Book of Abstracts

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The Isotope Workshop XV of the European Society for Isotope Research

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JUNE • 23-27 • 2019

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O-1

THIS IS WHAT STABLE ISOTOPES CAN DO FOR YOU IN WATER STUDIES

Grzegorz Skrzypek

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Many lakes, rivers and groundwater aquifers around the world are experiencing increasing water quality degradation arising from industrial pollution, municipal wastewater discharge and intensification of farming and agriculture [1, 2, 3]. In addition, manipulation of groundwater levels associated with water extraction for consumption, irrigation and mine site dewatering frequently induces undesired water mixing between different aquifers and acid rock drainage [2]. Therefore, the major question requiring an answer to address water quality problems is often: What are the fates of water molecules and solutes?

Traditional hydrochemical and hydrogeological techniques are inadequate when evaluating the relative contributions of water inputs from multiple sources, and the sources of pollution are often difficult to identify and distinguish. However, multiple stable HCNOS and Sr isotope tracers, in combination with major ion analysis, can disentangle many challenging environmental problems. Water and pollution sources can be decoupled by simultaneously analysing solutes and the stable hydrogen and oxygen isotope composition of water molecules [4]. The stable composition of water molecules can be used as a proxy for hydrological processes, thereby allowing the estimation of evaporative losses, the connectivity between different aquifers, and the relative contributions of different water pools [5]. The most commonly used stable isotope tracers in water quality studies are: 1) the solutes $\delta^{15}N(NO_3)$, $\delta^{18}O(NO_3)$, $\delta^{34}S(SO_4)$, $\delta^{18}O(SO_4)$ and $\delta^{13}C(DIC)$; 2) the particulate organic matter $\delta^{13}C(POM)$ and $\delta^{15}N(POM)$; and 3) water molecules $\delta^{2}H(H_2O)$ and $\delta^{18}O(H_2O)$ [4].

This presentation will provide an overview of the possible applications of stable isotope tracers and major ion hydrochemistry. Illustrative case studies will be introduced from various projects conducted in Western Australia, the USA, the Caribbean and Southeast Asia [1, 2, 3, 5].

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TRIPLE ISOTOPE ANALYSES OF WATER: EMERGING APPLICATIONS IN HYDROLOGY

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Stable isotopes of water (^2H and ^{18}O) are well-established tools in groundwater hydrology. They help to identify the origin of water (e.g. meteoric vs. non-meteoric, recent infiltration vs. infiltration under different climatic regime), they provide information about residence time of water, they help to quantify mixing patterns of various water types as well as serve as indicators of the elevation of recharge areas in mountainous regions and help to identify and quantify interactions between groundwater and dependent ecosystems, just to name few.

Because isotopologues of water containing the ^{17}O isotope ($^1H_2{}^{17}O$) occur in nature in significantly lower abundances compared to $^1H_2{}^{18}O$ and, consequently, are more difficult to measure, applications of stable isotopes of water have, from the beginning, focused on $^1H_2{}^{18}O$ and $^1H^2H^{16}O$ molecules. Only during the last decades, the potential of $^1H_2{}^{17}O$ isotopologue for studying water cycle has been gradually recognised [1,2]. Recent advances in laser spectroscopy resulted in the construction of commercial laser analysers capable of simultaneous analyses of ^2H, ^{18}O and ^{17}O content in water, with measurement uncertainties comparable ($\delta^{18}O$) or surpassing (δ^2H) those routinely achieved by off-line sample preparation methods combined with conventional IRMS technique [3, 4]. This creates opportunities for a wider use of triple isotope analyses of water in studies of the hydrological cycle.

We present here our ongoing efforts to explore in a systematic way the potential of triple isotope analyses of water in hydrology. We employ for this purpose Picarro L2140-*i* CRDS spectrometer capable of simultaneous, high-precision analyses of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ in water samples of various nature. The following examples demonstrating the potential of triple isotope analyses of water in hydrology will be presented and discussed in some detail:

(i) quantification of the extent of interaction between recent infiltration waters and diagenetic waters in the Wysowa Spa region (southern Poland),

(ii) assessment of the origin of heavy brines in the Klodawa Salt Mine (central Poland),

(iii) triple isotope balance of groundwater-dominated lake.

Reference will be also made to triple isotope monitoring of daily precipitation at two sites of contrasting characteristics, located in southern Poland: lowland urban site (Krakow) and high-altitude mountainous location (Kasprowy Wierch).

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TRITIUM AND STABLE ISOTOPES IN PRECIPITATION OF RM. VALCEA – ROMANIA

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The Romanian climate ranges from temperate to continental climate. Situated in the southeastern part of the Europe, midway to North Pole and equator on 45° parallel, it has various influences from Atlantic Ocean, Baltic Sea, Adriatic Sea and Black Sea. The relief induces significant modifications first of all due to its altitude and second of all due to the orientation of mountain chains: temperature drops depending on height and precipitation quantities increase at high altitudes. Valley corridors and depressions are responsible for deviations of air currents and "foehn effect", conducting to specific behavior of isotopes in precipitation in different country's regions.

Without being established a Romanian network of Isotopes in precipitation, one can find dedicated publications of stable isotopes composition of precipitation in north-west region [1], at Cluj, or north-east region [2], at Suceava, each locations having short period of observation of no more than 3 years. The longer data sets (δ^2H, δ^{18}O, ^{3}H) is for Rm. Valcea location (2012-2018), part of Global Network of Precipitation (GNIP). Tritium activity concentrations were published and evaluated until 2016 [3], establishing an annual mean around 10 TU, value similar with the records of Vienna station from GNIP. Therefore the main purpose of this paper is to present records of stable isotope composition in Rm. Valcea precipitation in relation to meteorological parameters (e.g. air temperature, precipitation amount) for the period 2012-2018, and to compare them with the published data from other country's regions.

The monitored location (237 m above sea level, latitude: 45°02'07" N, longitude: 24°17'03" E) has the particularities of Oltenia region which Rm. Valcea is part of. Oltenia is located in the S-W of Romania and it is at the crossroad of baric centers from Mediterranean Sea, Atlantic Ocean, Russian Plain, North Africa, and Scandinavian Peninsula. Winds have a higher frequency on the NS direction due to Sub-Carpathian Hills and Carpathian Mountain. The movement of air masses is along the Olt river (the surface water in the monitored area) on the NS direction and with average speeds not higher than 1-1.7m/s. The relative air humidity varies during a year, the highest values being recorded in the month of

December (92.5%) and the lowest in July and August (approx. 53%). The average value is around 75.8%.

The mean annual temperature for 2012-2018 period was between 11.4 °C in 2013 and 12.6 °C in 2015, with an average of the period of 11.9 °C (1.9 °C higher than the mean temperature of 1961-1990 period). The maximum monthly temperature of 26.3 °C was recorded in July 2012, and the minimum monthly temperature of -4.7 °C was recorded in February 2012. The annual amounts of precipitation varied between 624.8 mm in 2016, and 1095.7 mm in 2014, with an average of the period of 757.3 mm. The average level of precipitations recorded during 30 years period (1961-1990) for Rm. Valcea is 698.5 mm, the precipitation amount of the period 2012-2018 being with 8.4% above the normal level of this location. Three months without precipitation were recorded during this period, March 2012, December 2013 and December 2016. The minim amount of precipitation of 4.5 mm was recorded in January 2017, and a maximum of 233.8 mm was recorded in July 2014. Under these circumstances, the Köppen Climate Classification subtype for the city of Ramnicu Valcea is Dfb: Warm Summer Continental Climate [4].

The mean values for δ^2H and δ^{18}O were -59.76 ‰ and -8.24 ‰, and the weighted means to the amount of precipitation were -58.02‰ and -8.15‰. Deuterium excess values range between -23.7‰ and 24.2‰, with an amount weighted mean of 7.2‰ and a mean of 6.2‰, low values occurring during summer and high values during winter months.

The precipitation local meteoric water line using least square fit (LSF) results in $\delta^2H = (7.15\pm0.17)x\delta^{18}O - (0.5\pm1.37)$. The orthogonal regression (reduced major axis, RMA) give a local meteoric water line described by the equation $\delta^2H = (7.46\pm0.14)x\delta^{18}O + (1.6\pm0.26)$. The higher slope of the correlation of deuterium and ^{18}O data was obtained applying precipitation amount weighted least square regression (PWSLR), [5], conducting to $\delta^2H = (7.57\pm0.14)x\delta^{18}O + (3.64\pm1.25)$. The δ^2H and δ^{18}O values of the monthly precipitation and monthly air temperature (T) present a significant temperature dependent seasonality: $\delta^{18}O = 0.41T-13.31$ ($r^2 = 0.73$, n=81), and $\delta^2H = 3.06T-98.11$ ($r^2 = 0.72$, n=81), common behavior observed in other Romanian locations [6]. The same dependence seems to be on the amount of the precipitation, summer months having higher rainfall during the year, influence shown by the monthly mean of a long period of observations, not only for stable isotopes, but for tritium also [7]. This particularity and its significance in hydrogeological study have to be investigated into more details.

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O-4

ASSESMENT OF TRITIUM AND HYDROCHEMISTRY OF SURFACE WATER AND GROUNDWATER IN BABENI-VALEA MARE AREA – PRELIMINARY RESULTS

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Groundwater is one of the most important resources on earth, being crucial for human life. The quality of water depends on the geological environment, natural changes and movements and human activities. The demands for fresh water nowadays includes: irrigation, household consumption and industrial use. Giving the fact that small Romanian urban areas, like the Babeni-Valea Mare area, have a certain peculiarity regarding drinking water (use different water sources, from the county potable water provider to wells and springs in the area).

Tritium (3H), a radioisotope of hydrogen with a half-life of 4500±8 days, is an effective and useful environmental tracer for studying hydrological systems especially in identifying young waters contribution to the groundwater [1]. Its isotopic concentration is not undergoing any changes by chemical reaction in the aquifer, except decay and minor fractionation during phase changes. This minor change is insignificant in studying hydrological systems, and therefore can be neglected [2]. Tritium is an excellent indicator of modern recharge inputs in shallow groundwater and provides valuable information on processes involved in the past 70 years in the studied aquifer area [3].

A chemical parameter involved in the recharge of the aquifer can be considered concentration of dissolved oxygen (DO). Dissolved oxygen analysis measures the amount of gaseous oxygen (O_2) dissolved in an aqueous sample. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement), and as a waste product of photosynthesis [4], by itself giving some information about the movements of the studied groundwaters and their mixing with another type of water (surface water or precipitation). Among the physico-chemical parameters also used in hydrological studies can be mentioned: alkalinity, total dissolved solids, pH, electrical conductivity (EC), sulfate, chloride, nitrate, nitrite, ammonium and phosphate concentration, and main cation concentrations, like sodium, potassium, calcium and magnesium [3, 5, 6]. These parameters, together with tritium concentration in collected samples, can give information about drinking water sources vulnerability.

In this paper we identified some physico-chemical parameters that can be followed, including tritium concentration, in order to establish type of aquifer, confined or unconfined, contaminated locations, and general hydrochemical characteristics of Babeni-Valea Mare area, giving the local specific as small urban area. This area has a surface of approximately 32 km^2 and the sampling points were established as follow: 3 drillings, 4 springs, 19 wells and 6 surface waters (rivers and permanent streams). All the mentioned physico-chemical parameters were determined, in-situ (pH, conductivity, alkalinity as HCO_3^-, and DO, sulfate, phosphate, nitrite, nitrate and ammonium concentrations) or in the laboratories of our institute (tritium concentration or chloride concentrations, and also sodium, potassium, calcium and magnesium concentrations).

Tritium concentration was determined using liquid scintillation counting (LSC) method, with a low level scintillation spectrometer Quantullus 1220 from PerkinElmer. Concentration of DO, together with pH and EC, were determined using a WTW Multi 3630 IDS, directly from the water sources (drillings, springs or surface waters) or from the bottom of water collumn in the wells. A multiparameter HACH SL 1000 was used for in-situ determination of alkalinity, phosphate, nitrite and ammonium concentrations. Sulfate concentrations were determined with a portable equipment from HANNA Instruments (HI 96751C) and nitrate concentrations were determined with a portable photocolorimeter from HACH (Pocket Colorimenter II – Nitrate).

Preliminary results obtained for tritium concentration indicated that some of the drillings, springs or wells are influenced, more or less, to the precipitation, whose tritium concentration for our area is around annual average of 11 TU [7]. This information, correlated with the DO concentration, conducted to the establishing the locations witch are less influenced by the atmosphere and precipitations (Figure 1), the locations presenting lower tritium concentrations (<5 TU) and lower DO concentrations (< 3 mg/L) being the ones less exposed to the external environment.

Also the hydrochemical characteristics of all studied samples were within the normal range, for the type of water studied (drinking water or surface water), except two wells with higher nitrate concentrations (71 mg/L and 76 mg/L), more elevated than normal limit in drinking water (50 mg/L). In order to establish witch of the locations in the studied area are more exposed to the external environment we will have to do an one year survey.

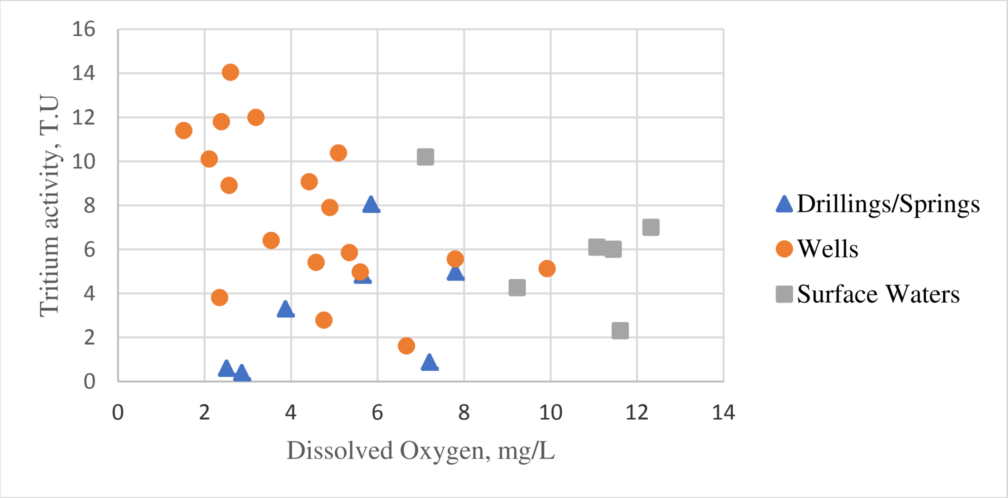

Figure 1. *Correlation between tritium activity and dissolved oxygen, in 31 locations from Babeni-Valea Mare area, Valcea County*

Acknowledgments: This paper was prepared in connection with the work done for project PN 18 12 03 04, part of Core Program ICSI 4E supported by the Romanian Ministry of Research and Innovation, and monitoring program of Tritium Removal facility PESTD.

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GROUNDWATER FLOW HISTORY IN THE BALTIC ARTESIAN BASIN (BAB) A SYNTHESIS OF NUMERICAL MODELS AND HYDROGEOCHEMICAL DATA

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In this study of the Cambrian aquifer system in the Baltic Artesian Basin (Fig.1), chemistry, stable isotopes, noble gases, and dating tracers were combined for a better understanding of flow and recharge dynamics of the system over the last one million years. We find that the variability in chemical composition, stable isotopes and noble gas concentrations in the basin is predominately controlled by mixing of three distinct water masses: Holocene and Pleistocene interglacial meteoric water, glacial meltwater, and a brine end member. Thanks to its inertness, constant atmospheric input function, and its insensitivity to degassing, ^{81}Kr turns out to be a nearly ideal dating tracer for such old waters. This is the first groundwater study with ^{81}Kr activities below the detection limit of the ATTA-3 instrument, currently at 2% of the atmospheric ^{81}Kr/Kr ratio[1]. Our results confirm that under normal conditions, underground production of ^{81}Kr is not affecting the ^{81}Kr dating results. However, the differing noble gas concentrations of the different water components, in particular the depleted noble gas concentrations of the brine, have to be considered when interpreting measured ^{81}Kr activities in terms of groundwater age. The radiogenic ^{4}He and ^{40}Ar concentrations provide additional age information,

Qualitatively they support and complement the age structure derived from the ^{81}Kr data as they “date” mainly the brine component, which is beyond the dating range of ^{81}Kr. The dating tracers ^{81}Kr, ^{4}He, and ^{40}Ar indicate a residence time of the brine component of more than 1–5 Ma. Some uncertainty about the brine formation process remains, but the combination of chemical and stable isotope composition of the brine, noble gas concentrations and dating results favours evaporative enrichment of seawater, implying a pre-Quaternary origin of the brine. Tracer ages of meteoric water and glacial meltwater are on the order of several hundred thousand years, so that the possibility of multiple reversals of the flow direction in the Cambrian aquifer system as a result of the paleoclimatology of the area has to be taken into account. Due to the cyclic changes in hydraulic conditions and potential reversals of flow direction, the aquifer was probably in a transient state over most of the last 1 Ma period, which needs to be considered in future modelling attempts. Finally, noble gas measurements from Estonia, where the proportion of glacial meltwater is high, noble gas derived infiltration temperatures and stable isotopes could be used to differentiate the glacial recharge mechanism.

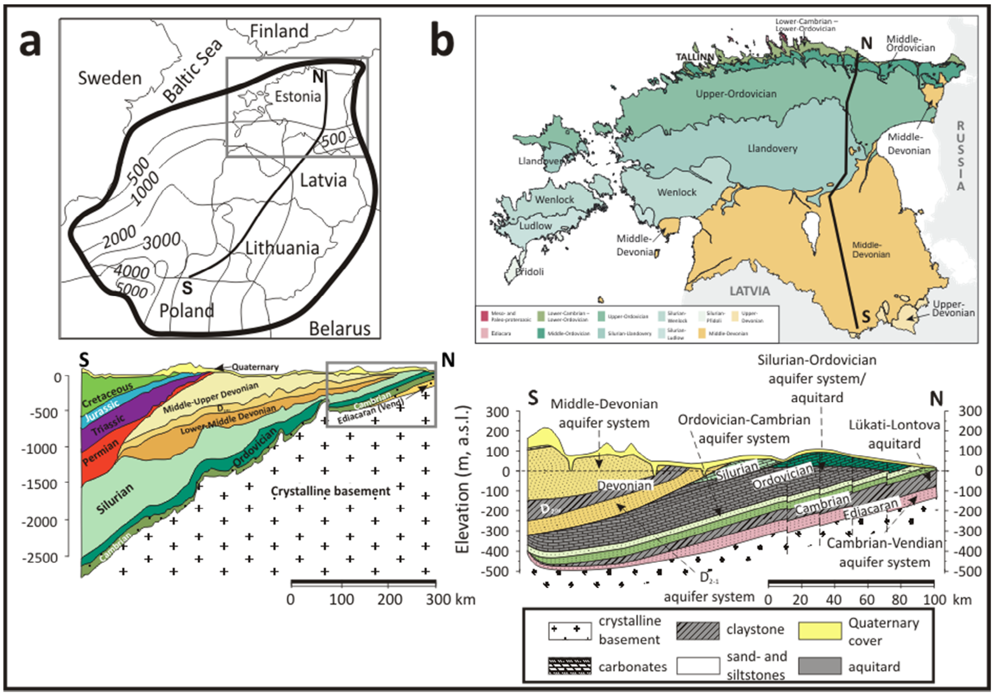

Figure 1: *(a) The location and boundaries of the Baltic Artesian Basin (BAB). Contour lines mark the depth of the crystalline basement in meters b.s.l. The geologic cross-section of the BAB along the line N-S is also shown. Abbreviations: D2-1 aquifer system – Lower-Middle Devonian aquifer system, D2nr – Narva regional aquitard, Q – Quaternary. (b) the close up (grey square) depicting the geological and hydrogeological setting in the northern part of the BAB (Estonia). [2]*

In order to reveal subglacial recharge conditions under the Fennoscandian ice-sheet two cross-sectional models crossing the northern BAB, one in Estonia, the other in the Gulf of Riga and in Latvia were developed, to assess whether subglacial recharge can explain the current distribution of $\delta^{18}O$. Groundwater flow was simulated over 28 ky, from the LGM to present-day, along with $\delta^{18}O$ transport for tracing meltwater and determining whether each simulation of subglacial recharge is in agreement with field data. The results show that subglacial recharge under the Fennoscandian ice-sheet can explain the distribution of $\delta^{18}O$ in the northern BAB as originally suggested by Vaikmäe *et al.* (2001). Many simulations provide a good fit between observed and computed values of $\delta^{18}O$, in particular those considering upper estimates of subglacial recharge, with maximum subglacial hydraulic heads averaging 2000 m and the duration of subglacial recharge reaching several ky, and less negative estimates of $\delta^{18}O$ in Fennoscandian meltwater, around -22.5‰ and -25.0‰[3].

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O-6

OXYGEN ISOTOPE EXCHANGE RATE BETWEEN BISULPHATE AND H_2O BELOW 100 °C: CASE STUDY OF THE BUDA THERMAL KARST, HUNGARY

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The oxygen isotope exchange between bisulphate and water is rather fast over cca. 200 °C [1], but it is exponentially decreasing by lowering temperature. With other words, the time needed for oxygen isotope equilibrium exponentially increases by decreasing temperature. Laboratory experiments are suitable in the time range from few days until about one year, but when the needed time is in the range of thousands of years, by means of laboratory experiments we can just estimate the equilibration time. Therefore the study of natural systems may help us to validate the laboratory based estimations.

