limnological review

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Study of Volatile Organic Compounds in Emission from Bottom Sediments of Three Lakes with Impact of Anthropopression Using the Proton Transfer Reaction Mass Spectrometry

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Abstract: Studies of volatile organic compounds (VOCs) emitted from the bottom sediments of three Pomeranian lakes in Poland: Łazienkowskie, Rychnowskie, and Jeleń were conducted. All three lakes are subject to anthropogenic pressure but to varying degrees. In 2021, bottom sediment samples were taken from the lakes studied and an analysis of the emission of 20 volatile organic compounds was carried out using a proton transfer reaction mass spectrometer (PTR-MS). Concentrations in emissions from the bottom sediments of VOCs with the following mass–charge ratio (m/z) were analyzed: 57, 61, 63, 69, 75, 81, 83, 85, 87, 95, 97, 99, 101, 109, 111, 127, 129, 137, 149, and 157. The obtained data were analyzed by performing statistical tests and multivariate cluster and PCA analysis. The analysis shows that the lowest concentrations of VOCs were observed from bottom sediments in Lake Jeleń, which is subject to the lowest anthropopressure among the studied lakes. The analysis shows that the lowest concentrations of VOCs were observed from bottom sediments in Lake Jeleń, which is subject to lower anthropopressure among the studied lakes. With the help of cluster analysis, it was possible to collect data on the VOC concentrations into clusters, which resulted in demonstrating similarities between Łazienkowskie and Rychnowskie lakes—lakes connected by an isthmus, and the different characteristics of Lake Jeleń. PCA analysis leads to similar observations. The tested m/z VOCs can be identified using additional analytical methods.

Keywords: VOC; PTR-MS; bottom sediments; Lake Rychnowskie; Lake Łazienkowskie; Lake Jeleń

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Citation: Antonowicz, J.; Wróblewski, T. Study of Volatile Organic Compounds in Emission from Bottom Sediments of Three Lakes with Impact of Anthropopression Using the Proton Transfer Reaction Mass Spectrometry. *Limnol. Rev.* **2024**, *24*, 205–216. https://doi.org/10.3390/limnolrev24030012

Academic Editor: Piotr Klimaszyk

Received: 25 May 2024
Revised: 25 June 2024
Accepted: 3 July 2024
Published: 6 July 2024

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1. Introduction

Bottom sediments that accumulate under natural conditions at the bottom of lakes are formed as a result of material collection from soil erosion and rock weathering in the catchment area. It is a deposition place for the dead remains of plant and animal organisms. Organic and inorganic compounds are precipitated from the water column into the lake's bottom sediments [1]. Chemical compounds such as biogenic substances are released into the water column by internal loading [2]. Human activity, the development of cities, and industry, including agriculture, result in the introduction of anthropogenic pollutants into the bottom sediments of lakes. A special place is given to organic compounds, the production of which has become common over the last century in the form of urban, post-industrial, and agricultural pollution. The most persistent and dangerous organic compounds include polychlorinated biphenyls, organochlorine pesticides, polycyclic aromatic hydrocarbons [1], petroleum compounds, phenols, and their derivatives. An important group of organic pollutants in lake bottom sediments are volatile organic compounds (VOCs). VOCs occur in bottom sediments and are emitted into the atmosphere, which is felt in the form of odor. The chemical composition of bottom sediments as well as their physical properties are closely related to the properties of the lake's catchment area. Substances constantly

precipitating into the reservoir are accumulated in bottom sediments. They are a source of information about chemical, biological as well as physical phenomena occurring both in the lake and its catchment area [3]. They are a source of information about lake pollution, both current and historical [4,5]. The pollution of lakes with organic compounds in urban areas is common [6,7]. Urban pollutants are delivered to surface waters mainly by surface runoff and meltwater. Meltwater and surface runoff carry pollutants such as dust, petroleum products, materials generated by the abrasion of car tires and asphalt, salts used to thaw ice, peeling off paints and varnishes, rust filings as well as fertilizers and herbicides used in the cultivation of urban greenery [1,8,9]

Lake eutrophication processes are determined largely by anthropogenic factors. Urban pollution is also a source of biogenic substances, which in turn lead to eutrophication processes and then the decomposition processes of organic matter in lake bottom sediments. These substances may be released from lake bottom sediments or accumulated in them [5]. The chemical composition of bottom sediments is determined by the lithology of the lake catchment, climatic conditions, and the method of the development and use of the catchment [1,3]. The chemical composition of a lake's bottom sediments provides information on the rate of eutrophication of the reservoir [2]. As a consequence of surface runoff, there is an increase in the concentration of biogenic substances, as well as other pollutants in lake waters, originating from agricultural activities [5], and in the case of lakes bordering the city, from urban infrastructure [1]. As a result of the immission of pollutants into the lake, changes in the chemical and phytoplankton composition in the water column are observed, which leads to quantitative and qualitative changes in the chemical composition of lake bottom sediments [5]. Due to nutritional connections, benthic organisms play an important role in the exchange of matter between the hydrosphere and the bottom sediment [5].

The composition of the bottom sediment, especially in its surface layer, is related to the chemical and biological composition of the water column. The development of laboratory techniques has enabled the search for methods of quickly analyzing the chemical composition of bottom sediments in order to find dangerous pollutants. The PTR-MS technique enables the examination of VOC emissions from environmental samples without the need for chemical treatment, and moreover, quickly as a form of screening or comparative studies.

Volatile organic compounds are carbonaceous chemicals that evaporate readily at room temperature, are lighter than air at room temperature, and have high vapor pressure and low water solubility [10]. The main sources of VOCs in urban areas are anthropogenic activities [11,12], which include coal combustion, the use of solvents, the petrochemical industry, vehicle exhaust emissions, biomass burning, and cooking. VOCs from the air can be transported to the aquatic environment in rainwater [13].

