic origin: propene, butanol, benzene and toluene. Acetaldehyde can have both natural and anthropogenic origin. It is well known, that plants have a capability to accumulate harmful compounds from ambient air. In the case of the sample from the Strohner Maarchen we can observe a possible anthropogenic influence in the region of the bog location. Probably sphagnum mosses in our sample contains accumulated pollutants as propene, butanol, benzene and toluene, which in some quantities can be registered be means of PTR-MS. Possible sources of this influence are agricultural machines and the traffic of the nearest roads: the VOCs are emitted directly from the tailpipe from incomplete combustion[4].

Undoubtedly, it is important to take into consideration that some VOCs can have both anthropogenic and natural origin, for example, acetaldehyde.

4. Conclusion

The application of PTR-MS method, specially developed for the VOCs detection in ambient air, allowed us to determine mass-spectrums of propene, acetaldehyde, acetone, isoprene, butanol, toluene and benzene in peat samples. High concentrations of isoprene and acetaldehyde, which are naturally characteristic for plants, were determined in both samples. It is important to outline that propene, butanol, toluene and benzene have much higher concentrations in the peat sample from the bog located in the agricultural and touristic region of Eifel. Acetone and acetaldehyde, emitted by the peat, can have both natural and anthropogenic origin. Acetone in our case does not exceed its concentrations in the purified ambient air. The present research allows us to observe anthropogenic influence on the environment in the place of Eifel region.

Taking into account opportunities of the PTR-MS for the VOC detection in peat, and wide implementation of sphagnum moss and peat in environmental studies, further research of VOCs in peat is necessary.

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References

1. Andrews E, Saxena P, Musarra S, Hildemann LM, Koutrakis P, McMurry PH, Olmez I, White WH. Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements. *J Air Waste Manage Assoc* 2000; **50**: 648–664.
2. Chow JC, Watson JG, Fujita EM, Lu ZQ, Lawson DR, Ashbaugh LL. Temporal and spatial variations of PM(2.5) and PM(10) aerosol in the Southern California air-quality study. *Atmos Environ* 1994; **28**: 2061–2080.
3. Elbert W, Weber B, Burrows S, Steinkamp J, Büdel B, Andreae MO, Pöschl U. Contribution of cryptogamic covers to the global cycles of carbon and nitrogen. *Nature Geoscience* 2012; **5**: 459–462.
4. Gaffney JS, Marley NA. The impacts of combustion emissions on air quality and climate – From coal to biofuels and beyond. *Atmospheric Environment* 2009; **43**: 23–36.
5. De Gouw J, Warneke C, Karl T, Eerdekens G, van der Veen C, Fall R. Measurement of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrometry Reviews* 2007; **26**: 223-257.
6. Hallquist M, Wenger JC, Baltensperger U et al. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos Chem Phys* 2009; **9**: 5155-5236.
7. Hansel A, Jordan A, Warneke C, Holzinger R, Wisthaler A, Lindinger W. Proton-transfer-reaction mass spectrometry (PTR-MS): on-line monitoring of volatile organic compounds at volume mixing ratios of a few pptv. *Plasma Sources Sci Technol* 1999; **8**: 332–336.
8. Hoyle CR, Boy M, Donahue NM, Fry JL, Glasius M, Guenther A, Hallar AG, Huff Hartz K, Petters MD, Petäjä T, Rosenoern T, Sullivan AP. A review of the anthropogenic influence on biogenic secondary organic aerosol. *Atmos Chem Phys* 2011; **11**: 321–343.
9. Kanakidou M, Seinfeld JH, Pandis SN, Barnes I, Dentener FJ, Facchini MC, Van Dingenen R, Ervens B, Nenes A, Nielsen CJ, Swietlicki E, Putaud JP, Balkanski Y, Fuzzi S, Horth J, Moortgat GK, Winterhalter R, Myhre CEL, Tsigaridis K, Vignati E, Stephanou EG, Wilson J. Organic aerosol and global climate modelling: a review. *Atmos Chem Phys* 2005; **5**: 1053–1123.
10. Krommer V, Zechmeister HG, Roder I, Scharf S, Hanus-Illnar A. Monitoring atmospheric pollutants in the biosphere reserve Wienerwald by a combined approach of biomonitoring methods and technical measurements. *Chemosphere* 2007; **67**: 1956-1966.
11. Hutchinson SM, Armitage R. A peat profile record of recent environmental events in the South Pennies. *Water, Air and Soil Pollution* 2009; **199** (1-4): 247-259.
12. Malm WC, Sisler JF, Huffman D, Eldred RA, Cahill TA. Spatial and seasonal trends in particle concentration and optical extinction in the United-States. *J Geophys Res-Atmos* 1994; **99**: 1347–1370.
13. Mezhibor A, Arbuzov S, Rikhvanov L, Gauthier-Lafaye F. History of the pollution in Tomsk Region (Siberia, Russia) according to the study of high-moor peat formations. *Int J of Geosciences* 2011; **2**: 493-501.
14. Rinnan R, Rinnan A, Holopainen T, Holopainen JK, Pasanen P. Emission of non-methane volatile organic compounds (VOCs) from boreal peatland microcosms – effects of ozone exposure. *Atmospheric Environment* 2005; **39**: 921-930.
15. Lindinger W, Hansel A, Jordan A. On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). Medical applications, food control and environmental research. *Int J of Mass Spectrometry and Ion Processes* 1998; **173**: 191-24l.
16. Roos-Barraclough F, Martinez-Cortizas A, García-Rodeja E, Shotyk W. A 14 500 year record of the accumulation of atmospheric mercury in

peat: volcanic signals, anthropogenic influences and correlation to bromine accumulation. *Earth and Planetary science Letters* 2002; **202**: 435-451.

17. Shotyk W, Cheburkin AK, Appleby PG, Fankhauser A, Kramers JD. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotropic peat bog profile, Jura Mountains, Switzerland. *Earth and planetary science letters* 1996; **145**: E1-E7.
18. Weiss D, Shotyk W, Kempf O. Archives of atmospheric lead pollution. *Naturwissenschaften* 1999; **86**: 262–275.