Water in the Buda Thermal Karst system is rich in sulphate and the age of water tapped by wells of varying depth is from few thousand years to more than 20 thousand years making this system suitable for checking exchange rate of oxygen between bisulphate and water. The outflow temperature of the studied water is below 100 °C.

The application of different cation geothermometers (Si, Na-K-Ca, etc) provides a tool for estimating the reservoir temperature. McKenzie & Truesdell [2] created a formula for calculating the half time of oxygen exchange between bisulphate and water at different pH and temperature. Using this formula we calculated the time needed for oxygen isotope equilibrium in the bisulphate-water system at neutral pH and at the temperature estimated by different geothermometers. This calculated time has been compared with the ^{13}C corrected radiocarbon ages. At several cases it seems that the isotopic equilibrium has been attained, and the bisulphate-water oxygen isotope geothermometer gave similar results as the cation geothermometers. In cases when cool water mixed to the ascending hot water the bisulphate-water oxygen isotope geothermometer gave different (significantly higher) temperatures than those calculated by cation geothermometers. In this case, when two components are mixed, neither the oxygen isotopic equilibrium in the bisulphate-water system, nor the cation equilibrium in the rock-water system was attained, but the former geothermometer gave an approximation for the hot component's reservoir temperature, while the latter geothermometer gave an approximation for the outflow temperature.

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O-7

^{39}AR DATING OF GROUNDWATER: STILL HARDLY AVAILABLE

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Numerous methods are available to study the age distribution of karst water bodies, if they are characterised by longer residence times. All these methods work in different time ranges. To investigate the past few decades, tritium, ^{3}H/^{3}He, SF_6, CFC's, ^{85}Kr age determination methods are frequently used to calculate the time elapsed since recharge. On the other hand, ^{14}C seems to be the only tool for studying water bodies having residence times of a few thousands or few tens of thousands of years. However, piston flow movement of groundwater occurs very rarely in aquifers longer than a few months. Rather, hydrodynamic dispersion and mixing might be significant along the flow lines of groundwater. Hence, based on isotope analyses there are cases when young (<70 years), not too old (few hundred years) and old (thousands of years) components are present in a groundwater system. The more age indicators we know , the more precisely we can determine the mixing ratios of the components of different ages (for example with lumped parameter modelling). While there are tools for 0 to 70 years, and for thousands of years, for the time scale of 100-2000 years ^{39}Ar dating is the only available method for the time being. ^{39}Ar is a cosmogenic isotope with a half-life of 269 (±3) years. The activity concentration of atmospheric argon is about 1.5 $mBq/dm^3{}_{Ar}STP$, it dissolves into groundwater during recharge. Along the flow line, its activity is decreasing due to the radioactive decay. Knowing the activity of the atmospheric and the dissolved argon, the "age" can be calculated. Nevertheless, due to the tremendously complicated analytical requirements it is limited only to a few laboratories in the world.

In our presentation, the details of the analytical procedure to determine ^{39}Ar/Ar will be shown. The technique consists of three steps: 1. extraction of at least 100 litres of dissolved gas in the field from the groundwater; 2. separation and purification of the argon from the gas; 3. determination of the ^{39}Ar activity concentration by a proportional counter system in an underground laboratory.

O-8

PALAEOENVIRONMENTAL RECONSTRUCTIONS BASED ON HIGH-RESOLUTION OXYGEN ISOTOPE PROFILES OF UPPERMOST JURASSIC VERTEBRATE TEETH AND OYSTER SHELLS

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The Owadów-Brzezinki quarry located in the Tomaszów Syncline in Central Poland is one of the most important uppermost Jurassic paleontological sites, which yielded exceptionally well-preserved marine and terrestrial, invertebrate and vertebrate fossils. The section is dated, based on ammonite fauna, to the Scythicus(=Panderi)–Virgatus zonal boundary of the Middle Volgian, which is an equivalent of the Fittoni–Albani zonal boundary of the Bolonian–Portlandian boundary [1], and should be correlated with a narrow interval of the Lower–Upper Tithonian boundary [cf. 2]. Depositional environments of the Owadów-Brzezinki basin varied from the offshore and the nearshore (Brzostówka marls, unit I limestones) to the coastal (units II, IV), and the lagoonal ones (unit III). The latter palaeoenvironment was characterized by high-amplitude variations in seawater salinities and oxygenation level of bottom waters, which favoured the preservation of soft tissue and fragile skeletal fossils [3, 4].

2 big oyster (*Deltoideum delta*) shells as well as 7 amiiform fish (*Caturus*) and 2 ichthyosaur (*Cryopterygius kielanae*) teeth were selected for microsampling. The samples were screened for the preservation state using cathodoluminescence studies and electron microprobe analyses. Oyster shells and enamel(oid) of studied teeth are found to be well-preserved; diagenetic alteration is, solely, observed in the porous, tooth dentine.

The *D. delta* oyster shells, which are derived from the lowermost part of the section, were microsampled (in ca. 0.5 mm step) in ligamental areas using a computer-controlled micro-drill (a MicroMill device) at the Institute of Geological Sciences, Polish Academy of Sciences. The oxygen and carbon isotope analyses have revealed variations of ca. 2‰ VPDB (mostly between -1 and 1‰ VPDB) in consecutive growth areas of the shells and a mean $\delta^{18}O_{calcite}$ value of ca. 0‰ VPDB. These results are broadly similar to the intershell range and the average $\delta^{18}O_{calcite}$ value of bulk oysters reported by Wierzbowski et al. [4]. The variations in oyster $\delta^{18}O_{calcite}$ may be linked to annual or seasonal changes in temperature and salinity of the sedimentary basin.

SHRIMP IIe/MC ion microprobe analyses conducted (in ca. 0.1 mm step) at the Micro-area Analysis Laboratory of the Polish Geological Institute–National Research Institute, have revealed a significant difference between oxygen isotope compositions of coeval ichthyosaur tooth enamel and oyster shells. This confirms the endothermy of ichthyosaurs, which was previously postulated based on the comparison between reptile and fish $\delta^{18}O_{apatite}$ values [5]. A juvenile portion of the ichthyosaur enamel was probably precipitated close to the oxygen isotope equilibrium with a relatively little respiratory oxygen isotope effect and might be used for the determination of the ambient water oxygen isotope composition, which is crucial for palaeoclimatic studies (Fig. 1). The tentative calculation shows that the ichthyosaurs may have lived in waters with $\delta^{18}O_{water}$ value of ca 1.1‰ VSMOW,

SHRIMP IIe/MC ion microprobe analyses of transverse section through the enameloid of *Caturus* fish teeth, belonging to the amiiforms (infraclass Holostei), which lived in a lagoonal environment of the unit III, have revealed high $\delta^{18}O_{apatite}$ values ranging from 23.6 to 26.5‰ VSMOW (mean 24.8‰ VSMOW). The high $\delta^{18}O_{apatite}$ values indicate that these creatures could have lived in waters of elevated salinities or even could have breathed air in hypoxic conditions. The latter feature is observed in a recent bowfin (*Amia calva*) – a counterpart of Jurassic amiiforms. This imposes re-interpretation of the habit of *Caturus* fishes, which were previously regarded as active marine predators [cf. 6].

Results of oxygen isotope analyses of 10 bulk *Caturus* teeth, using a standard thermal conversion elemental analyzer (TC EA) method, conducted at the GeoZentrum Nordbayern in Germany, are similar to the results of the SHRIMP IIe/MC microprobe analyses of the dentine, which form a major part of the tooth volume ($\delta^{18}O_{apatite}$ values of the bulk teeth and the dentine range from 19.3 to 21.6‰ VSMOW, and from 18.6 to 20.4‰ VSMOW, respectively). This confirms the reliability of SHRIMP IIe/MC ion microprobe analyses of all phosphate fractions of studied teeth.

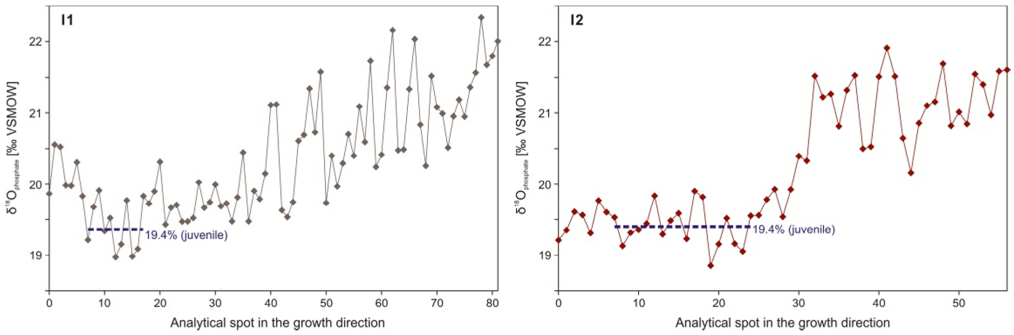

Figure 1: *$\delta^{18}O$ values of ontogenetic sections throughout the enamel of 2 ichthyosaur (C. kielanae) teeth measured using the SHRIMP IIe/MC. A juvenile portion of the teeth showing low $\delta^{18}O$ values (ca. 19.4‰ VSMOW) was presumably precipitated at low body weight and under a relatively slight effect of the isotope pool of respiratory oxygen.*

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O-9

HIGH RESOLUTION ISOTOPE TRACING OF GEO- AND ARCHEOLOGICAL PROCESSES BY LASER ABLATION MC ICP-MS

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The development of inductively coupled plasma mass spectrometer (ICP-MS) triggered the expansion of new tools which revolutionized chemical and isotopic studies of wide range of materials vital to earth sciences, archaeology, biology or medicine. The enhanced ionization efficiency of the plasma source not only enabled analyses of element abundances of virtually the entire periodic table but also permitted precise isotope composition measurement for wide range of elements. One of the biggest assets of the plasma source mass spectrometers is the possibility and relative ease of their coupling with the various sample introduction systems. Probably the most popular is laser ablation (LA) which coupled with a quadrupole or multicollector (MC) ICP-MS enabled routine high spatial resolution analyses at the detection limits in the low range of ppb, which earlier had been reserved to ion probes. While the analytical potential of LA (MC) ICP-MS has long been demonstrated and exploited, high precision and accuracy measurements remain a challenge. The roles of reference materials, normalization constants, or instrumental mass bias in precision and accuracy of measurements are still lively debated. In this study we tested various tuning parameters under wet and dry plasma conditions searching for the optimized setting that would provide the most precise and accurate isotope ratio measurements for Sr, Nd and Hf. The results unequivocally demonstrate non-exponential mass bias as a major source of inaccuracy, which appeared considerably more pronounced under the wet plasma conditions. The results obtained for the dry plasma conditions showed excellent long and short term reproducibility, without the necessity for the secondary normalizations. The measured isotopic ratios compared well with those obtained by, presumably more accurate, thermal ionization mass spectrometers. While the optimization of analytical parameters took place using highly purified standard solutions, we subsequently tested our setup on various matrices commonly applied in earth and archeological sciences using LA MC ICP-MS. Zirconium silicate (zircon), is the most commonly used accessory mineral in geology. It has relatively simple matrix and is enriched in U, Hf and heavy REE which are used for the dating purpose and reconstruction of the crystallization environment. Due to common inheritance of multiple growth stages, high spatial resolution analyses are of fundamental significance. Combined age estimates using U-Pb system with Hf isotope composition and trace element measurements made it one of the most useful minerals in deciphering evolution of the Earth's crust. While dating is still limited to about 1% precision, Hf isotope ratios can be measured with precision comparable to that achieved in the solution mode. Isobaric interferences are significant obstacle, but they can largely be overcome. Our results indicate the need for two different strategies in the data reduction protocols for minerals poor and rich in heavy REE. Additionally, LA ICP-MS element mapping preceding the isotopic analyses appeared very helpful and revealed domains undetected by the traditional imaging in cathodoluminescence.

Laser ablation (MC) ICP-MS analyses of archeological or paleozoological materials prove particularly important due to their virtually non-distractive nature. Measurements of element abundance combined with Sr isotope composition analyses of animal tissues appeared to be one of the most useful techniques bringing major advance in tracing habits of the extinct species. Bioapatite forming tooth enamel appears resistant to post-mortem alterations, and thus belongs to the most useful materials enabling the reconstructions of a life-time Sr and trace element signature of an animal. Despite numerous analytical difficulties in Sr isotope analyses, such as lack of globally used reference materials or particularly numerous isobaric interferences, accurate isotopic Sr composition can be recovered. Combination of histological studies with the high resolution LA MC ICP-MS Sr isotope data appeared very powerful in reconstructing migration paths of mammoths from the Spadzista site in Kraków, in Poland. Our results demonstrate 12 years record in a single mammoth molar representing cyclic changes in $^{87}Sr/^{86}Sr$ ratios interpreted as reflecting seasonal migration between warm and cold periods. The estimated time resolution is < 1 month, which shows that this method is perfectly capable of detecting even sub-seasonal changes. Analogue studies conducted on reindeers and horses whose teeth growth takes place over much shorter period of time, also allowed us to detect variations in Sr isotope composition and propose their migration paths.

The biggest remaining difficulty in applying isotopic tracing in reconstructing the animals mobility is insufficient large scale characterization of the potential migration sites. However, with the rapidly rising number of studies, this gap will certainly be rapidly filled.

O-10

CALCITE STANDARD FOR MICRO-AREA ANALYSIS ON SHRIMP IIE/MC

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Oxygen and carbon isotope compositions of calcite microfossils or high-resolution isotope traverse sections through calcite macrofossils may provide valuable palaeoenvironemntal data but are difficult to study using standard isotope techniques. High precision and accuracy measurements of oxygen and carbon isotope compositions of skeletal calcites can be conducted using an ion microprobe isotope (SHRIMP IIe/MC) based on repeated analyses of isotopically homogenized calcite standards. Available calcite references are, however, not tested for the isotope homogeneity in the microscale, and specific references used for the microprobe analyses, such as UWC-3 or Mex [1, 2], are prepared in small amounts only.

The oxygen isotope homogeneity of three commercially available calcite isotope standards (NBS 18, NBS 19, and IAEA-CO-1) provided by IAEA were compared with the UWC-3 ion microprobe reference (see Table 1).

Table 1. *Isotope data of calcite references tested*

Calcite standard	Mean $\delta^{18}O$ – reference value (‰ VPDB)	Mean $\delta^{18}O$ – SHRIMP IIe/MC analyses (‰ VPDB)	Number of SHRIMP IIe/MC analyses	Standard deviation of SHRIMP IIe/MC analyses (‰)
NBS 18	-23.20	-23.19	28	0.27
NBS 19	-2.20	-2.19	22	0.26
IAEA-CO-1	-2.40	-2.40	26	0.19
UWC-3	-17.82	-17.83	26	0.29

All the references are made of natural marbles. Several small grains of each reference, along with small fragments of two skeletal calcite samples were placed in the centre of the standard SHRIMP II mount (diameter of 35 mm) and carefully polished. A 15 kV, 9 nA Cs^+ primary beam was focused to 20 μm spot on the target producing a ~200 nA secondary beam. $^{16}O^-$ and $^{18}O^-$ were measured simultaneously on Faraday cups. An additional ~330 eV electron beam was used to neutralize surface charging.

Table 2. *Oxygen isotope data of skeletal calcites tested*

Calcite	Reference, δ18O (standard chemical method) (‰ VPDB)	Mean δ18O (SHRIMP IIe/MC calibrated to NBS 18) (‰ VPDB)	Mean δ18O (SHRIMP IIe/MC calibrated to NBS 19) (‰ VPDB)	Mean δ18O (SHRIMP IIe/MC calibrated to IAEA- CO-1) (‰ VPDB)	Mean δ18O (SHRIMP IIe/MC calibrated to UWC-3) (‰ VPDB)	Number of SHRIMP IIe/MC analyses
OK1	*-2.29**	-2.33	-2.50	-2.56	-2.36	8
BRT8	*-1.74**	-3.24	-3.50	-3.52	-3.30	10
NBS 18	-23.2		-23.02	-23.04	-23.14	28
NBS 19	-2.20	-1.90		-2.21	-1.97	22
IAEA-CO-1	-2.4	-2.11	-2.50		-2.17	26
UWC3	-17.82	-17.85	-17.81	-17.82		26

* Oxygen isotope compositions of the skeletal calcites measured using a chemical and microprobe method may differ due to internal inhomogeneity of the samples

Preliminary results show that two references: NBS 18 and NBS 19 show intermediate oxygen isotope homogeneities of (S.D. = ca. 0.3‰; Table 1). The same applies to an available portion of UWC-3 standard, provided by J. Valley. The better oxygen isotope homogeneity is documented for IAEA-CO-1 standard (S.D. = ca. 0.2‰; Table 1). This reference is, therefore, a promising material for the calcite standard, which can be used in the Micro-area Analysis Laboratory of the Polish Geological Institute – National Research Institute until a new reference characterized by high internal homogeneities of both oxygen and carbon isotope signals is selected and tested.

Multiple oxygen isotope analyses of two natural calcites and calcite references have revealed the presence of small to moderate differences in measured δ18O values during calibrations to different calcite standards (Table 2). These measurements confirm the importance of the selection of an appropriate reference material for the ion microprobe analyses of oxygen isotope composition of calcareous fossils.

Acknowledgement: We thank prof. John Valley for kind providing a UWC-3 ion microprobe standard of the University of Wisconsin-Madison (USA).

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O-11

LASER-BASED STABLE ISOTOPE MEASUREMENTS OF GROUNDWATER IN PGI-NRI (POLISH GEOLOGICAL INSTITUTE)

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The isotope composition of groundwater (hydrogen, oxygen) has been studied in the PGI-NRI starting from 2012, and since then the isotope composition became one of important parameters of groundwater measured in the monitoring groundwater network. The measurements have been performed by using the laser spectroscopic analyzer DT-100 made by Los Gatos Research against the laboratory reference waters. The analyzer uses the Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS), in which the optical beam passes through the cavity space more than 10000 times owing to High-Reflective (HR) mirrors, which multiplies the amplitude of absorption phenomena on water vapour molecules present in the cavity. Measured are relative intensities of absorption by three isotopologues of water: $H_2{}^{16}O$, $HD^{16}O$ and $H_2{}^{18}O$, and these are recalculated to isotope ratios $^{18}O/^{16}O$ and D/H. Subsequently, the obtained measurement data are processed by the dedicated Laboratory Information Management System software (LIMS) developed by Tyler Coplen (USGS) with collaboration with Leonard Wassenaar (IAEA), the "Lims for Lasers" [1]. This software combines the post-processing of data like normalisation to the international isotope standards, assessment of analytical errors, detection of faulty measurements, assessment of instrument drift etc. with the database functionality. Owing to long-term user-author collaboration, a number of improvements to the early versions of LIMS have been made.

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ISOTOPE AND CHEMICAL EVIDENCE FOR SECONDARY PHOSPHATE MINERALIZATION OF GRASPING SPINES OF LOWER PALAEOZOIC CHAETOGNATHA

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Chaetognaths (so called arrow worms) are small marine creatures, which are common in all modern oceans. Their grasping spines, found in Palaeozoic sediments, were erroneously included in conodonts due to the similar external appearance and phosphate mineralogy. Comparative studies of Lower [1, 2, 3, 4] and Upper Palaeozoic spines [5] have, however, shown a strict resemblance of these fossils to grasping spines of extant chaetognaths, which are built of chitin. It is likely that the chitin layers of chaetognath spines underwent phosphatisation, which is pervasive in many Palaeozoic sediments.

The mineralogy and the oxygen isotope composition of grasping spines of Lower Ordovician *Phakelodus* chaetognaths from Öland (Sweden) and various conodonts were investigated using an electron (CAMECA SX100) and an ion microprobe (SHRIMP IIe/MC) at the Micro-area Analysis Laboratory of the Polish Geological Institute–National Research Institute.

The results show that the studied *Phakelodus* spines are built of two layers: (i) a thin (up to ca. 10 µm), outer layer, which consist of densely arranged pure fluorapatite crystals (Ca ~38.3wt%, P ~17.6wt%, F ~3.1wt%, Fe ~2200 ppm, S ~ 900ppm), and (ii) much thicker middle layer (perhaps with traces of the inner layer; cf. [1]) of loosely bound, clouded structure (Ca ~29.1wt.%, P ~12.5wt.%, F ~3.4%, Fe ~2700 ppm, S ~6400 ppm), whose composition is similar to that of diaganetic apatite infillings occurring in some parts of the open, internal voids of the spines (Fig. 1). The ion microprobe analyses of 5 *Phakelodus* samples have shown low and variable $\delta^{18}O$ values, which range from 7.4 to 13.5‰ VSMOW. They are much lower than those of co-occurring *Cordylodus* conodonts (14.5 to 16.0‰ VSMOW). The scatter of *Phakelodus* $\delta^{18}O$ values is similar to the scatter (ca. 4‰) of diagenetically altered Lower Triassic conodonts (genera *Elisonia, Neospathodus*) from Svalbard. As the studied Lower Ordovician chaetognath spines and conodonts have low conodont alteration index (CAI) = 1 (<50–80°C), and show only dull cathodoluminescence, the low *Phakelodus* $\delta^{18}O$ values may be linked to specific processes of post-depositional apatite mineralization.