Various techniques are used to test VOC emissions. Most of them involve taking a sample to the laboratory and using gas chromatography [14] and "Purge-and-Trap" techniques [15]. The methods of extracting VOCs present in the sample using organic solvents are also used [16]. Another method that can be used to study VOCs in sediments is proton transfer reaction mass spectrometry (PTR-MS) [17]. The PTR-MS technique is based on the so-called soft chemical ionization, i.e., one for which the fragmentation processes of the tested chemical compounds are limited. In this case, this ionization occurs through the phenomenon of proton transfer from the hydronium ion to the detected volatile substance [18]. This is one of the so-called soft ionization methods, in which the tested substance acquires an electric charge as a result of the adduction of a proton from the hydronium ion H_3O^+. The big advantage of this technique is that the measurements are made on a chemically unprocessed sample, and the measurement takes only a dozen or so seconds. This reduces the risk of sample contamination and VOC reaction during the preparation process. The PTR-MS technique is characterized by high detection sensitivity (pptV). The disadvantage of this method includes the fact that PTR–MS does not allow for the clear identification of the VOCs emitted from the samples. Mass spectra only make it possible to determine the intensity of the ion signal (or determine the concentration) for a specific mass–charge ratio

(m/z). Despite this, this method seems to be useful in comparative VOC studies or in the determination of the so-called VOC "fingerprint" of the tested samples [19,20]. PTR-MS techniques have been used for analysis in various biological samples, e.g., the studies of VOC emissions from saffron [21], apple varieties [20], strawberries [22], agricultural soils [23], soils fertilized with slurry [24], during the decomposition of organic waste [25], and sludge from sewage treatment plants [26].

The aim of the study was to demonstrate the diverse nature of the composition of volatile organic compounds in the bottom sediments of the lakes Łazienkowskie, Rychnowskie, and Jeleń, along with the indication of the possibility of using PTR-MS tests to conduct comparative statistical tests in lake bottom sediment samples.

2. Materials and Methods

2.1. Study Area

Research on bottom sediments was carried out in three lakes in the Polish Pomerania: Rychnowskie, Łazienkowskie, and Jeleń (Figure 1). The morphometric features of the lakes are presented in Table 1. The largest in terms of surface area is Lake Rychnowskie—158.7 ha; Lake Jeleń is almost half the size—88.9 ha; and Lake Łazienkowskie covers 36.2 ha. All three lakes are characterized by a significant maximum depth, and the average depth ranges from 9.5 m for Lake Jeleń to 13.1 m for Lake Rychnowskie [27]. All three lakes are located near cities and are subject to significant anthropopressure.

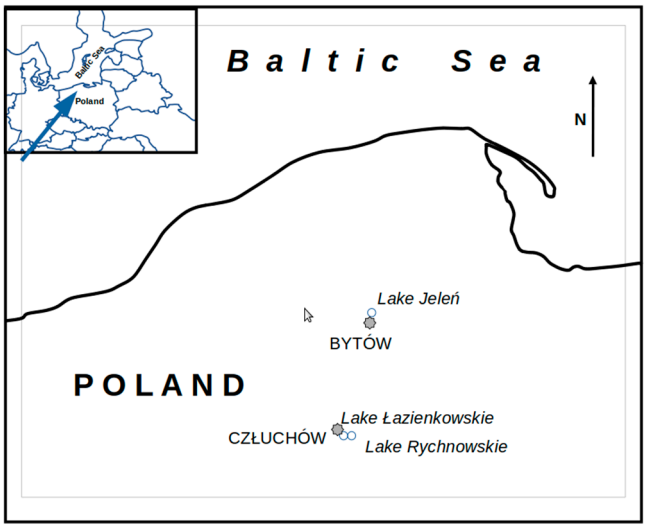

Figure 1. Location of the studied lakes on the contour map of the Polish Pomerania. The location of Pomerania on the map of northern Europe is marked on the left.

Table 1. The morphometric features of Lake Łazienkowskie, Rychnowskie, and Jeleń according to Jańczak [27].

	Lake Rychnowskie	Lake Łazienkowskie	Lake Jeleń
Latitude and longitude	53°40.5′–17°24.1′	53°38.9′–17°28.6′	53°49.6′–17°35.7′
Surface area [ha]	158.7	36.2	88.9
Volume [thous.—m^3]	20,823.0	3715.9	8461.1
Maximum depth [m]	31.5	20.5	33.2
Average depth [m]	13.1	10.2	9.5
Maximum length [m]	2565	1250	2025
Maximum width [m]	1025	405	750

Lakes Rychnowskie and Łazienkowskie are located in the Krajeńskie Lake District. They border the city of Człuchów, but Rychnowskie Lake to a much lesser extent. The Chrząstowa River flows through both lakes, connecting the lakes with an isthmus. They are dimictic lakes and undergo stratification in the summer [28]. The lakes near Człuchów can be used for tourism but according to data collected are polluted [29]. There are few studies of Łazienkowskie and Rychnowskie lakes in the literature. In the years 1994–1996, research was carried out on the water quality of these lakes. These studies showed that the waters of Lake Rychnowskie met the then standards of purity class III, while Lake Łazienkowskie was then classified as an out-of-class lake [28]. There is no heavy industry near the Człuchów lakes and the main sources of pollution in the nearby lakes are of urban origin [30]. Studies by Trojanowski and Trojanowska [28] also revealed a rapid progress in the eutrophication of these lakes and low oxygen concentrations in the layers of water above the bottom. In Lake Łazienkowskie, in the summer, a complete lack of oxygen in the hypolimnion and the appearance of hydrogen sulfide at the bottom were found. It was established that the main cause of such heavy pollution of these lakes was pollution flowing from the city [28].

Lake Jeleń is located in the Bytów Lake District in northern Poland. Lake Jeleń is one of the largest lobelia lakes in Poland. There are plant species typical of lobelia lakes, such as *Lobelia Dortmanna* and *Isoetes lacustris* [31], but trophically it is a eutrophic lake [32]. Lobelia lakes usually have landscape values that are attractive to tourists, i.e., clear waters, sandy bottom, and forested shoreline. As a result, such lakes are often subject to strong recreational pressure, which often leads to changes in the immediate catchment area [33]. Lake Jeleń is located within the city limits of Bytów and is used for tourism [32]. There is a municipal swimming area here. There is a constant deterioration of water quality in the lake caused by anthropopressure on the catchment area and directly on the lake [31].

2.2. Sampling of Bottom Sediments

Bottom sediment samples were collected in 2021 during the summer from the top layer of sediment using an Ekman grab (Eijkelkamp, Giesbeek, The Netherlands). Three research sites were designated on each of the lakes: Rychnowskie, Łazienkowskie, and Jeleń. Three samples of bottom sediments were collected at each research site. On Lake Rychnowskie, research stations were located in the eastern part (st. 1), in the middle part near the swimming area at the recreation center (st. 2), and st. 3 in the western part of the lake near the isthmus connecting with Lake Łazienkowskie. On Lake Łazienkowskie, research sites were designated in the eastern part near the isthmus connecting with Lake Rychnowskie (st. 1), in the central part (st. 2), and in the western part—closest to the urban buildings of Człuchów (st. 3). On Lake Jeleń, research sites were located as follows: st. 1—in the southern part—closer to Bytów, st. 2—in the central part, and st. 3—in the northern part.

2.3. Laboratory Analyses of Volatile Organic Compounds

The High Sensitivity Quadrupole Proton Transfer Mass Spectrometer (PTR-MS) from Ionicon Analytic GmbH (Austria) was used to examine the content of volatile organic compounds (VOCs) in fumes from bottom sediments. The bottom sediment samples weighing 15 g were placed in closed PTFE vessels with a fixed capacity of 50 mL. To avoid possible systematic memory effects from one measurement to the next, the apparatus was flushed with laboratory air between measurements. Before each measurement, mass spectra were also examined to control the signal decay to the background level [34]. The stabilized sample was connected to a tube and stable readings were used for calculations. A tube made of PTFE was inserted through the holes in the lids of the vessels, through which air from above the samples was sucked into the mass spectrometer at about 20 sccm of the gas flow rate. To avoid the condensation of VOCs on the pipe walls, it was heated to a temperature of 60 °C, similar to the work of Hansel et al. [35]. During measurements in the drift chamber, the pressure used was 2.2 mbar, temperature 60 °C, and voltage 600 V. This

corresponds to a reduced electric field value (E/N) of about 135 Td (1 Td = 10^{-17} V·cm^2). Four mass spectra were used for analysis in a stabilized atmosphere in the chamber from which the sample was aspirated. Positively ionized particles with the following mass to charge ratios (m/z) were analyzed: 57, 61, 63, 69, 75, 81, 83, 85, 87, 95, 97, 99, 101, 109, 111, 127, 129, 137, 149, and 157. 20 m/z with high concentrations were selected. When analyzing the given masses, it is taken into account that the m/z values are shifted by 1 due to the attachment of a proton to the tested molecule (e.g., m/z 57 = molecular mass 56 + mass of one proton). The results were given in the form of concentrations given by the device using the dedicated PTR-MS Viewer 3.2.12 software. Calculated estimated rating concentrations only apply to ions in the drift chamber and allow us to standardize the way the VOC results are presented according to Biasoli et al. [36]. The results given in the form of m/z concentrations in the emission from above the bottom sediments allow their normalization to the conditions prevailing in the drift chamber, i.e., pressure, temperature, and drift voltage [36]. For concentration calculations, the value of the reaction constant between the H_3O^+ ion and the molecules of the tested compounds was assumed for all m/z as 2×10^{-9} cm^3/s.

2.4. Statistical Analysis

The statistical analysis was performed in the Statistica (ver. 13.3) program [37] and in the Past (ver 4.13) statistical program using the studies of [38] and [39]. The statistical analysis included basic statistical parameters and multidimensional cluster analysis (Ward's method, Euclidean distance). To determine the type of the distribution of variables, the Kolmogorov–Smirnov test was used. If the sample had a normal distribution, ANOVA analysis with the RIR Tukey test was used. In cases of a lack of normal distribution, the non-parametric equivalent was used: the Kruskal–Wallis test and then the Dunn post hoc test.

3. Results

Table 2 presents data with the basic statistical parameters of the analyzed VOCs emitted from bottom sediments from the following lakes: Rychnowskie, Łazienkowskie, and Jeleń. The obtained average concentrations of VOC ionized particles from the three tested lakes are arranged as follows in order of increasing ion concentration for m/z: 157 < 129 < 149 < 99 < 101 < 127 < 85 < 137 < 69 < 81 < 111 < 109 < 83 < 87 < 97 < 95 < 75 < 61 < 57 < 63. High values of the coefficients of variation (CV) were observed for the following m/z: 57, 63, 75, and 97.

Table 2. Basic statistical parameters of studied VOC ionized particles [ppb] (Min—minimum value, Max—maximum value, CV—coefficients of variation).

VOC	Mean	Min	Max	CV
m/z 57	50.57	8.33	225.15	106.69
m/z 61	36.40	21.21	84.60	41.07
m/z 63	97.43	1.72	828.29	218.70
m/z 69	8.06	3.23	19.11	55.83
m/z 75	19.75	2.62	123.38	118.69
m/z 81	8.11	2.04	19.57	61.05
m/z 83	9.18	2.57	38.15	80.51
m/z 85	7.06	2.47	26.56	66.89
m/z 87	13.10	2.44	39.92	86.06
m/z 95	19.02	2.23	67.94	98.37
m/z 97	14.55	2.43	88.79	122.33
m/z 99	5.84	2.04	19.65	61.27
m/z 101	5.85	2.93	11.54	38.99
m/z 109	9.16	2.24	22.05	58.15
m/z 111	8.37	1.18	38.89	97.37
m/z 127	6.60	1.97	17.35	67.72
m/z 129	2.99	0.76	6.85	49.73
m/z 137	8.01	2.18	21.56	72.18
m/z 149	4.48	0.94	15.18	84.95
m/z 157	2.51	0.61	5.10	48.80

Statistically significant differences were found in the composition of VOCs emitted from the bottom sediments of the studied lakes. Tables 3 and 4 contain information about statistical differences between the examined sites. Statistical tests revealed significant differences between the studied lakes for 17 out of 20 VOCs analyzed (only in the case of m/z 75, 83, and 111 there were no statistical differences) (Tables 3 and 4). The clearest differences are visible for m/z: 57, 63, 75, and 97 (Figure 2). The highest VOC concentrations were found in Lake Rychnowskie for the following m/z: 57, 61, 69, 75, 81, 83, 85, 87, 101, 111, 129, 137, 149, and 157; Łazienkowskie: 63, 95, 97, 99, 109, 127. The lowest concentrations for all the tested masses were found in Lake Jeleń (Figure 2).