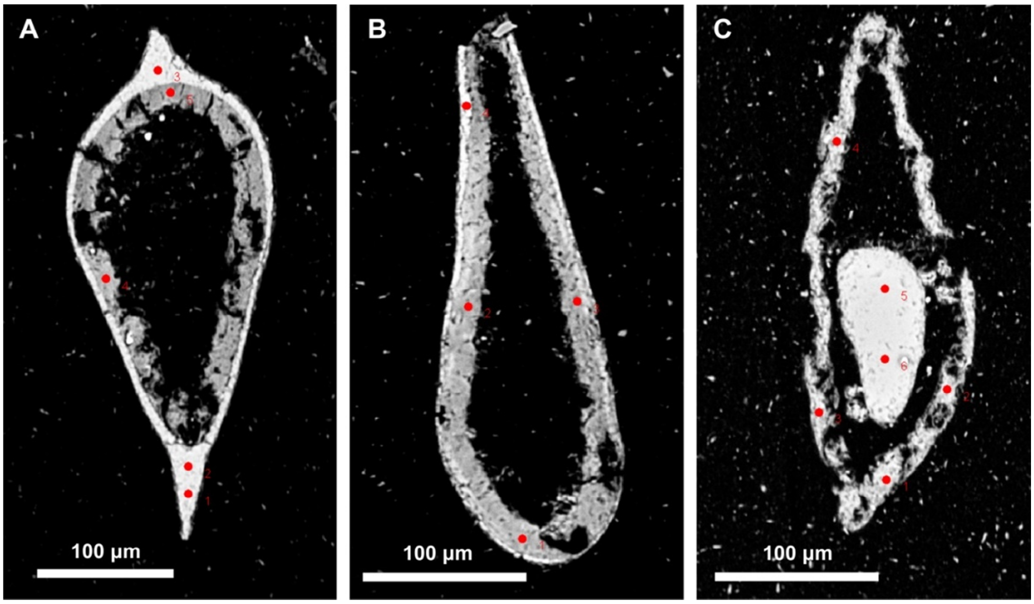

Figure 1: *Backscattered electron (BSE) images of transverse sections of Lower Ordovician Phakelodus spines. (A, B) Outer and middle spine layers are visible. (C) Middle layer and diagenetic, empty space infilling. Red spots – chemical analyses.*

Although a thin, outer apatite layer, which is a counterpart of the so called cuticle layer of modern chaetognath spines, might have been precipitated during the animal growth or additionally mineralised in very early submarine diagenetic processes it is too thin to form the sole structural support. It also seems to be not present in all samples. Besides, the observed deformations of the spines and wrinkles on their surface suggest the primary flexibility of grasping spines of Palaeozoic chaetognaths, which would not be possible if they were built of pure apatite [2, 5]. All the data confirm diagenetic phosphatisation of the spines.

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O-13

BARCODING THE EARLY EARTH: POTENTIAL CORRELATES IN POLAR REGIONS FROM ZIRCON GEOCHRONOLOGY

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The record of continent formation in the first half of the Earth's 4.5 billion-year history is obscured by the operation of plate tectonics in the latter half, which has repeatedly ruptured and reassembled continental crust into new configurations. In the plate tectonic regime, pre-existing continental fragments collide, forming orogenic belts composed of thickened crust with roots of metamorphosed rock, with new continent crust generated and accreted to continents along subduction zones. By the late Archean (2.7 – 2.5 Ga) such processes were already in operation [1]. How much further back plate tectonics operated is still a matter for debate, because early Archean terranes (*i.e.* >3.6 Ga) are scant and strongly affected by later orogenesis. This also makes it difficult to say whether these early Archean remnants were somehow related. However, each of these ancient terranes preserves timelines of geological events that occurred within and adjacent to early Archean crust. Such geochronological 'barcodes' can be compared to provide insights into possible relationships between terranes.

On the western margin of the sub-polar North Atlantic Craton (NAC), The Nain Province of Labrador, Canada, was assembled from early to mid-Archean components at *ca.* 2.7 Ga, as indicated by orogenic features such as widespread high-T metamorphism and ductile deformation [2]. Similar orogenic features are found in the conjugate part of the NAC on the coast of southwestern Greenland [3]. However, new dating of zircon and monazite in high-T metamorphic assemblages and in deformed granitoids indicate widespread orogenesis along the margin of the NAC also occurred at *ca.* 2.5 Ga, in both Labrador and parts of southwestern Greenland. Although *ca.* 2.8-2.7 Ga high-grade metamorphism and ductile deformation is widespread in Archean cratons, including the NAC, similar activity at *ca.* 2.5 Ga is less widely recognised. The Napier Complex (NC) of East Antarctica also contains remnants of early Archean crust [4]. Here the dominant metamorphism is at *ca.* 2.5 Ga, obscuring an earlier high-T metamorphism event at *ca.* 2.8 Ga. Both cratons also have zircon records of crustal development between 3.95 and 3.7 Ga, juxtaposed with ca. 3.2-3.0 Ga crust. These similarities increase the likelihood that the most ancient parts of both polar terranes (NAC and NC) share a common history up to the end of the Archean.

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O-14

LUBLIN REGION THROUGH PROTEROZOIC TIME – AN OVERVIEW OF U-PB ISOTOPE ZIRCON DATA

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Since Arthur Holmes published his basic book "The Age of the Earth" in 1913, in which the radiogenic isotope were applied for the first time to quantify a geologic time, the isotopic studies has become the mainstream of geological exploration, creating a separate scientific discipline. Currently, the isotope geochronology underpins a knowledge about the absolute age of terrestrial samples, especially for the fragmentary rock archive of the Precambrian crust. Such area, in which the geological recognition has been strongly improved by isotope geochronology, is the crystalline basement of the Lublin region. This part of the East European Craton (EEC) is completely covered by younger sedimentary rocks, including the Carboniferous coal-bearing series of the Lublin Formation with thickness of about 300 m. The structural architecture of the basement was approximated by various seismic surveys, acquired within SE part of Poland. The basement of the Lublin region represents the edge of EEC, relatively close to the major structure of the Teisseyre–Tornquist Zone (TTZ). Detected variation of the Moho depth together with specific assembly of the crust pointed by EUROBRIDGE '97, CEL05 seismic profiles in this area have been interpreted as a suture between two different crustal megablocks i.e. Fennoscandia and Sarmatia (merged with Volgo-Uralia), which finally formed the EEC.

In the Lublin region the eight boreholes reaching the crystalline basement were sampled and examined isotopically (Łuków IG 1, Radzyń IG 1, Parczew IG 10, Wisznice IG 1, Kaplonosy IG 1, Holeszów IG 1 and IG 2, and Niwa 1). The drill cores were taken from different depths of each drill section. The U-Pb-Th isotope age data of the basement within this border area were acquired using secondary ion mass spectrometry technique (SIMS). The representative zircon grains were analyzed on sensitive high resolution ion probe using four instruments of SHRIMP family, i.e. SHRIMP II and SHRIMP RG at Research School of Earth Science, SHRIMP II at Geoscience Australia, all three in Canberra, as well as SHRIMP IIe/MC at PGI-NRI, Warsaw.

The U–Pb age results revealed that the top of basement in the Lublin region has been formed during the Proterozoic time. There is no Archean structures. The oldest age of igneous protolith documents the range of 2.1–2.0 Ga. This age was recognized in Kaplonosy, Niwa, and Holeszów core sections. Their crystallization time well correspond with the ages of magmatic rocks known from northwestern Sarmatian active margin, where the Osnitsk-Mikashevichi Igneous Belt was formed between c. 2.00 and 1.97 Ga. The northern part of Lublin region consists of granitoids younger than 1.90 Ga (Radzyń IG 1, 1.88 Ga) [1]. This age, in contrast, suggests magmatic activity typical for Fennoscandia block. Later, the margins of both blocks were strongly influenced by the collision between Sarmatia and Fennoscandia, manifested mostly by magmatism at 1.81–1.78 Ga. This age of granitoids was recognized in a few sites between Łuków, Wisznice, Parczew and Holeszów. There is also a record of a high grade metamorphism in the Kaplonosy IG 1 borehole. Subsequent symptoms of intracratonic activity at about 1.49–1.48 Ga, visible only in the upper part of Parczew IG 10 section, represent in this part of EEC weak manifestations of Mesoproterozoic magmatism. Finally, in the Early Neoproterozoic, denudation of the cratonic surface along with the deposition of clastic sediments initiated early phase of breakup of the Rodinia supercontinent, which led to the formation of several continental plates, including Baltica and Amazonia, gradually separated by the Tornquist Ocean. The oldest Neoproterozoic sediments of the Lublin region, deposited directly on the basement surface, are represented by the siliciclastic Polesie Formation, that filled a tectonic grabens. After a long period of intense erosion, coarse-grained clastic sediments of the Żuków Formation were deposited above the Polesie Formation. Despite the Paleoproterozoic age of the crystalline basement on the EEC slope, the detrital material, however, was supplied exclusively from Mesoproterozoic sources, mostly younger than 1.5 Ga. The simple unimodal detrital zircon pattern from the clastic part of the Wisznice section (depth 424 m) peaked at 1482 Ga and bimodal zircon pattern from the Kaplonosy (depth 1809 m) peaked at 1525 and 1450 Ga are documented in a large number of measured detrital zircons (n=80) for each sample. This can be interpreted as evidence of the existence of a large source area of Mesoproterozoic age. The appropriate rocks with ages ≤1500 Ma_remains unknown in the TTZ slope of Baltica. Such rocks, however, are widespread in the Amazonia craton. Intrusive rocks with the age of 1500–1480 Ma, adjacent to the older crust, occur along the southern margin of Amazonia, corroborating the hypothesis of tectonic relationship between Baltica and Amazonia at that time. The geotectonic processes that occurred during the final stage of breakup of the Rodinia resulted in a dispersion of continental plates. Since that time Baltica was separated from Amazonia (?) by the Tornquist Ocean, whose opening was preceded by an extension.

The Neoproterozoic history of this part of Baltica includes the inboard rifting and passive margin siliciclastic succession, which was finally covered by the Late Neoproterozoic volcanogenic thick beds, composed of continental flood basalts (CFB) interbedded with pyroclastic horizon known from the Wisznice IG 1 and Kaplonosy IG 1 drill sections. The U-Pb SHRIMP dating of zircon from felsic pyroclastic rocks of the Lublin region allow to define the time frame of eruptive events cumulated between 566.9 ±4.6 Ma and 551.9 ±8 Ma and terminated until the end of Ediacaran. This volcanic activity is correlated with the Volhynian flood basalt province [2].

As a result of the studies of the U-Pb zircon age from drilling cores in the Lublin region, several important facts have been identified: the crust on the TTZ slope of Baltica (EEC) comprises at least two different units related to Fennoscandian versus Sarmatian affinity. The collision event was also recorded. Detrital zircon geochronology revealed a dominant input of Mesoproterozoic detritus, that thought to be derived from Amazonia craton. The zircon grains preserved the record of several global crust forming episodes i.e. sequential accretion, plate collision and then denudation and rifting of the Rodinia supercontinent, throughout Proterozoic time between 2010 Ma and 552 Ma.

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O-15

GEOGRAPHIC VARIATIONS IN THE SLOPE OF THE δD–δ^{18}O METEORIC WATER LINE OVER EUROPE: A RECORD OF INCREASING CONTINENTALITY

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Monthly weighted δD and δ^{18}O values of precipitation have been compiled from European IAEA stations excluding areas that are under the regional climatic influence of the Mediterranean basin. Those data allowed the calculation of the slopes S of the corresponding δD–δ^{18}O meteoric water lines to be determined for each station. Increasing S values with longitude ϕ from ≈5 (Portugal) to ≈9 (Russia) are positively correlated to relative air humidity, and continentality, the latter being quantified by the intra-annual amplitude of air temperatures and precipitation. On the basis of our knowledge of isotopic fractionation that takes place during water phase changes, slopes with values close to 9 are expected to reflect both hydrogen and oxygen isotope fractionation operating close to equilibrium during condensation of water vapour into liquid water or snow. Slope values that tend to decrease down to 5 are interpreted, in most cases, as the result of an increasing recycling of water vapour derived from the Atlantic Ocean, closed marine basins such as the Black Sea, and large freshwater lakes. In addition to this process, enrichment in heavy isotopes also most likely took place during the partial evaporation of water droplets during their fall in air of relative low humidity.

O-16

$\delta^{13}C$ VIS-À-VIS $\delta^{18}O$ OF SELECT PLANKTONIC FORAMINIFERAL SPECIES AND OF ORGANIC MATTER: A POSSIBLE INDICATOR TO DISCRIMINATE RAINFALL FROM THE SOUTH-WEST MONSOON

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Most of the Indian population is involved in agriculture and earn their livelihood out of the crop production. Indian agro based economy is largely dependent on the southwest monsoonal rainfall. While south-east Asia and Central Africa come under the domain of the monsoon in general (Williams *et. al.*, 2006), Indian subcontinent, in particular, witnesses vigorous reversing monsoon because of the presence of the Himalayan range in the north of the subcontinent. While, during the summers Indian subcontinent witnesses southwest monsoon, during the winters southwest monsoon subsides under the influence of stronger northeast monsoon. Nearly all of the workers on monsoon consider the monsoon and rainfall synonymous, which is probably not correct because of the following reasons: (i) While southwest monsoon, being formed over the Arabian Sea, carries moisture with it, resulting in rainfall on the Indian subcontinent; the northeast monsoon, which is devoid of moisture on most part of the Indian subcontinent, is incapable of producing rain, barring the southeastern parts of the southern India. (ii) Even if, the southwest monsoon carries enough moisture, it may not precipitate enough in the form of rain, as there are many other parameters, which are to be fulfilled for a rainfall to happen.

Sarkar *et. al.* (2000), Agnihotri *et. al.* (2003), and many others have worked on the summer monsoon with reference to Indian subcontinent, but none of them made any attempt to decouple the Indian summer monsoon and the resulting precipitation in the form of rainfall. A correlation between these two may result in the better understanding of the Indian rainfall system, which in turn may greatly help the Indian agriculture.

During summer monsoon, the upper surface of the sea is removed by the wind blowing towards the subcontinent resulting in the upwelling of the nutrient rich 'lower' water, which results in the increase in the productivity. Enhanced production should result in the removal of more ^{12}C from the sea surface water thereby increasing the $\delta^{13}C$ of the sea water. The select planktonic foraminiferal species tests growing in this water should have enriched $\delta^{13}C_{calcite}$, while the $\delta^{13}C_{organic\ matter}$ should be depleted. The $\delta^{18}O_{foraminiferal\ calcite}$ would depend on the influx of the rain water flowing into the sea in the form of the surface run-off. Understanding of the monsoon system requires the study of past long series of climatic data, which can be retrieved from the sediments deposited during the particular time. In the present work, an attempt would be made to understand the monsoon – rainfall relation based on the oxygen and carbon stable isotopic data obtained from off-shore sediment cores retrieved from the eastern Arabian sea.

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O-17

ISOTOPIC AND TIME SERIES INVESTIGATIONS OF RECENT STALAGMITES (1945-2018), SCHLOẞBERG TUNNELS, GRAZ, AUSTRIA: IMPLICATIONS FOR CLIMATIC FLUCTUATIONS

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During the World War II, between end 1943 and January 1945, labyrinth tunnels have been built across a hill situated the city of Graz, Austria. For the first time, we present an annual- to decadal-scale multi-proxy record of 70 samples including stable isotopes ($\delta^{18}O$, $\delta^{13}C$) and time series analysis of calcite stalagmites grown between 1945 and 2018 within the tunnel system. Speleothem records have proved to be very useful in reconstructing changes of environmental conditions as well as karst processes. For the present investigated stalagmites, the $\delta^{18}O$ value average 10.5‰ (VSMOW) with high-frequency variability of up to 8‰, and suggest variable climatic conditions since 1945. Meanwhile, the mean $\delta^{13}C$ value is low (~−26.7‰ VPDB) and related to percolation of water though the rocks and soil. The $\delta^{18}O$ and $\delta^{13}C$ values increase from the nineties onwards, the data being correlated with detailed temperature and precipitation amount records from a meteorological station situated near the hill. Anthropogenic influence is suggested for the steady increase of values.

STABLE ISOTOPIC COMPOSITION OF MAGNESITES AND DOLOMITES FROM THE PRECAMBRIAN EVAPORATE-BEARING FORMATIONS OF ASIA

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Magnesite is a stable carbonate phase in wide geological environments and is known in sedimentary exogenous formations, found in ultramafic rocks related to ophiolites and described in the mantle transition zone [3, 6, 7]. Magnesite occurrences are widespread in the different Phanerozoic structures and the Riphean sequences, where its form economically important deposits [3, 6, 8, 10]. Early Precambrian sedimentary magnesites are known only from a few of localities so far, e.g., the Pamir Mountains, the Sino-Korean Shield, and the Fedorovskaya Formation of the Precambrian Aldan Shield, etc.

Magnesite was analyzed for this presentation from stratiform and lenticular bodies and relatively younger skarns, pockets and veins, which most often developed after the primary metasedimantary rocks. The stratiform and lenticular carbonate rocks are restricted to the Goran Formation of the Pamir Mountains (Kukh-i-Lal noble spinel, clinohumite and Liadzhvardara lazurite deposits) [4], the Guanmenshan Formation of the Sino-Korean Shield (Ronrian and Simpkhun magesite and apatite deposits) [8] and the Fedorovskaya Formation of the Aldan Shield (group of apatite-carbonate deposits of the Seligdar type) [1]. The rocks are metamorphosed to the granulite and amphibolite faces. They conformably intercalate with gneisses and crystalline schists and have similar structural styles. Geological works in different sectors of the Aldan Shield revealed a wide distribution of anhydrite, barite, gypsum and celestine in metamorphic sedimentary rocks of the Fedorovskaya Formation, and salt-bearing sections of the Goran Formation [5]. Geological and mineralogical peculiarities of the observed objects are typical for young evaporate-bearing formations.

In contrast to almost pure magnesite marbles which are developed in area of Kukh-i-Lal (Fig. 1) dolomite marbles are typical primary carbonate rocks in different sectors of the Liadzhvardara lazurite deposit (Fig. 2).

Figure 1: *Kukh-i-Lal noble spinel and clinohumite deposit, the Pamir Mountains. Magnesite layer in contact with skarn (left), intercalations rich and poor in silicates marbles (center), spinel aggregates at the contact between magnesite marble and skarn (right).*

Presence of salt crusts within dolomite marbles of the Liadzhvardara lazurite deposit is unique feature of the upper part of the Goran Formation [4, 5]. Even after decades evidences of the salt formations had been detected during mapping of separate parts of the marble (Fig. 2). In addition to the salt founds distinctive fluorite debris have been described [4] within Khuduk sector. Rich in carbonate rocks sequences of the Goran Formation (or similar) are areas of exploration work on ruby, some of its promising manifestations have been discovered [9].

Figure 2: *Liadzhvardara lazurite deposit, the Pamir Mountains. Separate layer (left) of dolomite marble (between point 1 and 2) with lazurite undergrounds (black points within marble layer), inner structure of salt-bearing dolomite marble (right).*

Coarse or fine grained magnesite, with massive homogenous or sometimes banded structures, is main carbonate of lenses or layers in productive horizons of the magnesite deposits in Northern Korea (Fig. 3). In some objects rich in magnesite and apatite veins are determined.

Figure 3: *Magnesites from the North Korean deposits. Coarse grained (left), massive (center) and fragment of banded structure of magnesite (right). Scale – reduced two times from natural.*

In the diagram of Figure 4 $\delta^{18}O$ and $\delta^{13}C$ values group within discrete fields, corresponding to the types of deposits distinguished. The fields of carbonates from different varieties of stratiform and lenticular bodies commonly overlap.

Dolomites from marbles of the Liadzhvardara lazurite deposit have $\delta^{13}C$ and $\delta^{18}O$ values similar to those of the typical marine limestone carbonates and are limited in a relatively narrow field (Fig. 4), but data of magnesites from the North Korean apatite-carbonate deposit are located far from marine and freshwater limestones and have $\delta^{13}C$ and $\delta^{18}O$ values similar to skarn formations [1]. At the same time the highest $\delta^{13}C$ values are characteristic of magnesites from the North Korean Ronrian magnesite deposit, the $\delta^{18}O$ values vary from 11.0 to 19.1‰. The points plotting out-side suggested ranges represent magnesites from the Kukh-i-Lal deposit, which have $\delta^{13}C$ and $\delta^{18}O$ values similar to those of the typical marine and freshwater limestones carbonates, but are not limited in a relatively narrow field (Fig. 4).

Within heterogeneous rock volumes, in which carbonates of many morphogenetic types can occur simultaneously and the temporal succession of their formation was determined, the $\delta^{18}O$ and $\delta^{13}C$ values of early dolomite are always higher than the analogous values of the relatively late magnesite (Fig. 5). Siderite and calcite, which are deposited in an evolving mineralizing environment later than dolomite and magnesite, are characterized by low $\delta^{13}C$ values. The differences in the carbon and oxygen isotopic composition between earlier and later carbonates are commonly from 1 to 4‰.

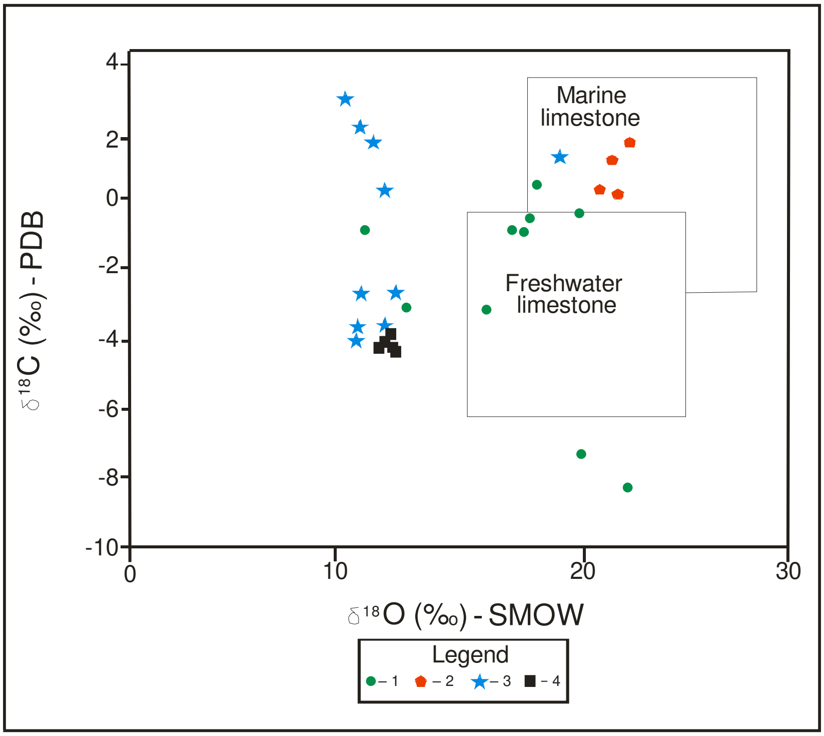

Figure 4: *δ^{13}C vs. δ^{18}O diagram shoving fields of the stable isotopes values in the measured carbonates concerning of the main nature carbon and oxygen reservoirs (after Hoefs, 2009). Legend: 1 – magnesite Kukh-i-Lal deposit, 2 – dolomite Liadzhvardara deposit, 3 – North Korean magnesite deposit, 4 – magnesite from the North Korean apatite-carbonate deposit.*

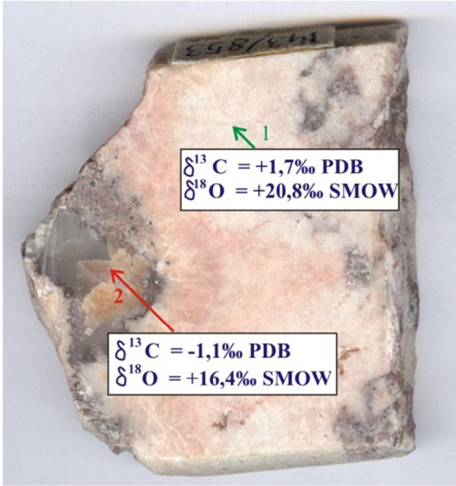

Figure 5: *Isotopic composition of primary dolomite (green 1) and relatively late magnesite (red 2) in the apatite-bearing Precambrian carbonate ores of the Seligdar deposit, Yakutia.*

The chemical environment in which the minerals of the studied carbonate rocks may have formed has been discussed in relation to the influence of carbonic acid concentration on the reaction of the major carbonate-forming elements (Ca and Mg). According to the constructed paragenetic diagrams the stabi1ity fields of the carbonate minerals follow the sequence dolomite > magnesite > calcite, but under limited concentration of calcium in the parent solutions it was involved with dolomite and calcite is absent.

The results of carbon and oxygen isotope studies performed on the different deposits confirm that each deposit represents a clearly defined and isotopically distinct sedimentary facies. The carbon and oxygen isotope data on magnesite and dolomite, as well as the chemical and mineralogical composition of different observed rocks, are in agreement with the hypothesis of a closed system in which a metamorphic fluid interacted with the rocks, whose protolith was produced chemogenically in shallow evaporate basins. The subsequent transformations of the primary rocks by meteoric waters and metasomatic fluids can be identified using low $\delta^{18}O$ and mainly negative $\delta^{13}C$ values.

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O-19

SUBSISTENCE STRATEGIES IN LATE MEDIEVAL TO EARLY MODERN COASTAL AND INLAND COMMUNITIES IN LITHUANIA REVEALED BY STABLE ISOTOPE DATA

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Carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) stable isotope analysis can now be considered as a “golden standard” in archaeological studies on food and nutrition [1]. Moreover, it can sometimes be the only source of evidence, when other sources are missing. Until now, only a few stable isotope investigations have been performed on Lithuanian bioarchaeological material, mainly dating to the Neolithic [2, 3] and most recently on one Late Medieval population [4].

To better understand the actual consumption and the distribution of various foods, stable isotope ($\delta^{13}C$ and $\delta^{15}N$) analyses were performed on skeletal remains from coastal and inland communities, ranging in date from the Medieval period to the early Modern ages (14th-early 20th c.). Elevated $\delta^{15}N$ values in coastal communities suggested a diet consisting of considerable amounts of freshwater fish, whereas marine resources were neglected due to relatively low $\delta^{13}C$ data. Meanwhile, inland communities had isotope values suggesting a high reliance on terrestrial resources and a “peasant” type of diet.

Measurements on modern samples can help to better understand the archaeological data. Therefore, several analyses were conducted on modern plant and human hair samples. Plant data provided valuable information on an isotopic “baseline” in certain environments, meanwhile hair data revealed some dietary preferences of modern males and females. Thus, modern samples provided valuable data to interpret the archaeological data.

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O-20

ISOTOPE GEOCHEMISTRY OF ACID MINE DRAINAGE: LESSONS FROM THE WIŚNIÓWKA AREA (SOUTH-CENTRAL POLAND)

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Keywords: Acid mine drainage, isotope geochemistry, isotope interactions, environmental impact

Determinations of stable isotope ratios in different media, i.e. $\delta^{34}S$ in pyrite and plants, $\delta^{34}S$ and $\delta^{18}O$ in dissolved sulfates and δD and $\delta^{18}O$ in waters enable a better understanding of different geochemical processes and interactions that occur in the rock/mineral-water-plant systems of acid mine drainage (AMD) sites, and assessing a potential impact of mine waters on the environment. The isotope determinations complement data derived from trace element measurements. The current isotope study encompassed pyrite mineralization zones exposed at Podwiśniówka and Wiśniówka Duża quarries, AMD water bodies (lakes, ponds, pools), and neighboring farmer's wells and rivers located in the Wiśniówka area (south-central Poland). For this purpose, different analytical methods were employed including stable isotope determinations (TIMS, SHRIMP, isotope water analyzer) combined with geochemical analyses of rocks and waters as well as petrographic and mineralogical examinations of minerals, rocks and sediments (optical microscopes, LA-ICP-MS, SEM/EDS, EMPA) (Migaszewski et al. 2008, 2013, 2018a).

The principal source of dissolved sulfates in acid pit lakes, ponds and intermittent pools is the predominant microscopic and locally framboidal arsenical pyrite that makes up at least two stratiform mineralization zones of the earliest and middle Late Cambrian age. These textural features of pyrite and the substitution of arsenic for sulfur in the crystal structure (FeS_2) expedite oxidation of this sulfide on exposed quarry walls and unvegetated historic and recent tailings piles (Migaszewski et al. 2018b, 2019). The lowermost Upper Cambrian pyrite (Podwiśniówka quarry) and the middle Upper Cambrian pyrite (Wiśniówka Duża quarry) show different $\delta^{34}S$ signatures with a mean of $-26.2 \pm 2.2‰$ and $-30.5 \pm 6.9‰$, respectively. These differences are also evidenced by the mean $\delta^{34}S\text{-}SO_4^{2-}$ values of AMD water bodies: $-15.3 \pm 1.0‰$ (Podwiśniówka) and $-10.0 \pm 1.7‰$ (Wiśniówka Duża). In contrast, springs, rivers and farmer's wells unaffected by AMD, exhibit distinctly positive $\delta^{34}S$ values (mean of $7.0 \pm 2.3‰$) resembling their equivalents from the Cambrian Main Range of the Holy Cross Mountains (mean of 6.2 ± 4.6‰) (Michalik, Migaszewski 2012). This isotope discrepancy allows an assessment of AMD impact on the environment and additionally the provenance of mining waste material (Migaszewski et al. 2018a). As opposed to metal(loid)s, sulfates are not immobilized by adsorption on Fe, Mn and Al oxyhydroxides, clay minerals and organic matter, and consequently may occur in clear acidic seeps reaching rivers and shallow aquifers. In this case only $\delta^{34}S\text{-}SO_4^{2-}$ values can fingerprint an AMD impact on fresh waters.

The sulfate efflorescences on pyrite surfaces display the same $\delta^{34}S$ signatures (Migaszewski et al. 2008). However, the negative $\delta^{34}S\text{-}SO_4^{2-}$ signatures shift toward more positive (less negative) values induced by bacterial (dissimilatory) sulfate reduction (BSR). This is documented by inversely proportional relationships between the $\delta^{34}S\text{-}SO_4^{2-}$ or $\delta^{18}O\text{-}SO_4^{2-}$ and sulfate concentrations. In addition, the comparison of $\delta^{18}O\text{-}SO_4^{2-}$ and $\delta^{18}O\text{-}H_2O$ values indicates that ferric iron is a dominant oxidant during pyrite oxidation under both aerobic and anaerobic conditions. This means that over 50% (range of 60–100%) of oxygen is derived from the water molecule (Migaszewski et al. 2013, 2018a).

The δD and $\delta^{18}O$ ratios of Wiśniówka water samples reveal progressive evaporative isotope enrichment. The high correlation coefficient ($R = 0.97$) between the $\delta D\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$ in river and farmer's well waters also indicates that both surface and underground waters are recharged by precipitation (Migaszewski et al. 2018a). The differences in O and H isotope signatures between individual water bodies can be attributed to their diverse shape, depth, as well as site topography and sunlight exposure.

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STABLE O-H-C ISOTOPES AND ^{1}H- AND ^{13}C-NMR SPECTROSCOPIC DATA FOR DIFFERENTIATION OF FRUITS – A PRELIMINARY STUDY

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The composition of fruits is the result of interactions between various factors, as the fruit class/varieties and growing conditions in terms of local climatic influences (e.g. temperature, precipitation, insolation), geographic (e.g. altitude, latitude, distance to sea, slope - for hilly regions) and geological (e.g. soil type, water, water retention in soil, soil drainage) features. Significant fractionation of heavy to light stable isotopes in biological matter can result during physical-chemical and biological processes such us photosynthetic fixation.

Plants have enzyme(s) that select against the less abundant and heavier ^{13}C isotopes relative to the ^{12}C isotopes. Factors like temperature, plant type (e.g., C3 *versus* C4 plants) [1, 2], and the environment [3] are also involved in stable carbon isotope fractionation, thus the $^{13}C/^{12}C$ ratios in plants may differ depending on latitude, location/altitude and climate (e.g. plants in humid areas take in more CO_2 and develop a lower ratio of ^{13}C to ^{12}C than in arid ones). Furthermore, fruits hydrogen and oxygen stable isotopes record the climatic conditions experienced by the plant and the isotopic composition of the plant's source water during fruit development [4]. As such, stable isotopes have been explored extensively for use in verifying claims of origin.

The hypothesis of this study is that classification of grapes, plums, apples, pears, strawberries, cherries, sour cherries and apricots, in terms of variety origin, year of production and harvest period, can be improved using stable isotope (D/H by SNIF-NMR, $\delta^{18}O/^{16}O$ and $\delta^{13}C/^{12}C$ by CF-IRMS) information fused with ^{1}H and ^{13}C NMR profiles. The combined data of 170 fruits samples collected from different regions of Romania were analysed using several multivariate statistical approaches including principal component analysis (PCA), discriminant analysis (DA), factor analysis (FA) and analysis of variance (ANOVA).

During our preliminary investigations, discriminant analysis was performed separately on the stable isotope ratios and the ^{1}H- and ^{13}C-NMR spectra for all the analyzed samples in order to obtain specific models for discrimination of fruit varieties, vintage and harvest period. This approach would be the most appropriate, because it would allow to provide a clear discrimination of a fruit sample based on its principal features. However, this first statistical modeling suggestion conduct us to the conclusion that the variations within the data sets (^{1}H-,^{13}C-NMR spectra and stable isotope data) are too important to be considered in one vector diagram regarding these major parameters. The uniqueness of each fruit sample should be investigated apart from its main characteristics, such as variety, harvest period (summer, autumn) and production year given the fact the data are influenced by the sample specificity. Enhancement of this type of profiling investigation includes the addition of other geographical areas, different agronomical practices (ecological *vs.* conventional) and additional fruit varieties.

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ISOTOPIC COMPOSITION OF MINERAL BOTTLED WATERS IN POLAND: IMPLICATIONS FOR THE ORIGIN AUTHENTICATION STUDIES AND QUALITY ASSESSMENT

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Keywords: bottled water, mineral water, healing water, water quality, origin of water, isotopic composition, chemical composition.

The waters used by bottling industry in Poland to produce natural mineral or spring bottled waters are the groundwaters in their origin and can be extracted by the wells or naturally flowing springs. The bottled waters on the market differ among each other not only by brands, labels and package types, but also by the total mineralization and the chemical composition, which determine the taste of water and its edible and refreshing qualities. In case of healing waters, which are also bottled an sold on the market in Poland, the water must additionally contain a specific pharmacologically active chemical compounds in an appropriate normalized amounts. Naturally occurring free CO_2 gas in the amount not less than 250 mg/L is one of such pharmacologically active chemical compounds which determines that the water becomes automatically considered as healing (according to Geological and Mining Low in Poland) and becomes the valuable resource regardless of the content of other chemical compounds. The questions of the quality of bottled waters, the appropriate method of their qualitative qualification as a "food product" and their origin authentication are still vital on the water market. These aspects are directly connected with competition on the bottled market and the protection of the own brand quality. In this field quite small attention is paid on the isotopic composition of bottled waters, namely the ratios of stable oxygen $^{18}O/^{16}O$ ($\delta^{18}O$) and hydrogen $^{2}H/^{1}H$ ($\delta^{2}H$) isotopes of two elements which built directly the water particles. In this paper the hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) isotopic composition of 42 bottled waters widely available on the market in Poland were measured in order (i) to evaluate the possibilities of application of water isotopic composition in complementary qualitative qualification of bottled waters and (ii) to determine precisely the origin of waters in the context of the authenticity verification. The waters studied belonged to three qualitative (marketed) groups: (i) natural mineral waters, (ii) spring waters and (iii) healing waters. All bottled waters marked as natural mineral waters and spring waters belong to wide range of meteoric waters of modern hydrological cycle with $\delta^{18}O$ in the range of -8.36 – -10.46‰ and $\delta^{2}H$ in the range of -62.4 – -72.9‰. Their isotopic composition reflect the physiographical localization of water intakes (mountain – lowlands) and aquifer hydrogeological conditions. The waters labeled as healing is usually sold by bottling companies connected with spas. Only four waters are analyzed with isotopic composition in wide range: $\delta^{18}O$ in the range of -0.61 – -8.79‰ and $\delta^{2}H$ in the range of -50.2 – -67.9‰. The $\delta^{2}H$ and $\delta^{18}O$ isotopic composition of healing waters in majority was characterized by the isotopic composition clearly enriched in the heavy isotopes of oxygen and hydrogen. The isotopic compositions of healing waters are strongly connected with their origin and the geochemical evolution in rock environment, which determine the genetic and qualitative uniqueness of such waters. Comparison of isotopic composition of Polish bottled waters with bottled waters of other European countries shows in some cases large similarities connected with similar climatic conditions of groundwater formation. The combination of at least two different indicators, for example the isotopic and the chemical one is better and more complete way of evaluation of the bottled water quality and hydrogeological origin.

ORIGIN OF HYDROCARBON GASES AND CARBON DIOXIDE IN DEVONIAN-CARBONIFEROUS STRATA OF THE UPPER SILESIAN AND LUBLIN REGIONS: ISOTOPIC, HYDROUS PYROLYSIS AND GEOLOGICAL APPROACH

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The objective of this study is determining the origin of hydrocarbon gases and carbon dioxide based on molecular and stable isotope (^{12,13}C in CH_4, C_2H_6, C_3H_8 and CO_2, ^{1,2}H in CH_4) compositions of natural gas of the Lublin Basin (LB), and coal-bed gases of the Upper Silesian Coal Basin (USCB) and Lublin Coal Basin (LCB), related to the geological setting of these basins. Five gas fields (Ciecierzyn, Komarów, Mełgiew, Minkowice and Wilga), and three oil and gas fields (Glinnik, Stężyca and Świdnik) were discovered in the Devonian and Carboniferous strata of the Lublin Basin. Six gas samples are collected from Gl-3 (Glinnik), Cn-1 and Cn-3 (Ciecierzyn), Mg-1 and Mg-8K (Mełgiew) and St-5K (Stężyca) wells. Stable isotope values range as follows: $\delta^{13}C(CH_4)$ from −49.0 to −34.4‰, $\delta^{2}H(CH_4)$ from −197 to −144‰, $\delta^{13}C(C_2H_6)$ from −37.5 to −33.5‰, $\delta^{13}C(C_3H_8)$ from −33.6 to −30.2‰, and $\delta^{13}C(CO_2)$ from −12.4 to −5.9‰ [1, 2]. Hydrocarbon gases and a large part of CO_2 from the Devonian and Carboniferous reservoirs of LB were generated during a low-temperature, thermogenic process, probably during two stages of transformation of Type-II and Type-II/III kerogen. In the years 2001-2019 sixty four coal-bed gas samples of the Pennsylvanian coal-bearing strata in USCB were analysed for molecular and isotopic compositions [1, 2, 3]. The analysed coal-bed methane varied significantly in the isotopic composition: $\delta^{13}C(CH_4)$ from −79.9 to −47.1‰, $\delta^{2}H(CH_4)$ from −294 to −211‰. Two samples of the coal-bed methane and carbon dioxide in the LCB characterize $\delta^{13}C(CH_4)$ −52.5 and −67.3‰, $\delta^{2}H(CH_4)$ −201‰ and $\delta^{13}C(CO_2)$ −13.7 and −11.9‰ [1].

To provide a better characterization of the origin of thermogenic gas, hydrous pyrolysis experiments were performed on five samples of USCB coals and one sample of LCB coal at 330 and 360°C for 72 h and compared with results of 13 HP experiments (11 coals from USCB and 2 coal from LCB) previously conducted at 360°C for 72 h [4, 5].

Thermogenic CH_4 is present within the Pennsylvanian coal-bearing strata of both USCB and LCB, and microbial CH_4 in USCB. Thermogenic gases were generated during the bituminous stage of coalification. This process was completed at the end of the Variscan orogeny and lasted a few Ma, being completed at the turn of the Pennsylvanian and Permian time. After Variscan uplifted coal-bearing strata were subjected to erosion and denudation, intensive degassing and emission of coalbed gases, mainly methane, to the atmosphere took place. In the southern part of USCB these processes lasted for about 290 Ma until the deposition of Miocene cover and in the LCB and central and northern parts of USCB for about 320 Ma up to today.

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SEASONAL VARIATION OF OXYGEN, CARBON AND NITROGEN ISOTOPE RATIOS OF COW MILK IN LITHUANIA

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Dairy products are of particular interest as a group of foods that play an important role in feeding the population. The composition of milk is fundamentally dependent on the feeding of the cows, and thereby on a particular environment. To better understand the amount of variation in $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ values in the milk from the same area, we measured stable isotope ratios in cow milk water, artesian water, and precipitation ($\delta^{18}O$) as well as in bulk milk samples ($\delta^{13}C$ and $\delta^{15}N$) collected in 2014 – 2016. Different water and food sources were available during the winter (artesian water only and dry grass) and summer (artesian water and fresh grass), and spring and autumn seasons reflected transitional periods. Oxygen stable isotope ratios in milk water were relatively lower in winter and transitional seasons and higher in summer, showing the dependence on the main water source. $\delta^{13}C$ values reflected particular food sources. This study shows the applicability of the stable isotope ratio method in linking cow milk to specific environments and reveals the amount of variation in stable isotope ratios in the same area. These results could be valuable for other studies on geographical origin determination of dairy products.