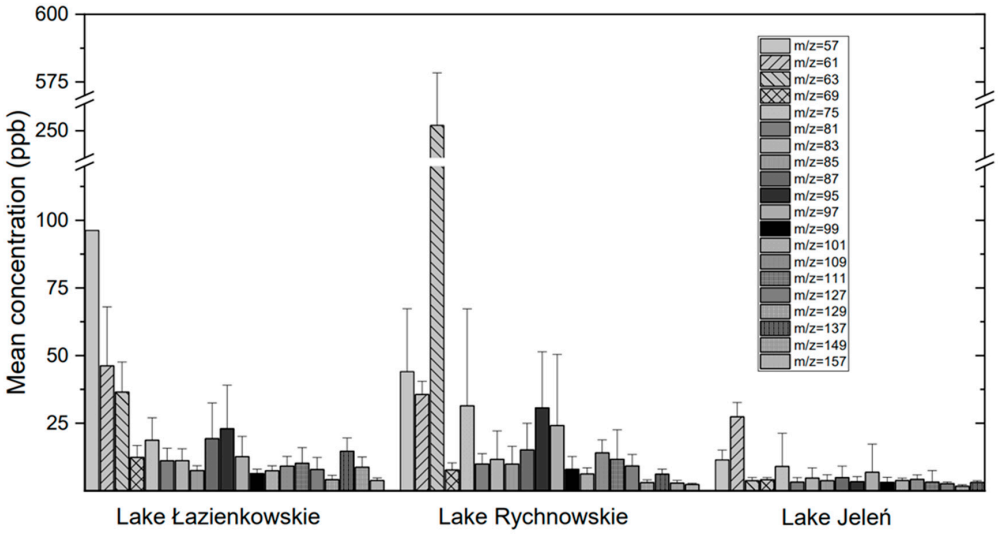

Figure 2. Mean values and standard deviations of the concentrations for the studied VOC ionized particles in the bottom sediments of Lake Łazienkowskie, Lake Rychnowskie, and Lake Jeleń.

Table 3. The result of the ANOVA test together with the Tukey RIR test calculated for the obtained m/z VOC concentrations, for which the existence of a normal distribution was demonstrated (n = 27).

ANOVA Test			RIR Tukey Test
VOC	**F**	***p***	
m/z 61	4.58	*	R-J
m/z 69	17.22	***	R-Ł, R-J, J-Ł
m/z 75	2.28	ns	ns
m/z 81	12.68	***	R-J, Ł-J
m/z 83	2.82	ns	ns
m/z 85	5.05	*	Ł-J
m/z 87	5.11	*	R-J
m/z 95	7.79	**	R-J, Ł-J
m/z 99	5.74	**	Ł-J
m/z 101	10.44	***	R-J, Ł-J
m/z 109	17.03	***	R-Ł, R-J, J-Ł
m/z 111	3.23	ns	ns
m/z 127	8.38	**	R-J, Ł-J
m/z 129	10.66	***	R-J
m/z 137	34.93	***	R-Ł, R-J
m/z 157	30.81	***	R-Ł, R-J, J-Ł

Explanations: R—Lake Rychnowskie, Ł—Lake Łazienkowskie, J—Lake Jeleń, ns—nonsignifiant, *—$p < 0.05$, **—$p < 0.01$, ***—$p < 0.001$.

Figure 3 shows the results of the cluster analysis. Two main clusters "A" and "B" were observed in the graphs for each lake. In the graph for data from Lake Jeleń, cluster "A" gathered VOCs with m/z: 57, 63, 69, 75, 81, 83, 85, 87, 95, 97, 99, 101, 109, 111, 127, and 129

and the cluster "B": 61, 137, 149, and 157. On the chart for Lake Łazienkowskie, cluster "A" included VOCs with m/z: 57, 61, 69, 75, 81, 83, 85, 87, 97, 99, 101, 111, 129, 137, and 149 and in cluster "B" with m/z: 63, 95, 109, 127, and 157, respectively, and on the chart for Lake Rychnowskie in cluster "A" the VOC masses were collected with m/z: 57, 61, 69, 81, 87, 95, 101, 109, 111, 127, and 129, and in cluster "B" with m/z: 63, 75, 83, 85, 97, 99, 137, 149, and 157. Visible VOC systems point to the origin of bottom sediments as well as the type of chemical components whose VOC concentrations correlate with each other. It was observed that the collected bottom sediments from each of the lakes, and even from the research site, have their own VOC compositions and correlation relationships. In addition, the VOC configurations of the collected bottom sediments from different lakes are likely to be felt as different odors.