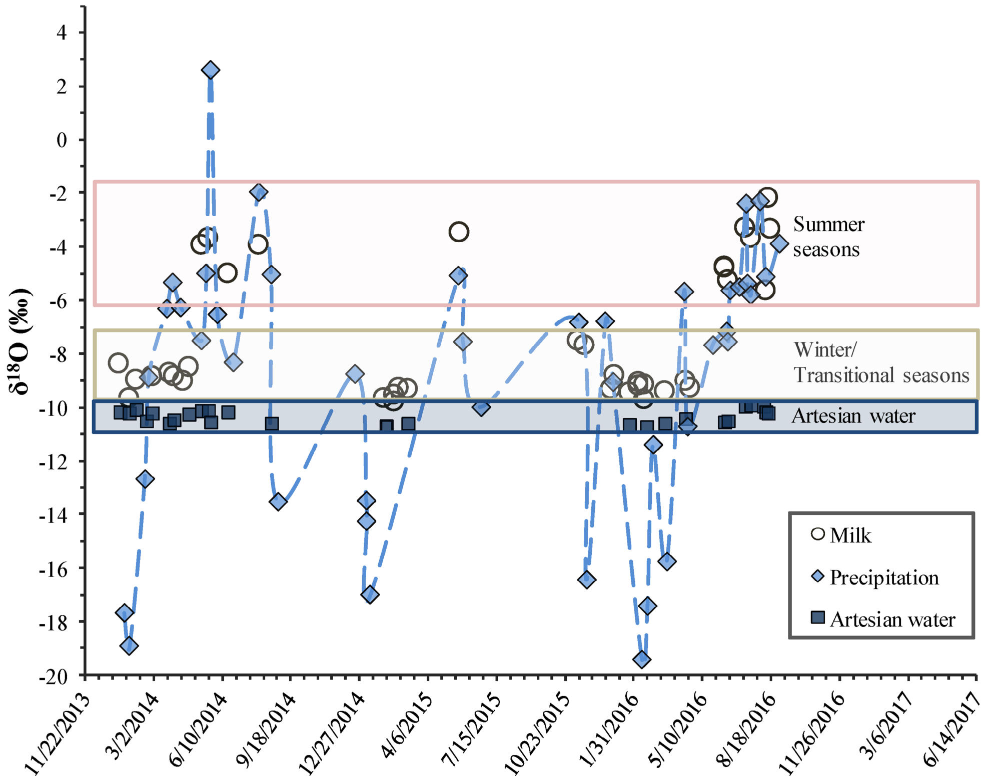

Figure 1: *Seasonal variation in δ18O values in milk water, artesian water, and precipitation water in the rural site in Lithuania during 2014–2016. Dashed blue line integrates measured δ18O values of precipitation. Boxes indicate which δ18O values of the cow milk fall into the range of summer or winter/transitional seasons.*

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TRACE HEAVY METAL AND PB ISOTOPIC COMPOSITION IN SCOTS PINE NEEDLES IN THE AREA NEAR CHEMICAL FACTORIES IN KĘDZIERZYN-KOŹLE (POLAND)

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We present the results of qualitative and quantitative elemental and Pb isotope analyses of pine growing in the urban forest area in South Poland. The annual pine needles (*Pinus Sylvestris* L.) investigated were formed in 2012 and collected in winter in 2013. Dendrochemical analysis for trace metal pollution is based on the assumption that element concentrations in tree represent element availability in the environment in which the tree grows.

The young annual needles of pine (Pinus Sylvestris L.) shoots were collected in three Polish cities/commune Sławięcice (KK_5), Rudziniec (KK_10) and Rudno (KK_15) in January 2013 (Fig.1.)

Figure 1: *Localization of the sampling sites (x) Sławięcice (KK-5, 50°20'15.7N 18°19'52 E), Rudziniec (KK-10; 50°20'3.6 N; 18°24'29E) and Rudno (KK-15; 50°21'26,4N 18°28'14E). The 2 chemical factories (i.e; ZAK S.A and Blachownia) are indicated on the map by the symbol *. KK-5 in Sławięcice is located ~5 km from ZAK S.A.), KK-10 in Rudziniec at ~10 km from ZAK S.A. and KK-15 in Rudno at ~15 km from ZAK S.A. and ~2 km far from motorway).*

Trace metal composition and Pb isotopes of pine needles were measured by ICP-MS and MC-ICP-MS, respectively, at Université Libre de

Bruxelles. Trace metal ^{52}Cr, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{208}Pb in pine needles record the impact of the pollution emitted *inter alia* by chemical factories, householders and traffic. Median concentration of trace elements in the pine needles has been observed in the following order: Cr<Pb<Cu<Zn. Similar order was observed in wood samples investigated in this area [1]. The variation in isotopic Pb composition reflects a mixing between different anthropogenic sources.

The authors wish to express their gratitude to everyone who contributed to making these investigations possible. The research was a part of: BIOPOL project "Trees as bioindicators of industrial air pollution during implementation of pro-environmental policy in the Silesia region" – funded by the National Science Centre allocated on the basis of the decision number DEC-2011/03/D/ST10/05251 (PI: B. Sensuła), WBI — bilateral agreements between Poland and Belgium (WBI 2017-2019; PI : B. Sensuła, N. Fagel).

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O-26

THE $\delta^{13}C$ OF CARBONACEOUS AEROSOL AS IDENTIFIER OF MAIN POLLUTION SOURCES

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Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources [1] . Fine atmospheric particles ($D_p < 1.0$ µm) have become a major public health concern [2, 3]. Discrimination between natural and anthropogenic particles in the atmosphere is increasingly difficult because the anthropogenic emissions can lead to an amplification in the secondary organic aerosol formation from naturally emitted precursors [4, 5]. Carbonaceous aerosols carry on the isotopic signature of their precursors (e.g., biogenic and fossil fuel hydrocarbons), thus their $\delta^{13}C$ value can be used as an indicator of an anthropogenic impact [6]. Consequently, the $\delta^{13}C$ value is a useful tracer to distinguish the origin of carbonaceous particle sources, as different sources generally exhibit rather unique $\delta^{13}C$ values ([7] and references therein).

Here we present a new approach for apportioning major source categories. In this study the results of the experimental research are presented by investigating the stable carbon isotope ratio ($\delta^{13}C_{TC}$) variations in fine fraction of aerosols in three sites in Lithuania (urban, coastal and forest). The study was conducted to identify and distinguish carbonaceous aerosol sources by an isotope mixing model.

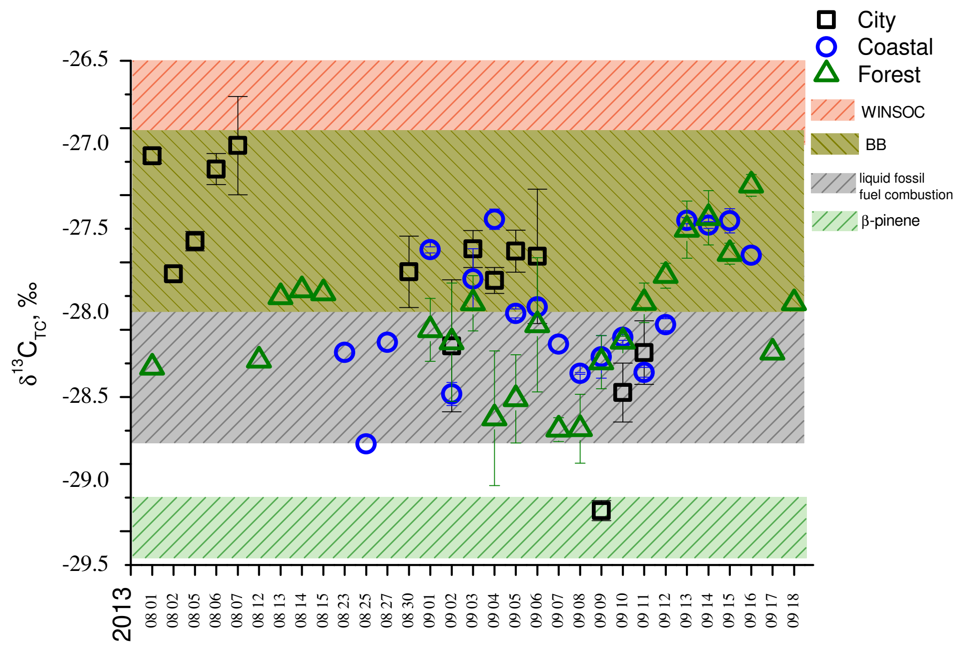

Figure 1: *$\delta^{13}C_{TC}$ variation of ambient aerosol samples collected at the city, coastal and forest sites. WINSOC values taken from [8], biomass burning values (BB) taken from [9], value of liquid fossil fuel combustion from [10] and value of β-pinene taken from [11].*

Figure 1 demonstrates the measured δ^{13}C values of TC that varies from -28.5 ± 0.2 ‰ to -26.6 ± 0.2 ‰ at urban site (average -27.6 ± 0.8 ‰), from -28.8 ± 0.1 ‰ to -27.2 ± 0.2 ‰ at coastal site (average -27.9 ± 0.5 ‰) and from -28.7±0.2 ‰ to -26.9±0.2 ‰ at forest site (average -28.0± 0.5 ‰). All these values fall into the range of the main carbonaceous aerosol sources (and most probably are the mix of it). The most enriched isotopic values (between -25 and -27‰) may be water soluble organic carbon (WSOC) as reported by [12]. The overlapping values may be from water insoluble organic carbon (WSOC) [8], biomass burning materials reported by [9] that varies from -24.7±0.2 ‰ to -28.0 ± 0.2 ‰. $\delta^{13}C_{TC}$ = -28.0 ± 0.9 ‰ attributed to fossil fuel combustion particles [10] and isotopic composition from -29.3 ‰ to -30.1 ‰ could be attributed to β-pinene [11].

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O-27

DIVERSITY IN SULFUR CONTENTS AND STABLE SULFUR ISOTOPE RATIOS IN SAMPLES OF PLANT SPECIES COLLECTED IN THE ACID MINE DRAINAGE-IMPACTED AREA

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Keywords: bioavailable sulfur, phytoremediation, pyrite weathering, stable sulfur isotopes

Sulfur content and sulfur stable isotope ratios were determined in the above-ground samples of 17 plants growing in the Wiśniówka acid mine drainage (AMD)-impacted area (south-central Poland). The vascular plants included the following species: *Betula pendula, Chamaenerion angustifolium, Frangula alnus, Juncus effusus, Oxalis acetosella, Pinus sylvestris, Populus tremula, Quercus petraea, Salix cinerea*, *Sorbus aucuparia, Tussilago farfara,* and *Vaccinium myrtillus*. Two samples of fern *Pteridium aquilinum* and one sample of each of the three following moss species *Drepanocladus aduncus, Mnium affine* and *Pleurozium schreberi* were also collected. Sampling was done in an area of about 100 x 100 m, where the AMD waters showed very low pH values (1.4-2.2) and extremely high concentrations of arsenic (max. 1548 mg/l) and rare earth elements (max. 24.84 mg/l) (Migaszewski et al. 2019).

Sulfur is one of the elements essential to all plants. It is usually taken up by plants as a sulfate ion, which subsequently undergoes biochemical reactions that produce important molecules including the amino acids and proteins, peptides, sulfolipids, sulfated polysaccharides and many others (Kopriva 2015). The AMD waters, which are a product of pyrite oxidation, are abundant in SO_4^{2-}. The highest content of this ion in the AMD study area was 91.8 g/l (Migaszewski et al. 2019). Sulfur concentrations in analyzed samples varied from 0.110% to 4.17%, with a mean of 0.597%. The lowest S contents were found in moss samples (0.11%-0.14%) and pine needles (0.137%). One species of the vascular plant (*Tussilago farfara*) exhibited approximately a ten-time enrichment in sulfur (4.17%). The high S content in this species was also reported by Wesołowski et al. (2001).

Considering the origin and fate of sulfate ions in the AMD areas, one can assume that stable sulfur isotope ratios of plants reflect those of pyrite. Because stable sulfur isotope determinations in plants from AMD sites are scarce, therefore, it is interesting to compare the $\delta^{34}S$ signatures in species naturally growing in such a harsh environment. The previous environmental studies carried out in the AMD-unaffected and relatively pristine areas of the Holy Cross Mts. region showed that all plant samples had the positive $\delta^{34}S$ values (Migaszewski 1998; Gałuszka 2005; Migaszewski et al. 2010), roughly reflecting isotopic composition of local precipitation, i.e. from +5.1‰ to +6.8‰ (Michalik and Migaszewski, 2012).

This study exhibited that stable sulfur isotope composition of plant samples collected in the Wiśniówka AMD study area was significantly enriched in the light sulfur isotope with an average $\delta^{34}S$ value of –10.5‰. The range of observed $\delta^{34}S$ values varied in individual plant species showing the highest negative values in fern (from –14.27‰ to –12.27‰; mean of –13.27‰), moderate values in vascular plant species (–16.14‰ to –7.06‰; mean of –11.37‰), and the least negative values in moss samples (from –1.97‰ to –7.67‰; mean of –4.91‰). It is noteworthy that there is a negative correlation between reciprocal S concentrations and $\delta^{34}S$ values ($R^2 = 0.87$). The obtained results are within the range of $\delta^{34}S$ values recorded in plants (from –10‰ to +20‰), but differ from those typical in terrestrial plants (from 0‰ to +5‰) (Finlay and Kendall 2007).

It may be concluded that the samples of different plant species growing naturally in the same environmental conditions have various levels of sulfur in their above-ground organs. The higher S content in the samples, the more negative $\delta^{34}S$ values. The practical meaning of this study is that the plant species that are able to uptake sulfate in the AMD-affected areas can be recommended for use in phytoremediation of contaminated soils and spoils. Of the plant species examined for the purpose of this study *Tussilago farfara* showed the highest concentration of S (4.17%) and the lowest $\delta^{34}S$ value (–16.14‰), which means that it can effectively uptake and transport a substantial amount of sulfur from the soil substrate to its leaves. This species does not have high requirements for soil quality and often grows in contaminated sites, which makes *T. farfara* an ideal plant for revegetation of AMD-impacted areas.

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DETERMINATION OF ENVIRONMENTAL ANTHROPOGENIC PRESSURE IN LOWER SILESIA (SW POLAND) BASED ON CARBON ISOTOPIC AND TC/OC/EC RATIO APPROACH IN ATMOSPHERIC PM$_{10}$

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In spite of last year's modernisation of many industry branches in Lower Silesia, the problem of air quality (especially with particulate matter – PM) is still crucial. The permissible level of 50 μg·m^{-3} for PM10 (particulate matter smaller than 10 mm in diameter) limited by CAFÉ Directive is exceeded many times over the year. Local government and ecological organisations as well as local community are perfectly familiar with the problem of low emission in Poland caused by local home heating (coal/wood etc.) and traffic/transport pollutants (diesel/gasoline). So it is necessary to correct remedial activities (e.g. local city ring project or replace old home heaters). We hypothesize that our investigations based on OC/EC/TC (organic/elemental/total carbon) in PM10 coupled with carbon isotopic analyses δ^{13}C of TC in PM10 provide new reliable quality and quantity monitoring tool.

The 173 (c.a. 25 for each of 8 sampling points) PM10 samples have been gathered in 2011 in Lower Silesia. Samples were collected by employees of VIEP (Voivodship Inspectorate of Environmental Protection) in: I group (two regional background stations) Osieczów (Oś) and Czerniawa (Cz); II group (one industrial influence station) Działoszyn (Dz) and III group (five urban background stations): Nowa Ruda (NR), Świdnica (Św), Polkowice (Po), Legnica (Le) and Zgorzelec (Zg). PM10 concentrations in each sampling point have been obtained based on gravimetric method. The specific carbon species (OC/EC/TC) concentrations were measured using Thermal-Optical Carbon Analyser, whereas carbon isotopic composition d13C was determined using EA-CF-IRMS.

Our results indicated that in 2011 the daily standard PM10 concentration has been exceeded. Extremely high PM10 concentrations reached e.g.: 157 μg·m^{-3} (NR), 152 μg·m^{-3} (Le) and 115 μg·m^{-3} (Św and Po). The coupled data of δ^{13}C values (especially calculated isotopic mass balance) as well as OC and EC composition yield a complex information and let to identify the quality and quantity sources of air pollution. Based on the mathematical calculation of the isotopic mass balance we drew conclusions as follow:

1. in the heating season a contribution of coal in total carbon pool in PM10 varied from 26.1 to 39.1% (I group), 49.1% (II group) and 40.6 to 97.3% (III group) whereas contribution of transport varied from 60.9 to 73.9% (I group), 50.9% (II group) and 2.7 to 59.4% (III group);
2. in vegetative season the contribution of coal in total carbon pool in PM10 oscillated about 2.8% (I group), 23.2% (II group) and 21.8 to 87.9% (III group), whereas contribution of transport input was equal around 96.6% (I group), 65.5% (II group) and 7.6 to 73.8% (III group). The biogenic input estimated to be around 0.6% (I group), c.a. 11.4% (II group) and from 0.3 to 4.5% (III group).

Finally, using percentage contribution of PM10 specific sources it was possible to calculate their real quantity input in the total mass of PM10 described in [μg˙m-3].

Coupled carbon isotopic signatures and OC/EC ratio in PM10 let to conclude: (i) throughout the year in each considered localisation dominated the fossil fuels combustion input (coal used in heating/energy production and diesel/gasoline used in transport) nevertheless with different proportion depending on local area specification; (ii) surprisingly biogenic input in total PM10 fraction was negligible on each of the measurement station and can be excluded as a potential important PM10 source in the Lower Silesia region.

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O-29

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Jarosław Grodowski

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- Field and laboratory deployable with no consumables
- Installed and operational in minutes
- Rugged and insensitive to changes in ambient temperature, pressure or vibration

O-30

HALOGEN STABLE ISOTOPE EVOLUTION DURING EXPERIMENTAL EVAPORATION OF SEAWATER-TYPE BRINES

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Chlorine (Cl) isotope fractionation during precipitation of salt from saturated brines is one of the most studied subjects in chlorine isotope geochemistry [1,2,3]. These studies indicate that during the stage that halite is the most prominent precipitating salt a relatively Cl isotope large fractionation of about +0.35‰ is observed. During later stages, when K and Mg chlorides precipitate the fractionation is much smaller. The isotope fractionation of bromine (Br) has been studied significantly less, but recent studies show fast progress of our knowledge in this field [4,5]. These studies suggest that Br isotope fractionation may be even larger than Cl isotope fractionation.

It is well known that the chemical composition of the oceans has varied considerably over the Earth's geological history [6,7,8]. These variations are characterised by alternation of seawater with SO_4^{2-} concentrations larger than or smaller than Ca^{2+} concentrations during the Phanerozoic, SO_4^{2-} poor (and perhaps CO_3^{2-} rich) seawater during most of the Pre-Cambrian and extremely Ca^{2+} rich seawater during the earliest stages of the Earth's history [8,9]. The compositional variations have significant influences on the composition of salt precipitating from it as well as the Cl and Br isotope composition of this salt.

In order to understand these differences, we prepared brines that were composed of different salts in the proportions they were present in seawater from different periods in the Earth's history. In total we studied 7 different mixtures representative of: 1/ Modern seawater ($SO_4^{2-} > Ca^{2+}$; results in all Ca^{2+} removed early by gypsum precipitation; 2/ Early Paleozoic seawater ($Ca^{2+} > SO_4^{2-}$; results in all SO_4^{2-} removed early by gypsum precipitation; 3/ Archean bicarbonate rich seawater (Ca^{2+} and Mg^{2+} poor seawater) [10]; 4/ Soda ocean [11,12]; 5/ MORB brine (endmember following the Spencer-Hardie evolution of seawater model [13]); 6/ River water (other endmember following Spencer-Hardie model [13]) and 7/ Early Archean seawater with higher Ca^{2+} than Na^+ concentration [8].

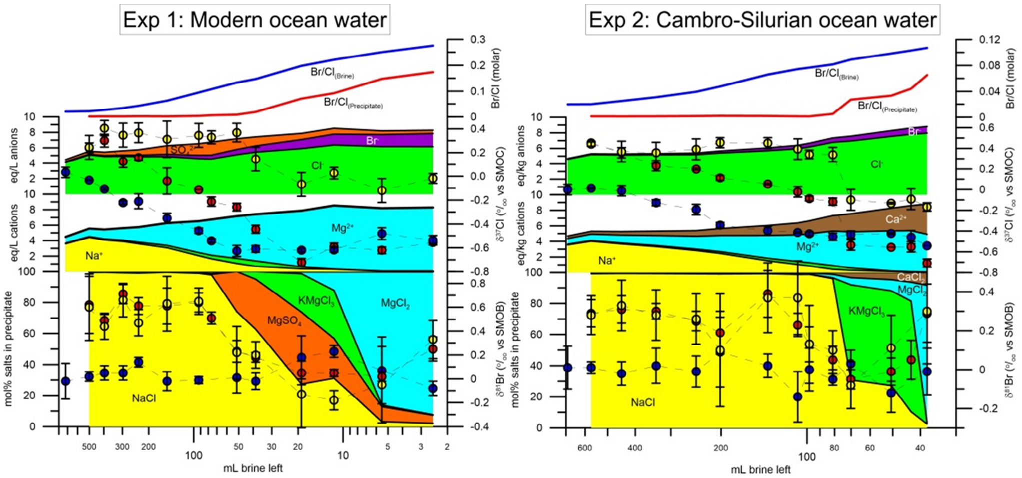

Figure 1: *Trends observed in Exp 1 (left) and Exp 2 (right). The different panels indicate the different trends observed, from the original seawater at the left to the final stage at the right. The panels show the Br/Cl ratios, the brine composition, the salt composition, the Cl isotope and the Br isotope data measured.*

Indeed, the evaporation trends, the minerals that precipitate and the Cl and Br isotope variations differ from experiment to experiment. Variations that were observed in exp. 1 are shown in the left of Figure 1. This brine is equivalent to modern seawater. The trends observed are clearly the same as observed when modern seawater is evaporated, for example in salt pans [14]. The salt precipitation sequence is halite, magnesium sulphates, carnallite and bischofite. The isotope compositions also show expected trends [1,2]. During the precipitation of halite, the δ^{37}Cl of the salt was about 0.35‰ higher than that of the brine. Due to a Rayleigh fractionation process the δ^{37}Cl values decreased in later stages. During the precipitation of carnallite and bischofite only little isotope variation was observed. This experiment also taught us about the largely unknown isotope fractionation of Br during evaporation of modern seawater. In the left figure we observe that during the precipitation of halite the δ^{81}Br is about 0.6‰ higher in the salt than in the brine, during precipitation of carnallite Br fractionation is strongly (about 0.4‰) negative, while during precipitation of bischofite again a relatively large positive fractionation is observed with the δ^{81}Br in bischofite about 0.4‰ above that of the remaining brine.