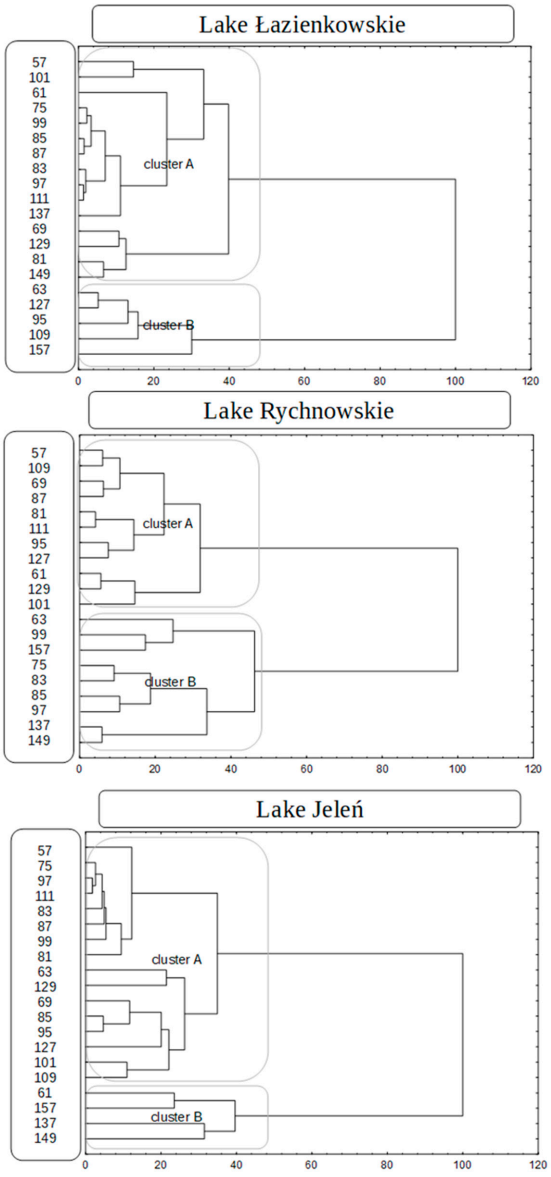

Figure 3. Multidimensional cluster analysis (calculated in Statistica software, added explanations) for m/z concentrations of VOCs obtained from bottom sediments collected from Lake Łazienkowskie, Rychnowskie, and Jeleń (Ward's method, Euclidean distance).

Table 4. The result of the Kruskal–Wallis test together with the post hoc Dunn test calculated for the obtained m/z VOC concentrations, for which the existence of a normal distribution was demonstrated (n = 27).

Kruskal–Wallis Test			Post Hoc Dunn Test
VOC	**H**	p	
m/z 57	18.84	***	R-Ł, R-J
m/z 63	17.824	***	R-Ł, R-J
m/z 97	11.25	**	R-Ł, R-J
m/z 149	18.75	***	R-Ł, R-J

Explanations: R—Lake Rychnowskie, Ł—Lake Łazienkowskie, J—Lake Jeleń, **—$p < 0.01$, ***—$p < 0.001$.

PCA analysis was performed (Figure 4). In the diagram, the clustered m/z of VOC information is observed in three areas. The data area visible on the left side of the graph (J1–J3) shows data from the bottom sediments of Lake Jeleń. The middle and right parts of the graph show data from Lake Łazienkowskie (Ł1–Ł3) and Lake Rychnowskie (R1–R3). The VOC data areas from Lake Rychnowskie partially overlap with the data area from Lake Łazienkowskie.

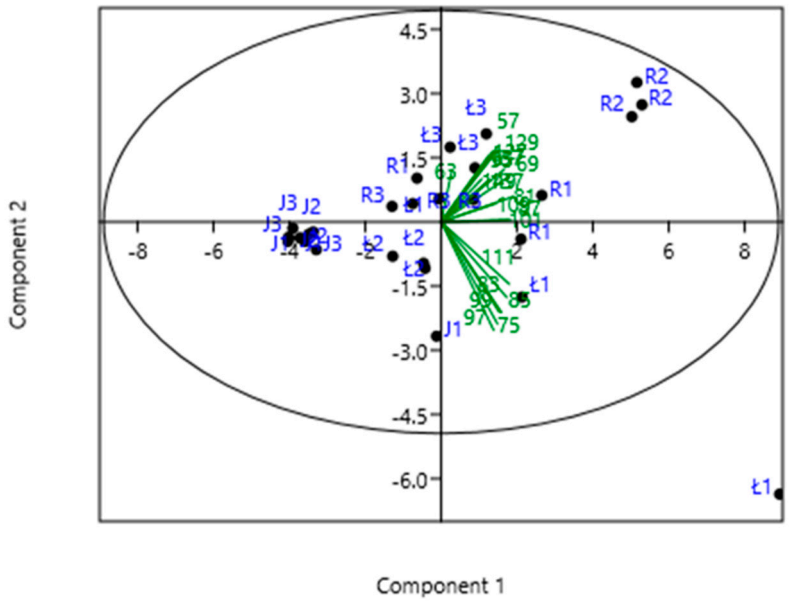

Figure 4. PCA analysis graph (calculations in the Past statistical software) for ionized VOCs taken from the Łazienkowskie Lake (Ł1–Ł3), Rychnowskie (R1–R3), and Jeleń (J1–J3) research stations. Green numbers indicate m/z VOCs.

4. Discussion

The PTR-MS method used is characterized by a very high sensitivity of detected m/z VOCs and the ability to simultaneously examine the concentration of a large number of ionized VOCs in a wide m/z range simultaneously in a short time and without the need for the chemical processing of the sample [34]. This method can be practically used in comparative studies, screening tests, and for determining the so-called "fingerprint" based on VOCs emitted from samples [19,20]. The presented work uses PTR-MS analyses to compare the odor compositions selected for the m/z analysis of VOCs emitted from the bottom sediments of three lakes using statistical methods.

The statistical analyses of the concentrations of VOCs emitted into the atmosphere made it possible to distinguish bottom sediment samples and attempt to identify them with their place of origin, i.e., lakes Jeleń, Łazienkowskie, and Rychnowskie (Tables 3 and 4). It can be noted that the statistical analysis indicates a clear distinctiveness of VOCs emitted

from the bottom sediments of Lake Jeleń in terms of the obtained VOC concentrations, which in this lake were the lowest among the analyzed bottom sediments.

All three studied lakes are lakes subject to varying degrees of anthropogenic pollution: Łazienkowskie and Rychnowskie lakes border the city of Człuchów [28] and Jeleń borders the city of Bytów [31,33]. Among the studied lakes, the one subjected to the strongest anthropopressure was Lake Łazienkowskie, which directly borders urban development, and in previous decades its waters were polluted with domestic sewage and were characterized by very polluted waters [28]. The Chrząstawa River flows through Lake Łazienkowskie and Rychnowskie, thanks to which water and pollutants are exchanged between the lakes. Lake Jeleń, although it is used as a municipal swimming area, does not directly border the main buildings of the city of Bytów and is within its forest area used for tourism [31,32]. ANOVA and Kruskal–Wallis analysis of variance, along with Tukey and post hoc Dunn tests, respectively, provided information on statistically significant differences in the observed concentrations for the individual m/z of VOCs from the bottom sediments from Lake Jeleń, Łazienkowskie, and Rychnowskie.