In the right figure the same trends for early Paleozoic seawater are shown. In this period the SO_4^{2-} concentration was lower than the Ca_2^+ concentration so that all SO_4^{2-} was removed from the brine through gypsum precipitation. Here precipitation starts with halite and when most Na^+ has been removed from the brine mostly carnallite precipitates.

At room temperature $CaCl_2$ almost does not precipitate due to its hygroscopic character. The Cl isotope trend shows positive $\delta^{37}Cl$ for the salt during precipitation of halite, and negative during precipitation of carnallite. Br again shows largely positive $\delta^{81}Br$ values during precipitation of halite and less (to negative) fractionation during precipitation of carnallite.

In our presentation we will summarise the differences in chemical and isotope evolution for the different experiments and we will try to link the differences to the variability in the brine compositions. Further we will examine the currently not well understood Br isotope fractionation in brine evaporation evolution and salt deposits.

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O-31

SEASONAL STABLE ISOTOPE COMPOSITION OF ATMOSPHERIC PRECIPITATION IN SOUTH WESTERN SIBERIA (RUSSIA)

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Water stable isotope analyses of precipitation are a powerful tool for characterization of regional moisture regimes and budgets. On the vast territory of Russia, at different times, there were only about 40 functioning stations GNIP, where atmospheric precipitation was sampled and then analyzed for stable isotopes. In this study we present the results of isotope composition of precipitation collected in Barnaul city (South Western Siberia, Russia) during five winter (2013-2014, 2014-2015, 2015-2016, 2016-2017, 2017-2018) and four summer (2014, 2015, 2016, 2017) seasons. The isotopic composition of precipitation varies widely, about 38‰ for $\delta^{18}O$ and 280‰ for δD. We defined local meteoric water lines for winter (snowfall) and summer (rainfall) precipitation (Fig.1) and the overall precipitation $\delta D = 7.63 \times \delta^{18}O - 1.17$ ($n = 508$, $R^2 = 0.99$).

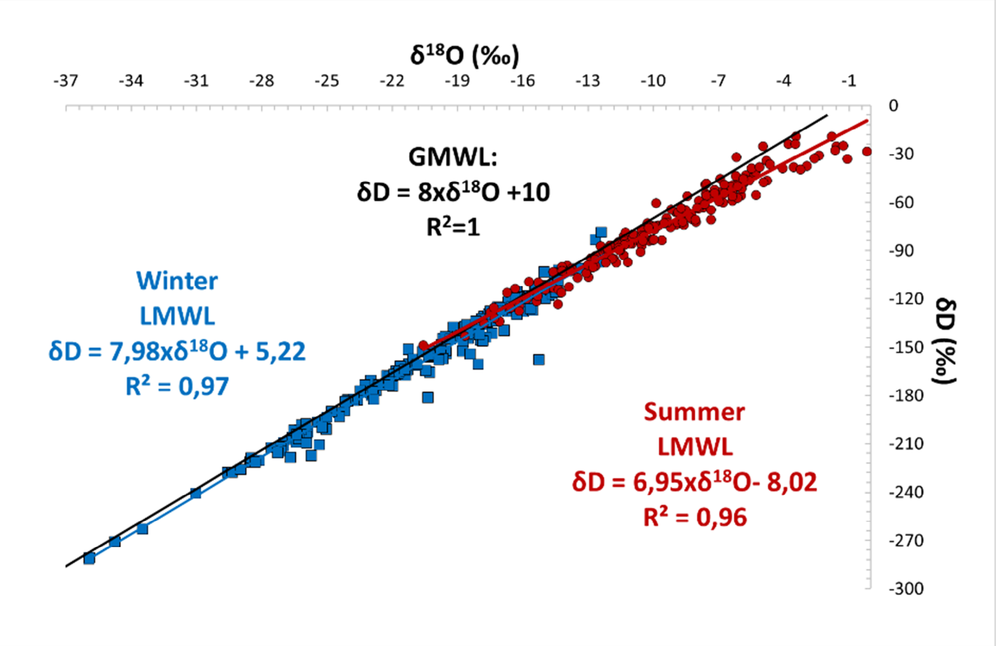

Figure 1: *Local meteoric water lines for winter (2013-2014, 2014-2015, 2015-2016, 2016-2017, 2017-2018) and summer (2014, 2015, 2016, 2017) precipitation in South Western Siberia*

Seasonal patterns of isotopic composition of precipitation were the following: higher isotopic values in a summer ($\delta^{18}O$ = -9.7‰, δD = -75.1‰) and lower isotopic values in a winter ($\delta^{18}O$ = -20.8‰, δD = -160.5‰). These seasonal patterns of isotopic composition were largely linked to different regional moisture sources determined by Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) backward trajectories calculated for heights at the lower limit of clouds. Five regions have been identified as sources of the atmospheric moisture which precipitated in Altai foothills. It has been shown that Atlantic and Arctic Oceans are the dominant source (>50%) of precipitation, but in the warm season Central Asian sources make a significant contribution (up to 15%).

O-32

VARIABILITY IN STABLE CARBON ($\delta^{13}C$) AND NITROGEN ($\delta^{15}N$) ISOTOPE RATIOS AT THE INTERINDIVIDUAL AND INTRAPOPULATION LEVEL IN RED DEER (*CERVUS ELAPHUS*)

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Keywords: stable isotopes, carbon, nitrogen, red deer, collagen

Ratios of stable carbon and nitrogen isotopes in tissues of large herbivorous mammals give information about their habitat and diet. Value of $\delta^{13}C$ indicates the habitat, in which the animal was foraging (forest or open land), while value of $\delta^{15}N$ points out the group of plants, which dominated in diet (woody or soft-tissue vegetation). The stable isotope analysis is useful for paleoecological investigation of species. In such studies the bone collagen (time resistant protein structure) extracted from fossil samples is used. However, such studies have limitations. Firstly, due to scarcity of fossil samples, it is assumed that all bones in the skeleton have the same ratio of stable isotopes. Secondly, the sex and age of individuals are usually not known. Thirdly, it is assumed that one or few individuals are good enough representation of the whole population.

The aim of our study is to investigate the variability in stable carbon and nitrogen isotope ratios within different bones in the skeletons of individuals of red deer *Cervus elaphus*, and among individuals of different age and sex within the same population. We studied individuals from 4 populations in Poland (Szczecin Pomerania, Bieszczady Mountains, Volhynia Polesie and Western Polesie). We measured $\delta^{13}C$ and $\delta^{15}N$ in: (1) ten mandibles with three subsamples: Coronoid Process, Mandibular Angle, Corpus; (2) three different bones (finger bones, mandibles, metatarsal bones) in each of the 13 deer; (3) bones of 65 individuals with known age; and (4) bones of 120 individuals with known sex (58 males and 62 females). Samples of bone collagen were isotopically analysed in Gliwice Mass Spectrometry Laboratory (Institute of Physics – Centre for Science and Education Silesian University of Technology in Gliwice, Poland) using continuous flow IsoPrime mass spectrometer coupled to EuroVector elemental analyzer. Values of $\delta^{13}C$ and $\delta^{15}N$ are reported in per mil (‰) relative to VPDB and AIR standards, respectively. Each sample was run in triplicate, with analytical errors of 0.1‰ and for $\delta^{13}C$

and 0.2‰ for $\delta^{15}N$. All isotope measurements were made on well-preserved collagen, as determined by collagen C/N ratios. The atomic C/N ratios calculated for almost all of the samples in this study were between 2.9 and 3.6, which is within the range expected for pure collagen.

Values of $\delta^{13}C$ and $\delta^{15}N$ in mandibles and finger bones collected from the same individuals were correlated ($r = 0.97$ and 0.68, respectively). Differences in $\delta^{13}C$ and $\delta^{15}N$ in bone collagen between males and females from the same population were not statistically significant. We did not find any relationship between the age of the studied individuals and the ratio of stable isotopes in their bones, either. Ratios of stable isotopes were not influenced by the sex and the age of individuals.

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O-33

OPTIMIZING EA-IRMS: GETTING MORE FOR LESS BY ULTRA-HIGH SENSITIVITY

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The Thermo Scientific™ EA IsoLink™ IRMS System has revolutionized EA-IRMS by introducing temperature ramped gas chromatography with a single GC column and a helium management system that reduces cost per analysis. These innovative features open doors to push research boundaries at new levels, especially for the analysis of nitrogen, carbon and sulphur concentrations less than 5 µg and on very high C/N and C/S ratio samples (Figure 1), whilst delivering automated routine analysis. In figure 1, complete baseline separation is shown with sound background correction and sharp peak shapes for very large (7000 µg C) and very small (11 µg N and 0.8 µg S) analyte amounts. For 5 replicate measurements on wood, $\delta^{13}C$ = -24.10±0.06‰; $\delta^{15}N$ = 3.20±0.23‰ and $\delta^{34}S$ = 5.92±0.26‰.

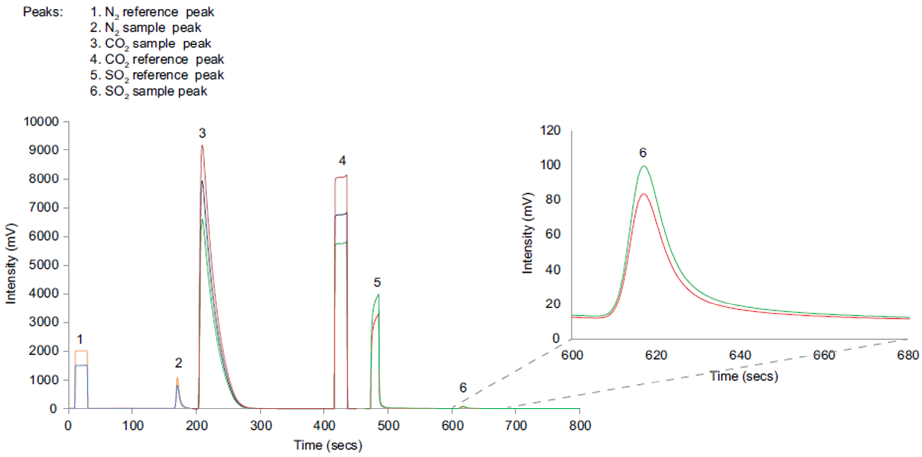

Figure 1: *Simultaneous NCS analysis of wood (C/S ratios >7900:1) from a single sample drop using the EA IsoLink IRMS System. Analysis time <10 minutes using <1.4 liters of helium.*

This presentation will focus on the analysis of small concentrations of carbon, nitrogen and sulphur and illustrate with data, how the EA-IRMS utilizes chromatographic principles to routinely increase the sensitivity on NCS measurements and reduce cost per analysis. An example of the gains in sulphur sensitivity will demonstrate measurements on 1 mg of bone collagen, where data precision is significantly better than 0.3‰.

P-1

TRIPLE ISOTOPE EFFECTS ACCOMPANYING EVAPORATION OF WATER: NEW INSIGHTS FROM DEDICATED LABORATORY EXPERIMENTS

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Stable isotopes of hydrogen and oxygen (^{2}H and ^{18}O) have been often used for quantification of water budgets of lakes and other surface water bodies, in particular for the assessment of underground components of those budgets which are very difficult to quantify using classical hydrological methods [1]. Recent advances in laser spectroscopy resulted in the construction of commercial laser analysers capable of simultaneous analyses of ^{2}H, ^{18}O and ^{17}O content in water, with measurement uncertainties comparable (δ^{18}O) or surpassing (δ^{2}H) those routinely achieved by off-line sample preparation methods combined with conventional IRMS technique [2,3]. This opens up the doors for improving reliability of isotope-aided budgets of surface water bodies by adding third isotope tracer (^{17}O). This, however, requires good knowledge of triple isotope effects accompanying evaporation of water, in particular the kinetic isotope effect related to evaporation of $^{1}H_{2}{}^{17}O$ isotopologue.

Here we present the results of a dedicated laboratory experiment aimed at quantification of triple isotope effects accompanying evaporation of water. The experiment was designed to simulate evaporation of water under natural conditions. Identical containers with predefined mass of water of known isotopic composition were placed in an isolated chamber with controlled parameters during the experiment (temperature, relative humidity, flow of nitrogen). In regular time intervals (ca. one week) samples with partially evaporated water were removed one by one from the chamber, the remaining mass of water in the removed container was determined gravimetrically, and the water was stored under controlled conditions for subsequent isotope analyses. The experiment lasted three months.

The results of the experiment were interpreted in the framework of Craig-Gordon model of evaporation [4]. It turned out that the assumption often used in the description of isotopic effects accompanying evaporation process which says that the liquid phase is isotopically homogeneous during the process, leads to conflicting results for all three isotopes. However, if surface enrichment of the liquid phase, different for each heavy isotopologue ($^{1}H^{2}H^{16}O$, $^{1}H_{2}{}^{18}O$, $^{1}H_{2}{}^{17}O$) is included in the model, consistent results for all three isotopes can be obtained, with kinetic fractionation factor for $^{1}H_2{}^{17}O$ isotopologue equal 14.84 ± 0.40 ‰, which, within the quoted uncertainty, agrees well with the value of 14.60 ± 0.30 ‰ obtained by Barkan and Luz [5].

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THE POSSIBILITIES OF P SOURCES IDENTIFICATION BASED ON CHEMICAL AND ISOTOPIC ANALYSES ON THE EXAMPLE OF ZAKRZÓWEK RESERVOIR - PRELIMINARY STUDIES

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Anthropogenic eutrophication is one of the biggest problems of recent decades, hence studies which can improve water quality are very important. Phosphorus, like nitrogen, belongs to the elements limiting of biomass multiplication. Therefore possibility of P sources identification and broader understanding of processes occurring in phosphorus cycle can be used to protect our drinking water resources and also to their revitalization.

Phosphorus has only one stable isotope, ^{31}P, but in most its compounds is strongly bonded with oxygen (3 stable isotopes, with mass 16, 17 and 18). Without biological activity the O-P bond is not broken and isotopic fractionation associated with abiotic processes is not greater than 1‰ [1] so we can measured δ^{18}O-P as an indicator of P source. PO_4^{3-} ions can be easily absorbed by organisms, therefore their excessive amount is a danger to quality of water resources. Nowadays, development of analytical techniques allows us to measure the isotopic composition of oxygen in samples with micromolar oxygen content, so isotopic analysis of phosphates extracted from water has been gaining popularity in recent years (i.e. [2, 3, 4, 5]). The different PO_4^{3-} sources could have a similar δ^{18}O values and recognition of the phosphates origin could be difficult; to distinguish between natural and anthropogenic sources of phosphates we are looking for deviations from equilibrium line δ^{18}O-PO_4^{3-} - δ^{18}O-H_2O (eg. [1, 6]) in seasonal cycle.

Here we present and briefly discuss the first results of isotopic analysis of dissolved inorganic phosphates (δ^{18}O-PO_4^{3-}) in small retention reservoir in Zakrzówek near Lublin (S-E Poland). The results of our preliminary studies could be useful to identification of phosphates source in this reservoir in studied period.

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NATURAL CHEMICAL AND ISOTOPIC GROUNDWATER CHARACTERISTICS IN URBAS LANDSLIDE RECHARGE AREA IN THE KARAVANKE MTS. (NW SLOVENIA)

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Abstract

The purpose of the research on natural chemical and isotopic groundwater composition in Urbas landslide is to determine the groundwater origin in the landslide body and obtain information on the groundwater flow pattern. Groundwater sampling with field parameters measurements in four springs and two wells were carried out. Groundwater samples for isotope analysis were taken six times in year 2018, three times in dry period and three times in wet period. The measured average values of $\delta^{18}O$ are dependent on weather conditions and altitude. Based on determined Ca-HCO_3 type of groundwater and estimated range of altitude (2,190 – 1,370 m a.s.l.) of the water origin the carbonate rocks of Belščica hill (up to 2,105 m a.s.l.) are interpreted as a main Urbas landslide groundwater recharge area (1,300 – 1,150 m a.s.l.).

Key words: *Hydrogeochemistry, oxygen-18, deuterium, water origin, altitude effect*

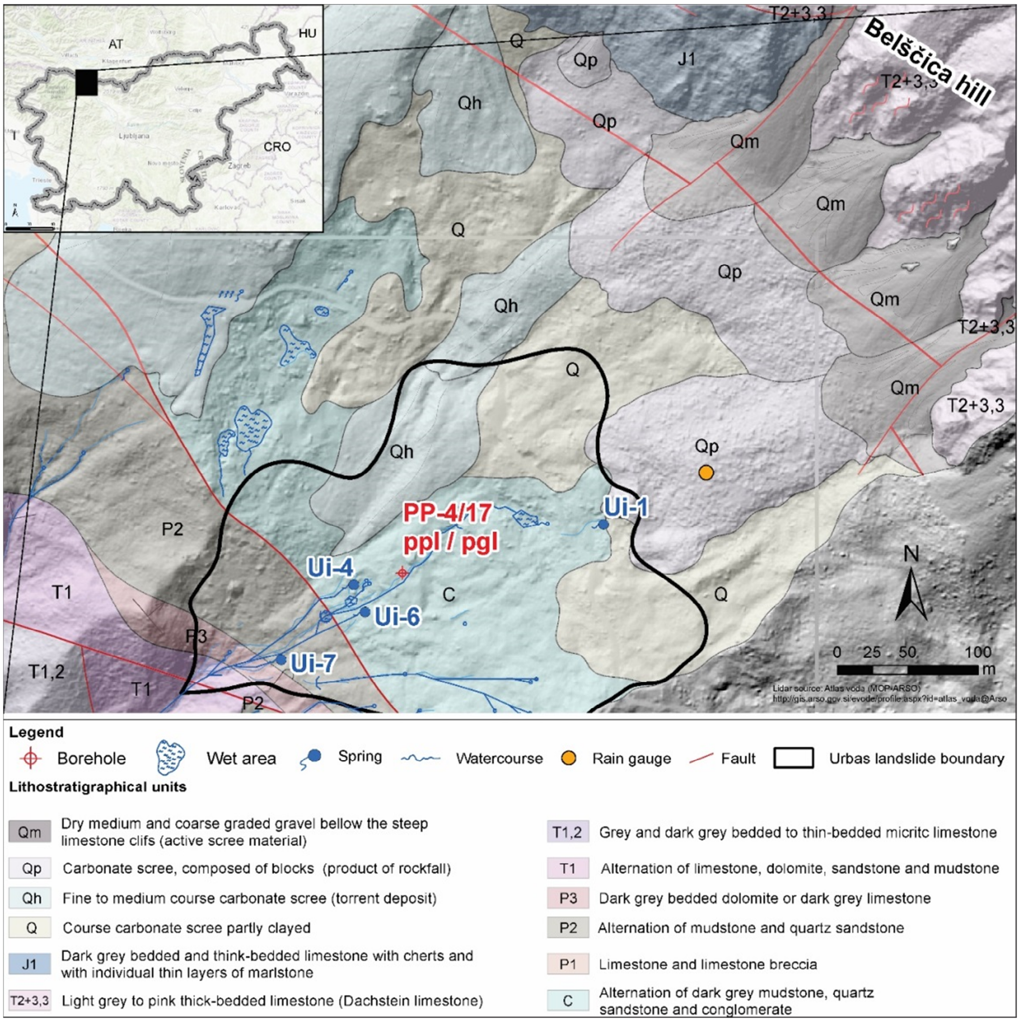
Introduction

Hydrogeological conditions have an important role in the stability of slopes [1]. Their interpretation is often complex and require multiple sources of information. Natural chemical and isotopic groundwater composition contains information, which can be efficiently used for characterisation of hydrogeological conditions in the landslide body and its recharge area [2]. This paper presents the first chemical and isotopic data from the Urbas landslide area. The main goal of the research was to get an insight into hydrogeological features of the landslide and its recharge area.

Settings

The research area lies above the settlement of Koroška Bela in the Karavanke Mts. (NW Slovenia), in the area (Fig. 1) which is highly prone to slope mass movements and poses a high risk for the safety of the settlement. The landslide extends from an elevation of 1,150 to 1,300 m with a gradient ranging generally from 30 to 70 ° [3]. Average annual precipitation is 2,000 – 2,600 mm (at Javorniški Rovt (939 m a.s.l.)) and has two precipitation peaks, with the main one in autumn, and the second one in spring. The average annual air temperature is 3 – 5 °C [4]. The sliding mass is composed of tectonically deformed and weathered Upper Carboniferous and Permian clastic rocks covered with a large amount of talus material which originates from upper laying Triassic to Lower Jurassic carbonate rocks [5, 6].

Observed large fluctuations of springs discharges and of groundwater levels in observation wells are highly dependent on meteorological conditions [3]. Hydraulic conductivity in the upper parts of landslide body of predominantly gravel layers, is highly permeable (2×10^{-3} to 1×10^{-5} m/s), and in general higher than in the deeper clayey gravel parts (3×10^{-5} to 1×10^{-7} m/s) [3].



Lidar source: Atlas voda (MOP-ARSO)
http://gis.arso.gov.si/evode/profile.aspx?id=atlas_voda@Arso

Figure 1. *Study area (modified after [3]).*

Methods

Above the Urbas landslide, a rain gauge for automatic daily precipitation measurements was placed in June 2018. At the same time, the groundwater samples in permanent springs (Ui-1, Ui-4, Ui-6 and Ui-7) and observation wells (Pp-4Ppl and Pp-4Pgl) for chemical and isotopic analysis were taken (Figure 1). Field parameters were measured with portable WTW Multimeter pH/Cond. 340i/SET (pH value - SenTix 41, electrical conductivity and temperature - TetraCon 325 [7]) and WTW Multi 3410/set C (redox potential - SenTix ORP [8], oxygen content - FDO 925 [9]). Analysis of major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}; SIST EN ISO 14911:2000) and anions (Cl^-, SO_4^{2-}, NO_3^-; SIST EN ISO 10304-1:2009; and HCO_3^-; ASTM D 1067-B mod.) were performed at Vodovod-Kanalizacija d.o.o. accredited laboratory (Table 1). Stable isotope analysis ($\delta^{18}O$ and δD) were performed with Picarro L2130-i [10] at Geological Survey of Slovenia. Individual sample was measured five times, the final result represents an average value of the fourth and fifth measurements. The results were calibrated to three internal and two Picarro standards.

Based on measured precipitation, dry and wet periods were defined. In case when four days before sampling less than 0.2 mm of precipitation was accumulated, the period was determined as dry (samplings in June, August and October). Samplings in July, September and November were performed in wet periods.

Results and Discussion

Measured groundwater temperature at the springs and boreholes is in the range 3.9 – 7.7 °C, electrical conductivity (EC) 181 – 251 μS/cm, pH value 7.8 – 8.3 and redox potential (Eh) 372 – 486 mV (Table 1). The chemical analyses show that the content of Na^+ is low (1 – 1.5 mg/L), also concentration of SO_4^{2-} (<1.5 – 3.84 mg/L), K^+ (<0.25 – 0.35), Cl^- (<0.75 mg/L), NO_3^- (<2.2 mg/L) and Mg^{2+} (4.5 – 5.7). The concentration of Ca^{2+} is higher (32 – 44 mg/L) as well as concentration of HCO_3^- (123 – 157 mg/L). The spatial comparison of chemical composition shows no significant difference in major ions concentration between upstream and downstream sampling points (Table 1). According to the major ions, the groundwater is of $Ca-HCO_3$ type [11]. This indicates that the groundwater in Urbas landslide originates mainly from limestone, which points out Belščica hill as a most probable recharge area.

Water isotope composition ($\delta^{18}O$ and δD) depends on the altitude (temperature effect) and continental effect, governed by the amount of the precipitation [12]. The results (Table 2; Figure 2) show that average values of $\delta^{18}O$ from upstream to downstream measuring points are mainly changing according to weather conditions (dry period: -11.76‰ to -

11.42‰, wet period: -11.23‰ to -10.34‰). Altitude effect in the Alps and the Coastal region of Slovenia is determined as: Y=399.66X – 2,679 [13], so the recharge area of our samples is estimated at 2,190 – 1,370 m a.s.l., which corresponds to the elevation of Belščica hill (2,105 m a.s.l.).

Table 1. *Physical-chemical field parameters and main ions in groundwater measured on the 21th of June 2018*

Sampling point	**Ui-1**	**Pp-4-Pgl**	**Pp-4-Ppl**	**Ui-6**	**Ui-4**	**Ui-7**
Object type	Spring	Well	Well	Spring	Spring	Spring
Altitude (m a.s.l.)	1275.4	1229.7	1229.7	1218.5	1237.45	1195.8
Object depth (m)	/	15.2	6	/	/	/
Temp. (^{0}C)	3.9	6.4	6.9	5.2	5.1	6.6
EC (μS/cm)	175	322	209	217	211	235
pH (/)	8.3	8.1	8.1	7.9	7.9	8.0
DO (mg/L)	11.9	10.0	10.5	11.0	11.3	10.7
O_2 (%)	105.3	94	99.3	100	102.4	100.4
Eh (mV)	347	365	378	469	440	442
HCO_3^- (mg/L)	123	143	143	150	143	157
Na^+ (mg/L)	1.0	1.4	1.3	1.4	1.1	1.5
K^+ (mg/L)	<0.25#	0.32	0.35	0.31	< 0.25#	0.35
Ca^{2+} (mg/L)	32	38	38	40	39	44
Mg^{2+} (mg/L)	4.5	5.6	5.5	5.5	5.5	5.7
SO_4^{2-} (mg/L)	< 1,50#	3.30	3.06	3.45	1.89	3.84
Cl^- (mg/L)	< 0.75#	< 0.75#	< 0.75#	< 0.75#	< 0.75#	< 0.75#
NO_3^- (mg/L)	< 2.2#	<2.2#	< 2.2#	< 2.2#	<2.2#	< 2.2#
Water Type	$Ca-HCO_3$	$Ca-HCO_3$	$Ca-HCO_3$	$Ca-HCO_3$	$Ca-HCO_3$	$Ca-HCO_3$

 # - <LOQ

Table 2. *Isotopic composition of precipitation and groundwater samples taken in selected springs and wells.*

Date	**21.06.2018**		**2.07.2018**		**7.08.2018**		**3.09.2018**		**1.10.2018**		**9.11.2018**	
Precipitation	0 mm		7.4 mm		0 mm		52.2 mm		0 mm		11 mm	
	$\delta^{18}O$ (‰)	*δD (‰)*	*$\delta^{18}O$ (‰)*	*δD (‰)*	*$\delta^{18}O$ (‰)*	*δD (‰)*	*$\delta^{18}O$ (‰)*	*δD (‰)*	*$\delta^{18}O$ (‰)*	*δD (‰)*	*$\delta^{18}O$ (‰)*	*δD (‰)*
Rain gauge			-8.87	-61.1	-6.59	-39.8	-9.75	-63.4	-7.30	-43.6	-8.58	-51.2
Ui-1	-11.87	-80.5	-11.74	-80.6	-11.90	-80.9	-11.21	-75.5	-11.51	-77.9	-10.74	-72.3
Pp-4Pgl	-11.90	-81.1							-11.28	-76.4	-10.36	-69.0
Pp-4Ppl	-11.91	-81.3										
Ui-4	-12.18	-83.5	-12.27	-84.9	-12.15	-83.4	-11.68	-79.4	-11.65	-79.6	-10.81	-72.8
Ui-6	-11.68	-80.1			-11.67	-79.6	-10.55	-70.6	-11.11	-75.1	-10.13	-66.9
Ui-7	-11.69	-79.7	-11.32	-77.2	-11.57	-78.6	-10.54	-70.1	-10.99	-74.2	-10.04	-66.2

** – ΣPrecipitation (mm) 4 days before sampling*

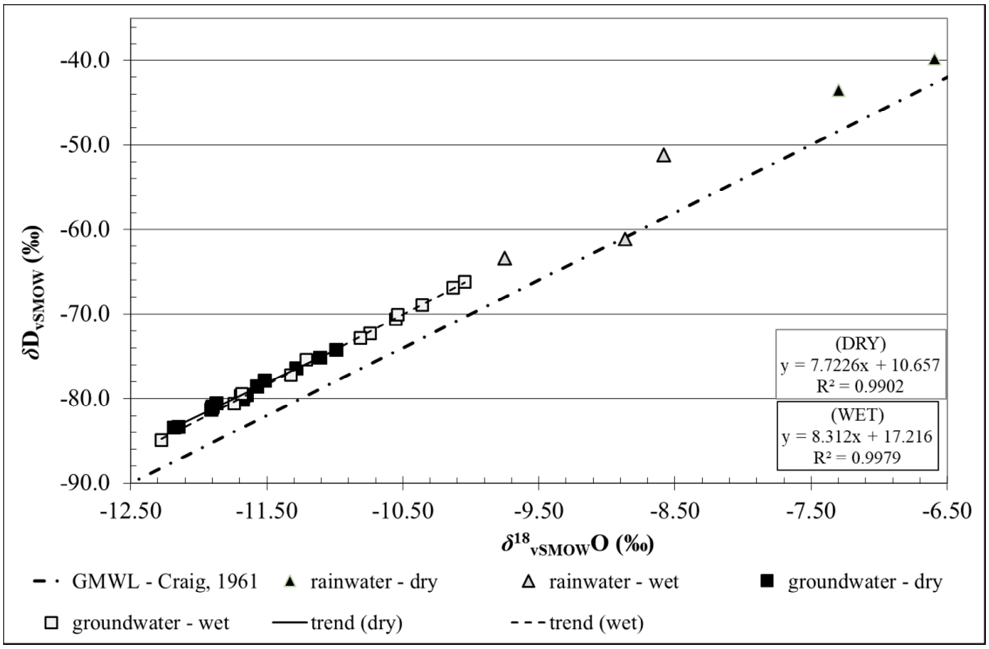


Figure 2. *Measured values of $\delta^{18}O$ and δD in samples.*

Conclusions

The paper presents first indicative survey, focused on chemical and isotope composition of groundwater in the wider Urbas landslide area. It has indicated Belščica hill as most probable recharge area of the Urbas landslide. To confirm this hypothesis further investigations are planned. They will include more frequent and long-term sampling. For defining portions and residence times of rapid runoff components [14] a high temporal resolution (at least weekly) sampling of δ^{18}O from precipitation and groundwater is planned. Additionally, analyses of sulphur, strontium, boron and carbon isotopes, and tritium activity in groundwater may give additional information about their origin.

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CHARACTERIZATION OF GEOTHERMAL RESOURCES IN SLOVENIA BASED ON NEWEST MONITORING RESULTS

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Abstract

Groundwater levels, temperatures and abstraction rates are measured continuously within an hourly interval at sites with granted concessions for thermal water use in Slovenia. Beside, chemical (field parameters, main and trace elements, organics and pesticides) and isotopic (tritium, oxygen and deuterium in water) analyses of thermal water are performed annually and once in a lifetime (noble gases); temperature and quantity of waste water is monitored continuously; pumping (step) tests have to be made periodically etc. All these data are interpreted annually in a standardized report form which is then approved by the Environmental Agency of Slovenia. This has mostly been established at all Slovenian sites in 2019 and makes a firm ground to be able to provide, the first time ever, a reliable hydrogeological characterisation of our geothermal aquifers.

Keywords: production monitoring, water analysis, natural variability, over-exploitation, data uncertainty

Introduction

There are more than 50 sites with thermal water (20 - 75 °C) in Slovenia emerging in the extensive Pannonian sedimentary basin and its Alpine surroundings: i) warm spring systems in fissured mostly carbonate aquifers, ii) aquifers in fissured carbonate and metamorphic rocks in basement below sedimentary basins, and iii) intergranular aquifers in sedimentary basins. Most are rather local but two regional systems with multiple users and a threat of overexploitation also exist: the sandy Upper Pannonian aquifer in the Mura-Zala sedimentary basin in NE Slovenia and the dolomite basement aquifer in the Kriško-Brežice sedimentary basin in SE Slovenia.

Geothermal resource estimation and characterisation can be made with various uncertainties. In the regions with traditional use of thermal waters as in the Pannonian basin [1], it is expected that at least some measurements exist. The quantitative and qualitative assessment of aquifers, independent of national borders, is also important in the framework of groundwater body assessment within the River Basin Management Plans required by the Water Framework Directive (2000/60/EC). Production and surveillance monitoring systems are the appropriate tools for this and may differ in detail based on the type of observed geothermal system.

Monitoring of geothermal aquifers was rarely the case in the wider Pannonian basin region [2, 3]. Some indications on over-exploitation of the transboundary low temperature Upper Pannonian sandy geothermal aquifer have been investigated on a local [4] and regional scale [5, 6, 7], however, it was also very difficult to gain comparable monitoring data from the neighbouring countries.

Two types of concessions can be granted for the use of thermal water. If total reinjection (a geothermal doublet) is established, the mining concession based on the Mining Act is being granted by the Ministry of Infrastructure. If this is not the case, a water concession under the Water Act is being granted by the Ministry of the Environmental and Spatial Planning. The latter producing sites with granted concessions are obliged to perform monitoring of abstracted quantities, impacts of water use and of hydraulic properties of geothermal objects.

It is worth emphasising that only one mining concession is granted for geothermal use even in 2019, for a doublet in the district heating system of the town Lendava. As these monitoring requirements significantly differ from the ones listed in water concessions (the first being less rigorous), we will focus only on the situation with the water concession.

Methods

Due to various legislative complications most thermal water users gained their water concessions only in 2015. Their Decrees on Water Concession have had prescribed several types of monitoring:

1. monitoring of abstracted quantities,
2. monitoring of impacts of water exploitation and use,
3. monitoring of hydraulic properties of geothermal objects.

Consequently, groundwater levels, temperatures and abstraction rates in production and observation wells with concessions have to be measured continuously with at least an hourly interval of data collection, sometimes also with daily transmission of data to the Environmental Agency of Slovenia. The requirement is also that only 5% of data can be missing otherwise (also financial) measures can be taken.

Moreover, chemical analyses (field parameters, main and trace elements, organic substances and pesticides) and isotopic analyses (activity of tritium, stable isotopes of oxygen and deuterium in water) of thermal water must be performed annually, while composition of noble gases in water is analysed only once, preferably in the first year when the concession is granted. Accredited labs are required to perform the analyses. After the first three years of full inspection of composition and when the natural variation of composition is expected to be reliably evaluated, modification of the parameters list can be made in the monitoring programme which has to be submitted to the Environmental Agency of Slovenia every three years. This approach is expected to be a cost-effective and data-reliable way, acceptable to both parties, the concessionaire and the surveillance agency.

The temperature and quantity of waste thermal water have to be monitored continuously, with at least daily recording. Large efforts are now being put into the harmonisation of requirements and harmonisation with the emission monitoring.

Monitoring of hydraulic properties of geothermal wells should be performed by running pumping (step) tests periodically. The first one should be made in the first year when the water concession is granted, the second in the third year, and the next ones every six years.

Exceptions in all these requirements are possible either when survey was already properly performed prior the concession has been granted and duplication is, of course, not needed or of there are some technical issues which would cause unreasonable costs to establish a fully-monitored system.

All required monitoring data has to be interpreted annually in a standardised Excel-form report and submitted to the Environmental Agency of Slovenia which approves (or not) it.

We had 67 geothermal objects available for analysis, 51 active and 16 inactive ones. Based on lithology (carbonate rocks, metamorphic rocks, Ptuj-Grad Formation, Mura Formation, Špilje Formation, mixed rocks), porosity (intergranular, fissured), geothermal system type (warm water system, aquifer in the sedimentary basin or in the basement of the basin) and location (SE Slovenia, NE Slovenia, other) we grouped them into eight classes for which we identified the main statistical properties based on monitored parameters.

Results and Disscusion

In three years (2015-2018) of establishing such production monitoring systems, several challenges have had to be solved, technically and legislatively.

In practice, artesian wells with high free CO_2 gas content and/or methane emissions still pose a technological challenge for the long-term operation of monitoring equipment. Such wells have pressure and temperature probes installed at the wellheads, which causes several issues which have to be accounted for within interpretation: i) temperature is often dependent also on the ambient air temperature, showing higher temperatures in the summer season; ii) when the well is not in operation, it cools down and the temperature cannot be used to calculate the thermal efficiency of the system, iii) pressure can vary dependent on the scaling effects or gas outbursts etc. Such gas wells also have huge problems with the water meters. Based on several manual discharge rate measurements, these meters can show 1.8 to 2.6-times larger yields as there is the actual water outflow rate.

There are also some modifications on monitoring the quantities of natural thermal springs. Here, the total outflow usually cannot be measured due to costly need for re-working of the capture to install a water meter. It even happened that even though the natural spring was discharging directly into a swimming pool (it was built above the spring), the user has built a concrete pool above it instead and fills it with water from a well, just to easily measure the actually used thermal water quantity. Spring also show the highest tritium activity of thermal waters in Slovenia due to the mixing of thermal and shallow groundwater, however, it is still often well below 3 TU.

One of the greatest challenges was posed by doing the short-term (step-drawdown) pumping tests. In most cases, they were not successful the first time (prior to 2017) and this occasion was the first example when the hydrogeologist and the utilization-system-operator at the site have discussed in very details how the wells are operated, what-kind are the submersible pumps and how they are controlled (many but not all have frequency regulators). Since 2016, step test were performed in more than 40 wells in Slovenia by two different methodologies. The first one is of a traditional type – 3 steps with increasing 3 quantities being pumped for approximately the same time each (30 to 120 minutes, depending what was the time slot the user provided from the test – how large were its thermal water needs). Within the second method we tried to have 4 steps, sometimes with a pause in between the each step. This forms an unique database of data where from not only engineering solutions on specific capacity and its changes in time for each well were evaluated, but we plan also to make a scientific assessment of joint interpretation of gained results based on differenced for such test performance in regards to the aquifer's porosity type.

Previous investigation on chemical and isotopic composition of thermal water [8] showed a generally stable situation over at least one-year period. Still, at some locations long-term trends in decreasing mineralization, emerging natural gas emissions and similar were indicated, implying local deterioration of the aquifer. This has been confirmed by production monitoring analyses also. The greatest issue here was how to provide comparable methods and sampling procedures over time, to be able to compare the data in a long-term and be really sure that chemical trends are not a consequence of a measurement uncertainty and similar. We have learned that careful investigation of the analytical results is needed each time, and some errors can be identified only after several analyses have been performed, therefore we found this annual sampling approach extremely valuable to really be able to define what is the natural variation of thermal waters' composition and what are random or systematical measurement errors.

The requirements have resulted in much better care for thermal water wells in general, as many well-logs and camera inspections were made to establish a reliable status of the casing (and its leakage) to plan well rehabilitation. Many users installed also additional heat pumps to reduce the waste thermal water temperature, now approaching 20-25 °C and not 30 °C anymore. This is favourable for keeping good aquifer's status and also enhanced use of direct geothermal energy, respectively.

We analysed only categories with more than 5 objects with available datasets. This summed to 41 objects from warm water systems in carbonate rocks, carbonate aquifers in the basin in central and west Slovenia and Mura formation in NE Slovenia.

The lowest dynamic piezometric water level was measured at the Coast at -168,7 m a.s.l., while the highest in Cerkno at the Alps with 570,4 m a.s.l. The average change of dynamic water level during the pumping is about 21 m. The heads generally decrease towards east which follows the general topography of the country.

Warm water systems have the water outflow temperature up to 40 °C, carbonate aquifers in west and central Slovenia up to 43 °C, while in SE Slovenia between 40 and 63 °C. The NE Slovenia with siliciclastic Miocene formations produces the hottest water, between 37 and 78 °C.

As the average waste water temperature is often below 30°C, the average thermal efficiency is quite high, 64 %, and still indicated possibilities for some improvements.

Discharge rates clearly distinguish among aquifers: carbonate aquifers in central and west Slovenia are most productive and produce 47% of all thermal water. Only little smaller share is attributed to NE Slovenia, where the Mura Formation has produced about 37% of all thermal water in 2017. The carbonate basement aquifer in SE Slovenia was reported to produce 10% of total thermal water production, but it might be higher. Other aquifers are more local and have minor productivity.

Conclusions

The Slovenian requirements for production monitoring are rather extensive and strict, however, almost all thermal water concessionaires have had it properly established in 2019. Based on first such data from 2017 we were able to make the first reliable national characterisation of the Slovenian geothermal aquifers which will be much improved in the following years.

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P-5

CARBON ISOTOPE VARIATIONS IN LAKE TAPELIAI SEDIMENTS CAUSED BY ENVIRONMENTAL FACTORS

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Anthropogenic activities such as agricultural practices, dam constructions wastewater discharge, greenhouse gas emissions, and changes in atmospheric pollutant deposition affect lake ecosystems by changing the import and export of organic and inorganic matter. This includes ongoing transformation processes within the system, as well as CO_2 exchange rates with the atmosphere. In this study, we examined how land use and urbanization changes in adjacent areas affected biological productivity and carbon cycling in a lake system over 100 years, and how these changes are reflected in carbon isotope variations. As an object for our research was chosen a running, shallow Lake Tapeliai (N 54°46'28", E 25°26'45") attributed to a sandy glacial tunnel valley near the Neris River and located in suburb of Vilnius City, Lithuania. Lake Tapeliai is a part of the lake chain connected by a brook with lakes Juodis (54°46'49"N, 25°26'29"E) in the North and by a ditch with Lake Lydekinis in the South. It is known that this ditch was opened between 1879 and 1923. In the 1960s an inflowing ditch connecting the former first original water body of Lake Lydekinis (54°46'11"N, 25°27'23"E) with Lake Tapeliai was blocked by a sand buffer, so Lake Tapeliai became the first original water body in the entire lake chain. During spring flood periods or after long-term rains, the lake is fed by an inflow of coloured water from the surrounding watershed mires.