It was observed that there were statistical differences for most of the tested m/z of VOC. Differences were found for 17 of the analyzed 20 m/z VOCs. It was found using the RIR Tukey and post hoc Dunn tests for half of the cases that there are statistically significant differences in the emitted m/z VOCs between the examined bottom sediments from lakes Jeleń, Łazienkowskie, and Rychnowskie. Of these, 21 out of 33 different results concerned VOC results from the bottom sediments of Lake Jeleń compared to Człuchów lakes. The statistical analysis of PCA (Figure 4) shows that there is a difference between the bottom sediments of Lake Jeleń and the lakes Rychnowskie and Łazienkowskie. Moreover, VOC emissions from Lake Rychnowskie and Łazienkowskie were partly similar. These similarities are probably due to the common source of pollution for all the Człuchów lakes, which is the city. It is noticeable that in Figure 4 presented PCA analysis, the symbols of the position R2 are significantly distanced on the graph from the other symbols. This is probably due to anthropogenic pollution of the R2 site (on Lake Rychnowskie). The R2 site is located near the bathing area and recreational centers, which probably provide pollution to the lake. In addition, tourists using the bathing area probably disturb the lake bottom by releasing substances accumulating in the bottom sediments into the water.

It is probable that some of the VOC compounds emitted from bottom sediments were related to urban and tourist pollution. The literature analysis shows that the presented m/z values may correspond to the following chemical compounds: acetic acid (m/z = 61) and dimethyl sulfide (m/z = 63) [40], methylketene and butene (m/z = 57) [41], methyl acetate (m/z = 75) [42], dimethyl disulfide and phenol (m/z = 95) [24], propanoic acid (m/z = 75), hex-2-enal (m/z = 99), trans-hex-2-en-1-ol, cis-hex-2-en-1-ol, hexanal (m/z = 101), benzyl alcohol (m/z = 109), 3-phenyl propanol (m/z = 137) [43], as well as butanol, which is fragmented during ionization to m/z = 57 [14]. Some of these compounds are the natural products of organic matter decomposition, such as acetic acid, propanoic acid, and methyl acetate. However, phenols and their derivatives are anthropogenic pollutants [44]. Dimethyl disulfide may appear in bottom sediments with poor oxygen conditions [45] as soon as in wastewater and manure [46]. In the Łazienkowskie and Rychnowskie lakes, poor oxygen conditions and even oxygen deficits were observed. With this in mind, it is likely that the dimethyl sulfide exist in the bottom sediments of these lakes.

The analysis of statistical differences calculated using statistical tests combined with cluster analysis provide further information about the VOC samples studied. Cluster analysis presents correlation relationships [39] between VOCs occurring in the same areas and mutually correlating concentrations.

PCA analysis combined with variance analysis (Tables 3 and 4) are tools indicating the distinctiveness of the tested m/z VOC concentrations in bottom sediments from Lake Jeleń, Rychnowskie, and Łazienkowskie. Although the tested VOCs occurred in each of the studied lakes, they differed significantly from each other, and PCA analysis (Figure 4) showed that bottom sediment samples from the studied lakes showed different concentra-

tions of the same VOCs. PCA analysis indicates a clear difference between VOCs emitted from the bottom sediments of Lake Jeleń and the bottom sediments of Lake Rychnowskie and Łazienkowskie. Clear differences were visible between Lake Jeleń and the Człuchów lakes, which are subject to stronger anthropogenic pressure. In their research, Trojanowski and Trojanowska [28] indicated a high degree of urban pollution in Człuchów lakes and recommended recultivation procedures for Lake Łazienkowskie.

5. Summary

PTR-MS analysis is an interesting alternative to other measurement techniques. Not only does it enable the quick and effective examination of bottom sediments directly in the sample without chemical interference, but it also limits the fragmentation of the molecular ions of the tested substances, which facilitates the analysis of mass VOC and reduces errors made in chemical analysis. It allows us to quickly scan the fumes of VOC and adjust selected peaks to create a "fingerprint", which helps identify pollutants or the type of bottom sediments. However, the main disadvantage of the method is the inability to directly identify the composition of the sample. Identification is possible when this technique is combined with chemical methods such as gas chromatography (GC). However, thanks to the use of PTR-MS, it is possible to quickly identify anthropogenic pollutants. In the studied lakes, higher concentrations of the tested VOCs were found in the Człuchów lakes than in the Lake Jeleń. VOC research using PTR-MS has so far been used, among others, to analyze water pollution, sewage, and sludge from sewage treatment plants. To the authors' knowledge, in this work, this technique was used for the first time for the comparative analysis of VOCs emitted from lake bottom sediments.

Author Contributions: Conceptualization, J.A. and T.W.; methodology, J.A. and T.W.; software, J.A.; validation, T.W.; formal analysis T.W., investigation, J.A. and T.W.; resources, J.A. and T.W.; writing—original draft preparation, J.A. and T.W.; writing—review and editing, J.A. and T.W.; visualization, J.A. and T.W.; project administration, J.A.; funding acquisition, J.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by internal Pomeranian University in Słupsk grant, no. 21.4.14.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the author/s.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bojakowska, I.; Dobek, P.; Kucharzyk, J. Geochemical characteristics of sediments of reservoir zadębie in Skierniewice. *Biul. Państwowego Inst. Geol.* **2017**, *470*, 9–16. [CrossRef]
2. Szymański, D.; Dunalska, J.; Łopata, M.; Bigaj, I.; Zieliński, R. Characteristics of bottom sediments of Lake Widryńskie. *Limnol. Rev.* **2012**, *12*, 205–210. [CrossRef]
3. Aleksander-Kwaterczak, U.; Kostka, A. Lead in the environment of Lake Wigry (NE Poland). *Limnol. Rev.* **2011**, *11*, 59–68. [CrossRef]
4. Januszkiewicz, T. Chemistry of recent sediment of Grabowskie Lake in Kustubian Lakes District in northern Poland. *Pol. Arch. Hydrobiol.* **1980**, *27*, 319–336.
5. Trojanowski, J.; Bruski, J. Chemical and physical characteristics of bottom sediment top layer in Rzuno lake. *Arch. Environ. Prot.* **2003**, *29*, 135–148.
6. Sekabira, K.; Origa, O.H.; Basamba, T.A.; Mutumba, G.; Kakudidi, E. Assessment of heavy metal pollution in the urban stream sediments and its tributaries. *Int. J. Environ. Sci. Technol.* **2010**, *7*, 435–446. [CrossRef]
7. Bojakowska, I.; Lech, D.; Jaroszyńska, J. Heavy metals in sediments of water bodies in the Służew stream catchment (Warsaw area). *NREI* **2014**, *25*, 27–33. [CrossRef]
8. Legret, M.; Pagotto, C. Heavy metal deposition and soil pollution along two major rural highways. *Environ. Technol.* **2006**, *27*, 247–254. [CrossRef]
9. Guney, M.; Onaya, T.; Copty, N. Impact of overland traffic on heavy metal levels in highway dust and soils of Istanbul, Turkey. *Environ. Monit. Assess.* **2009**, *164*, 101–110. [CrossRef]
10. Carroll, G.T.; Kirschman, D.L. A peripherally located air recirculation device containing an activated carbon filter reduces VOC levels in a simulated operating room. *ACS Omega* **2022**, *7*, 46640–46645. [CrossRef]

11. Legreid, G.; Lööv, J.B.; Staehelin, J.; Hueglin, C.; Hill, M.; Buchmann, B.; Prevot, A.S.H.; Reimann, S. Oxygenated volatile organic compounds (OVOCs) at an urban background site in Zürich (Europe): Seasonal variation and source allocation. *Atmos. Environ.* **2007**, *41*, 8409–8423. [CrossRef]
12. Norris, C.; Fang, L.; Barkjohn, K.K.; Carlson, D.; Zhang, Y.; Mo, J.; Li, Z.; Zhang, J.; Cui, X.; Schauer, J.J.; et al. Sources of volatile organic compounds in suburban homes in Shanghai, China, and the impact of air filtration on compound concentrations. *Chemosphere* **2019**, *231*, 256–268. [CrossRef] [PubMed]
13. Kuráň, P.; Soják, L. Environmental analysis of volatile organic compounds in water and sediment by gas chromatography. *J. Chromatogr. A* **1996**, *733*, 119–141. [CrossRef]
14. Bianchi, A.P.; Varney, M.S.; Phillips, J. Analysis of volatile organic compounds in estuarine sediments using dynamic headspace and gas chromatography—Mass spectrometry. *J. Chromatogr. A* **1991**, *542*, 413–450. [CrossRef]
15. Campillo, N.; Aguinaga, N.; Viñas, P.; López-García, I.; Hernández-Córdoba, M. Speciation of organotin compounds in waters and marine sediments using purge-and-trap capillary gas chromatography with atomic emission detection. *Anal. Chim. Acta* **2004**, *525*, 273–280. [CrossRef]
16. Amaral, O.C.; Olivella, L.; Grimalt, J.O.; Albaiges, J. Combined solvent extraction-purge and trap method for the determination of volatile organic compounds in sediments. *J. Chromatogr. A* **1994**, *675*, 177–187. [CrossRef]
17. Blake, R.S.; Monks, P.S.; Ellis, A.M. Proton-transfer reaction mass spectrometry. *Chem. Rev.* **2009**, *109*, 861–896. [CrossRef] [PubMed]
18. Romano, A.; Capozzi, V.; Spano, G.; Biasioli, F. Proton transfer reaction–mass spectrometry: Online and rapid determination of volatile organic compounds of microbial origin. *Appl. Microbiol. Biotechnol.* **2015**, *99*, 3787–3795. [CrossRef] [PubMed]
19. Roslund, K.; Lehto, M.; Pussinen, P.; Hartonen, K.; Groop, P.H.; Halonen, L.; Metsälä, M. Identifying volatile in vitro biomarkers for oral bacteria with proton-transfer-reaction mass spectrometry and gas chromatography-mass spectrometry. *Sci. Rep.* **2021**, *11*, 16897. [CrossRef]
20. Ciesa, F.; Höller, I.; Guerra, W.; Berger, J.; Dalla Via, J.; Oberhuber, M. Chemodiversity in the Fingerprint Analysis of Volatile Organic Compounds (VOCs) of 35 Old and 7 Modern Apple Cultivars Determined by Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) in Two Different Seasons. *Chem. Biodivers.* **2015**, *12*, 800–812. [CrossRef]
21. Nenadis, N.; Heenan, S.; Tsimidou, M.Z.; Van Ruth, S. Applicability of PTR-MS in the quality control of saffron. *Food Chem.* **2016**, *196*, 961–967. [CrossRef] [PubMed]
22. Granitto, P.M.; Biasioli, F.; Aprea, E.; Mott, D.; Furlanello, C.; Märk, T.D.; Gasperi, F. Rapid and non-destructive identification of strawberry cultivars by direct PTR-MS headspace analysis and data mining techniques. *Sens. Actuators B* **2007**, *121*, 379–385. [CrossRef]
23. Schade, G.W.; Custer, T.G. OVOC emissions from agricultural soil in northern Germany during the 2003 European heat wave. *Atmos. Environ.* **2004**, *38*, 6105–6114. [CrossRef]
24. Feilberg, A.; Bildsoe, P.; Nyord, T. Application of PTR-MS for Measuring Odorant Emissions from Soil Application of Manure Slurry. *Sensors* **2015**, *15*, 1148–1167. [CrossRef] [PubMed]
25. Mayrhofer, S.; Mikoviny, T.; Waldhuber, S.; Wagner, A.O.; Innerebner, G.; Franke-Whittle, I.H.; Märk, T.D.; Hansel, A.; Insam, H. Microbial community related to volatile organic compound (VOC) emission in household biowaste. *Environ. Microbiol.* **2006**, *8*, 1960–1974. [CrossRef]
26. Byliński, H.; Barczak, R.J.; Gębicki, J.; Namieśnik, J. Monitoring of odors emitted from stabilized dewatered sludge subjected to aging using proton transfer reaction—Mass spectrometry. *Environ. Sci. Pollut. Res.* **2019**, *26*, 5500–5513. [CrossRef] [PubMed]
27. Jańczak, J. *Atlas Jezior Polski*; Tom 1 and 2; Bogucki Wydawnictwo Naukowe: Poznań, Poland, 1997.
28. Trojanowski, J.; Trojanowska, C. Stan zanieczyszczenia jezior człuchowskich. *Arch. Environ. Prot.* **1999**, *25*, 91–109.
29. Kołsut, B. *Chojnicko-Człuchowski Zespół Miejski. Poziom Rozwoju i Wzajemne Powiązania*; Bogucki Wydawnictwo Naukowe: Poznań, Poland, 2012; p. 82.
30. Antonowicz, J.P.; Kozak, A. Phytoneuston and Chemical Composition of Surface Microlayer of Urban Water Bodies. *Water* **2020**, *12*, 1904. [CrossRef]
31. Klimaszyk, P.; Borowiak, D.; Piotrowicz, R.; Rosińska, J.; Szeląg-Wasielewska, E.; Kraska, M. The Effect of Human Impact on the Water Quality and Biocoenoses of the Soft Water Lake with Isoetids: Lake Jeleń, NW Poland. *Water* **2020**, *12*, 945. [CrossRef]
32. Klimaszyk, P.; Kraska, M.; Piotrowicz, R. Jeziora lobeliowe w badaniach Zakładu Ochrony Wód UAM. In *Ekosystemy Wodne. Funkcjonowanie, Znaczenie, Ochrona i Rekultywacja*; Budzyńska, A., Dondajewska-Pielka, R., Rosińska, J., Kozak, A., Kowalczewska-Madura, K., Eds.; Bogucki Wydawnictwo Naukowe: Poznań, Poland, 2019.
33. Kraska, M.; Dąbrowska, B.B.; Pełechaty, M. Roślinność oraz stężenia substancji biogennych i humusowych w ekotonach wybranych jezior lobeliowych. In *Ekotony Słodkowodne: Struktura—Rodzaje—Funkcjonowanie*; Radwan, S., Ed.; Wydawnictwo UMCS: Lublin, Poland, 1998; pp. 89–98.
34. Wróblewski, T.; Kamińska, A.; Włodarkiewicz, A.; Ushakou, D. Studies of volatile organic compounds emission from fragaria vesca and fragaria ananassa using proton transfer reaction mass spectrometry. *Acta Phys. Pol. B Proc. Suppl.* **2020**, *12*, 899–906. [CrossRef]
35. Hansen, M.J.; Adamsen, A.P.S.; Feilberg, A. Recovery of Odorants from an Olfactometer Measured by Proton-Transfer-Reaction Mass Spectrometry. *Sensors* **2013**, *13*, 7860–7871. [CrossRef]

36. Biasioli, F.; Gasperi, F.; Aprea, E.; Mott, D.; Boscaini, E.; Mayr, D.; Märk, R.D. Coupling proton transfer reaction− mass spectrometry with linear discriminant analysis: A case study. *J. Agric. Food Chem.* **2003**, *51*, 7227–7233. [CrossRef]
37. StatSoft Inc. *Statistica (Data Analysis Software System)*; Version 13.3; TIBCO Software Inc.: Palo Alto, CA, USA, 2017.
38. Hammer, Ø.; Harper, D.A.T.; Ryan, P.D. PAST: Paleontological Statistics software package for education and data analysis. *Palaeontol. Electron.* **2001**, *4*, 1–9.
39. Hammer, Ø. PAST. In *Paleontological Statistics. Reference Manual*; Natural History Museum, University of Oslo: Oslo, Norway, 2023.
40. Mancuso, S.; Taiti, C.; Bazihizina, N.; Costa, C.; Menesatti, P.; Giagnoni, L.; Arenella, M.; Nannipieri, P.; Renella, G. Soil volatile analysis by proton transfer reaction-time of flight mass spectrometry (PTR-TOF-MS). *Appl. Soil Ecol.* **2015**, *86*, 182–191. [CrossRef]
41. Jordan, A.; Haidacher, S.; Hanel, G.; Hartungen, E.; Märk, L.; Seehauser, H.; Schottkowsky, R.; Sulzer, P.; Märk, T.D. A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). *Int. J. Mass Spectrom.* **2009**, *286*, 122–128. [CrossRef]
42. Jardine, K.; Wegener, F.; Abrell, L.; Van Haren, J.; Werner, C. Phytogenic methyl acetate. *Plant Cell Environ.* **2014**, *37*, 414–424. [CrossRef]
43. Pyysalo, T.; Honkanen, E.; Hirvi, T. Volatiles of wild strawberries, Fragaria vesca L., compared to those of cultivated berries, Fragaria x ananassa cv. Senga Sengana. *J. Agric. Food Chem.* **1979**, *27*, 19–22. [CrossRef]
44. Wang, M.; Zhang, Y.; Sun, J.; Huang, C.; Zhai, H. Current status of phenolic pollution in urban lakes and its toxicity to cells—A case study of Xi'an, China. *Arch. Environ. Prot.* **2023**, *49*, 63–73.
45. Lomans, B.P.; Smolders, A.; Intven, L.M.; Pol, A.; Op, D.; Van Der Drift, C. Formation of dimethyl sulfide and methanethiol in anoxic freshwater sediments. *Appl. Environ. Microbiol.* **1997**, *63*, 4741–4747. [CrossRef]
46. Lee, C.-L.; Brimblecombe, P. Anthropogenic contributions to global carbonyl sulfide, carbon disulfide and organosulfides fluxes. *Earth—Sci. Rev.* **2016**, *160*, 1–18.

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