We performed radiocarbon (^{14}C) activity and stable carbon isotope ratio analysis in two organic fractions: humin and humic acids of lake sediment. Additionally, we performed pigment and diatom analysis, determined the carbonate and organic matter (OM) content in sediments, as well as the C/N ratio in sedimentary OM.

Over the last century, the estimated radiocarbon reservoir age (RRA) in both sediment organic fractions varied from 1136±112 y to 5733±122 y. The increase in the RRA by 1175±111 y was related with higher inputs of pre-aged organic carbon and ^{14}C depleted hard water due to the opening of the channel connecting two lakes. Nuclear weapons tests caused an increase in RRA of up to 5421±135 y and 5733±122 y in humin and humic acids, respectively.

^{13}C values in the humic acid fraction showed a tendency to decrease, depending on the content of autochthonous versus allochthonous OM in sediments, while changes in the sources of OM had a minor impact on the stable carbon isotope composition in the humin fraction. ^{14}C depleted organic and inorganic carbon inflow and changes in the sources of sedimentary OM affected the ^{14}C activity difference in both fractions by 1-5 pMC.

P-6

SEASONAL CHANGES OF LEAF CELLULOSE δ^{13}C AND δ^{18}O IN CO-OCCURRING DECIDUOUS OAK SPECIES

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Seasonal variations of cellulose yield and stable isotope composition (δ^{13}C and δ^{18}O) were assessed of foliage samples of *Quercus cerris* and *Q. petraea*. Leaf samples were collected biweekly from two individuals for both species from the same stand located at Eger-Almár (Hungary) during two consecutive growing seasons (2014 & 2015). It is hypothesized, that if any inter-species differences occur in either the yields or stable isotope seasonality during the growing season, that has to be attributed to the physiological differences between the species. In addition, any contrast between the consecutive growing seasons might indicate different plant physiological response of the studied oak species to the distinct environmental conditions prevailing in 2014 and 2015.

The analyzed leaf material was separated to vein and blade, and cellulose extracted using the Jayme-Wise method [1, 2]. It was found that there:

1. is a high increase in cellulose yield in vein and blade in after budburst for two to three weeks around the turn of April & May allowing to identify transitions times from juvenile to mature phase in leaf development of the two species;
2. is a clear difference in the cellulose yield between leaf tissues for both species (vein showing higher values than the blade samples).
3. are seasonal differences in cellulose yields in foliage development through growing seasons of 2014 and 2015 comparing *Q. cerris* & *Q. petraea* i.e. unexpected variations were detected in 2015 the cellulose yield which was not documented before in any study.

The stable oxygen isotope ratio in vein cellulose slightly decreased from the beginning of the growing season of 2015 (from 31.32‰ to 27.69‰) until the first week of May in *Q. cerris*, then the values remained rather constant (Fig. 1A). While δ^{18}O values in the blade suggest a small gradual enrichment in the youngest leaves changing from 34.93‰ to 39.62‰ until 1 June, afterwards the δ^{18}O decreased to ~34‰ and remained at this level (Fig. 1A).

In *Q. petraea*, δ^{18}O increases in the blade from 35.43‰ to 41.26‰. The highest value was reached by 21 May, and then decreased to the level of ~34‰. The vein cellulose δ^{18}O of *Q. petraea* slightly decreased from 28.44‰, reaching 26.20‰ by late summer (Fig. 1B).

The stable carbon isotope ratio followed a pretty parallel trajectory in blade and vein cellulose for both oak species in 2015 (Fig. 1C, D) . In these case for both leaf tissues (vein and blade) δ^{13}C values tended to decrease precipitously from -24.87‰ to -27.58‰ (until 15 August) for the blade whereas in the vein it dropped from -24.68‰ to -27.05‰ (1 July,) for *Q. cerris* (Fig. 1C). A similar decreasing tendency was observed also in *Q. petraea* from ~-25‰ to ~-27‰, and then the values slightly increased in August (Fig. 1C) just as in *Q. cerris* (Fig. 1C). The average difference between midrib and blade of *Q. petraea* was ~-0.56‰.

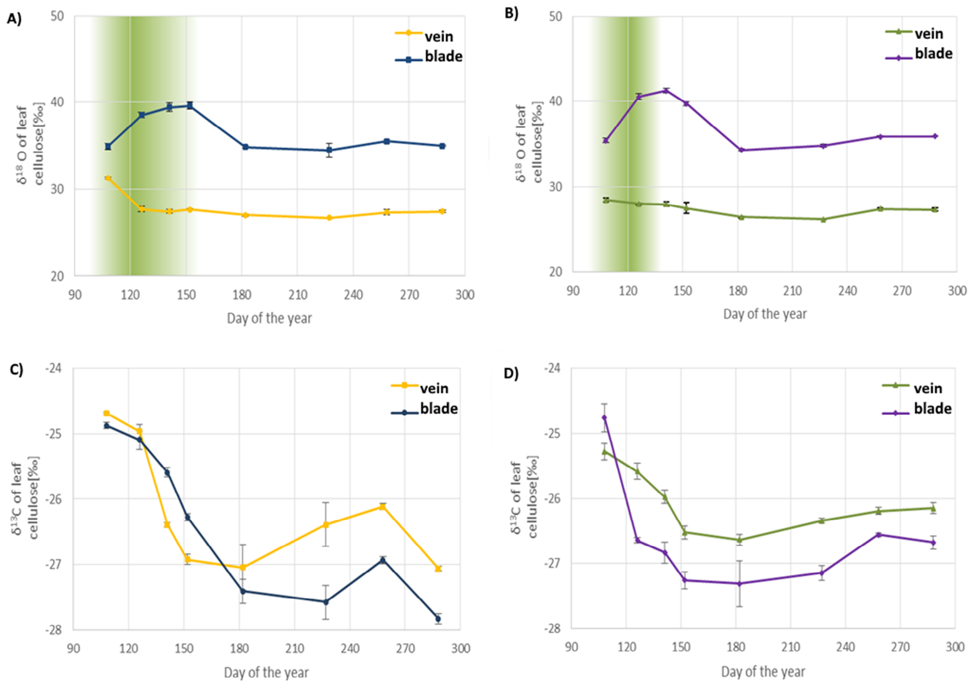

Figure 1: *Seasonal development of stable oxygen A), B) and carbon C), D) isotopic compositions [‰] of Querrus cerris and Querrus petrea in 2015 respectively according to major leaf tissue types (midrib & blade). The foliage samples were collected from a stand in Eger-Almár, Hungary The green shaded area in panels A) & B) show the length of the juvenile phase, DOY represents the day of the year in 2015.*

The seasonal changes in stable carbon and oxygen isotope composition of the cellulose material throughout the growing season of 2015 for both studied oak species (*Q. cerris* and *Q. petraea)* followed the seasonal cycle described for another oak species (*Q.* robur) [3]. The observed seasonal changes can be explained by the processes that fractionate these stable isotopes were associated with the heterotrophic – autotrophic transition which affects the δ^{13}C [3] and the transpiration process for δ^{18}O [4].

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APPLICATION OF RADIOCARBON MEASUREMENTS TO FRESHWATER ECOSYSTEM FOOD WEB ANALYSIS

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The freshwater reservoir effect (FRE) is the imbalance between the radiocarbon isotope ratio ($^{14}C/^{12}C$) in the atmosphere and water bodies. This difference in ^{14}C concentration in different specimens is caused by processes that affected the freshwater ecosystem. Both natural factors and anthropogenic pollution can lead to changes in FRE. These external factors of the environment affect the processes in lake ecosystems which determine the fractionation of carbon isotopes in freshwater systems. This changes the reservoir effect and results in systematic errors in radiocarbon dating. A number of studies have been conducted to show the differences in FRE in different locations, in time, in the same lake or river, in different aquatic plants and animals or even in single fish species of the lake [1–3]. Therefore, the aim of this research was to evaluate the redistribution of ^{14}C between specimens of different trophic levels.

Recent studies have used stable nitrogen and carbon isotope ratios ($\delta^{15}N$, $\delta^{13}C$) as indicators to describe the trophic level and food source of an organism, respectively. A combination of these two isotopes can describe food web structure [4,5]. However, it is not easy to identify carbon sources (autochthonous or allochthonous) in the food webs of freshwater ecosystems only on the basis of stable carbon and nitrogen isotope ratios. Therefore, additionally we have used the ^{14}C concentrations which greatly improved these estimations.

We measured ^{14}C, $\delta^{13}C$ and $\delta^{15}N$ of 18 fish samples (8 different species) from Lake Tapeliai using a 250 kV single stage accelerator mass spectrometer (SSAMS, NEC, USA) and isotope ratio mass spectrometer (IRMS, Thermo Scientific Delta V Advantage) in the Center for Physical Sciences and Technology, Vilnius, Lithuania. The results show large freshwater reservoir effects in the study area. In the Lake Tapeliai, fish species present a wide range in ^{14}C ages, from 119 ± 37 yr BP for common carp up to 749 ± 33 yr BP for ruffe.

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PREVAILING WIND DIRECTION IMPACT ON RADIOCARBON ACCUMULATION IN BIOSPHERE NEAR NPP

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Human activities and natural processes produce radiocarbon which oxidates and enters carbon cycle. Nuclear objects, like power plants or nuclear waste recycling facilities are common known as significant anthropogenic source of ^{14}C. Usually there are no efficient filters applied to cach $^{14}CO_2$, therefore released gas with radiocarbon contamination is noticeable consumed by biosphere mostly in nuclear object surroundings.

In order to evaluate Ignalina nuclear power plant (NPP)(Lithuania) exploatation impact on environment, there were extracted 9 pine tree cores around the NPP which were separated to 410 tree ring samples (time span 1980-2017) to determine the overall increase of radiocarbon concentration in NPP surroundings as compare to 3 tree cores from background rural area at Vaikšteniai. Samples were physically and chemically (BABAB) prepared [1], graphitized with AGE-3 (IonPlus AG) coupled with elemental analyzer (Vario Isotope Select, Elementar, GmbH) [2] and measured at Vilnius Radiocarbon SSAMS (NEC, USA) facility [3].

Radiocarbon analysis of tree samples collected from multiple locations within 1.8-2.6 km around INPP provides a unique data reflecting anthropogenic radiocarbon contamination and transport from the NPP. Directional analysis in three different sites from NPP exhibited high correlation between ^{14}C concentration in tree rings, wind rose and declared radiocarbon releases from NPP (see Figure 1).

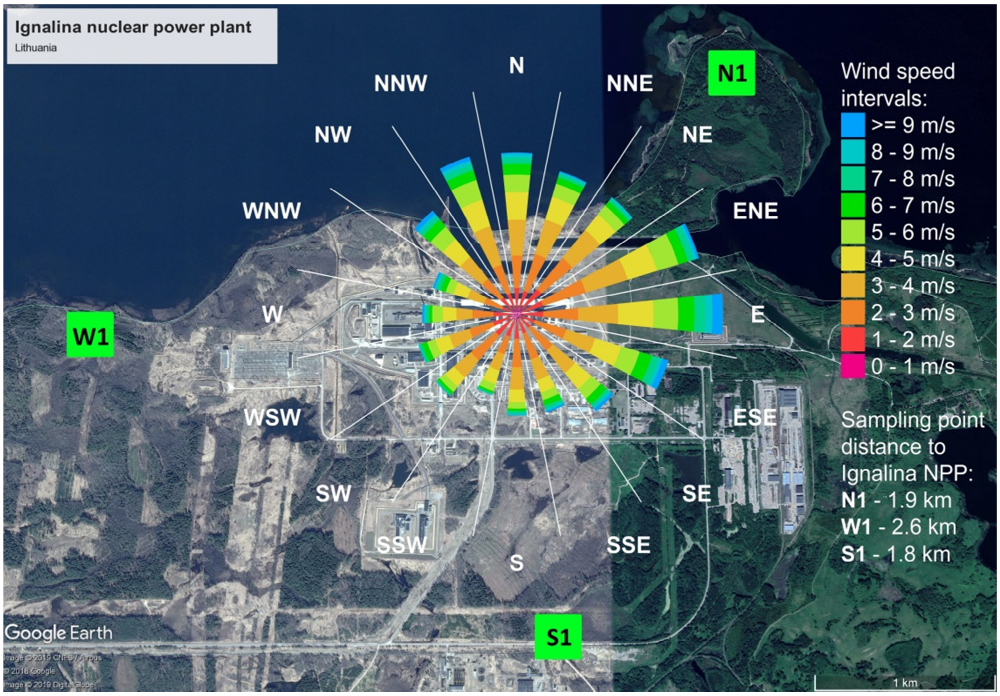

Figure 1: *Sampling sites around Ignalina NPP and local wind rose.*

Application of the high sensitive ^{14}C measurement technique applied for tree rings samples, is a reliable and convenient tool for the NPP anthropogenic impact assessment over long periods.

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AIR QUALITY ASSESSMENT IN ŚWIĘTOKRZYSKI NATIONAL PARK (POLAND) BASED ON OC/EC CONCENTRATION AND CARBON ISOTOPIC COMPOSITION OF ATMOSPHERIC DUST AND BIO-PASSIVE INDICATOR *ABIES ALBA* NEEDLES

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The problem of atmospheric pollutants, especially of particulate matter (PM) is still crucial and very current. The active methods (gravimetric, optic, beta-attenuation) are commonly used but they need specific equipment and are relatively expensive. In montane and woody regions the applied of active sampling is very often impossible. Therefore, the proposed bio-passive sampling method of atmospheric dust will be an possible answer to access the air quality in inaccessible regions. We hypothesize that dust (atmospheric particles) adsorbed on *Abies alba* needles save original pollutant signal possible to identification.

Samples of *Abies alba* needles were collected in 2013 in 20 different localizations in Świętokrzyski National Park. The needles were divided by age into 3 groups: older than 2012, 2012 and 2013. The division was made taking into account the growth of needles on the branch and the noticeable separation of individual annual increments. The particles of the dust were washed out from the surface of the needles using distilled water. PM were obtained from washing water using vacuum filtration of the suspension particles and deposited on Quartz filters for further investigations. The concentration of dust [μg/g] was calculated from the weight difference of particulate matter on filters and weight of dry needles.

To distinguish possible bio-organic dust (crushed needles) contaminated PM derived directly from atmospheric PM, $\delta^{13}C$ of needles and $\delta^{13}C$ of adsorbed dust have been analyzed. The idea is that differences between $\delta^{13}C_{needle}$ and $\delta^{13}C_{dust}$ indicate an anthropogenic impact on the air quality. We expected that $\delta^{13}C$ of C3 plants vary from -34‰ to -22‰ (average -27‰). The $\delta^{13}C$ of possible anthropogenic PM, reported in literature, are: (i) coal, ranging from -24.2‰ (poor quality coal) to -25.7‰ (high quality) in Poland, while the $\delta^{13}C$ of its soot is -24.5‰ [1]; (ii) unleaded fuel particles, varying between -24.2‰ [2] and -26.8‰ [1]; (iii) diesel particles, ranging from -26.5‰ [2] to -28.3‰ [1]. We expected also that PM will be enriched in ^{13}C comparing to natural bio-particles and needles.

For better understanding carbon distribution in PM from our bio-passive sampler total carbon (TC), elemental carbon (EC) and organic carbon (OC) have been analyzed using thermo-optical analysis (TOT). Elemental carbon appearing in atmospheric dust usually comes from the incomplete combustion of fossil fuels or biomass whereas OC may come directly from anthropogenic sources as well as from natural sources (e.g. bacteria, viruses, pollen). Our geochemical analyses showed that the contribution of EC in TC is low and varies seasonality. On the contrary, contribution of OC in TC was characterized by higher input. The highest OC values were obtained from the dust washed out from needles older than 2012. Concentrations of OC in this period were elevated by a large amount of accumulated organics. It can suggest that using needles older than one year is not useful. The variations of OC/EC ratio may derive from the higher adsorption of organic particles (increase in the proportion of OC) on the surface of the needles, as well as the variability of the EC concentration caused by changes of emission sources. Calculated primary and secondary organic carbon indicated that: (i) in the samples older than 2012 concentration of POC and SOC were similar; (ii) in 2012 SOC was significantly higher than POC while (iii) in 2013 POC was higher than SOC. It may suggest that concentration of SOC is higher during heating season and lower during vegetative season.

The obtained $\delta^{13}C$ values of the analyzed 3 generation of needles ranged from -34.5‰ to -29.4‰. Following factors can contribute on this wide range of $\delta^{13}C$ values: humidity, amount of precipitation, air temperature and altitude (through high concentrations of ozone). The obtained $\delta^{13}C$ values of the PM from 3 generation of needles varied from -31.3‰ to -27.2‰. To distinguish influence of crushed needles on final signal reported in PM the isotopic mass balance (IMB) was calculated. Based on isotopic signal of sources calculated from IMB we can draw a conclusion that two main air pollution sources dominated: (i) anthropogenic, characterized by $\delta^{13}C \approx -27.5$‰ (in 2012), depending on localization, which indicated high probability of home heating/transport sources and (ii) natural organic, characterized by $\delta^{13}C \approx -31.0$‰. Comparing spatiotemporal $\delta^{13}C$ values results from our investigation area we can conclude that one-year-old needles are the most useful, as they "save" vegetation period and heating period on their surface. Using older needles is not useful due to the large amount of organic particles or fungi contained in the dust (confirmed by OC/EC/TC analysis). To sum up, our coupled analysis based on OC/EC and carbon isotopes indicated possible useful of bio-passive sampling method and can be recommended in air quality assessment. Moreover it indicates that anthropopression can be noticed even in very clean area like National Park.

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P-10

PARTICIPATION OF TRIBUTARIES TO THE ODER IN THE FORMING OF THE QUALITY OF ITS WATERS IN THE AREA OF WROCŁAW DURING THE RECONSTRUCTION OF THE WROCŁAW WATER KNOT

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The aim of the presented studies was to determine if tributaries affect the quality of water in the Oder River and if a reconstruction of the Wrocław Floodway System is important in this case. The study area included the section of the Oder River with its seven tributaries located in the center of Lower Silesian Voivodeship in the areas of the Wroclaw city. Studies have been conducted in the years 2014 and 2015 and included three sampling series, where following biological (chlorophyll "a" and total number of bacteria), physico-chemical (temperature, dissolved oxygen, total suspended solids, organic and inorganic suspended solids, pH and conductivity) and isotopic (isotopic composition of dissolved inorganic carbon (DIC) and suspended particulate organic matter) parameters were examined.

The results showed considerable differences in isotopic composition of dissolved inorganic carbon between the Oder and its tributaries. Most water samples from the Oder River analyzed in this study had $\delta^{13}C_{DIC}$ values fluctuating from -12‰ to -9‰, whereas $\delta^{13}C_{DIC}$ from tributaries varied in the large range from -23‰ in Trzciana River. The isotopic composition of suspended organic matter varied from -34.00‰ to -26.91‰. The concentration of chlorophyll “a” varied from 0.0 $\mu g\ m^{-3}$ to 7.7 $\mu g\ m^{-3}$. Total bacteria number was similar in most research stations except one located in the Bystrzyca River. Statistically significant positive correlation was found between $\delta^{13}C_{OM}$ and water temperature (r=0.60; p=0.000).

Physico-chemical parameters and the isotopic composition of carbon differed between the Odra River and its tributaries. Parameters measured in the Widawa, Bystrzyca and Oława Rivers confirmed better water quality, therefore, those rivers have potentially a positive effect on the Oder River. However, Ługowina, Trzciana and Ślęza Rivers, which have demonstrated worse values of parameters of water could potentially have a negative impact on water quality in the Oder River. It has also been observed that the Odra river’s tributaries may have a slight influence on the isotopic composition of its waters.

Due to hydrological drought, low water discharge in rivers coincided with an increase of electrolytic conductivity in waters, depending more or less on the size of the watercourse, the nature of the watercourse's contact with groundwater or the catchment area usage. Electrolytic conductivity and pH were positively related with temperature ($r=0.42$, $p=0.003$; and $r=0.42$, $p=0.004$, respectively).

On the basis of the obtained results, the state of the Odra River can be described as good. According to the International Odra Project and Voivodship Inspectorate of Environmental Protection, the state of the Odra river and its tributaries has been gradually changing from bad to good starting from the year 1997. The reason of these changes was, among others, the modernization of sewage treatment plants, the improvement of municipal management in cities and the elimination of major pollutants, which had posed a serious threat to the quality of surface water.

P-11

ASPECTS ON PLANT DEVELOPMENT IN DIFFERENT GROWTH CONDITIONS - THE VARIATION IN H-O ISOTOPES SIGNATURE

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In this work, waters with different isotopic H-O concentrations, in association with different growth substrates, were used to test their influence to the development of plants. The tests, performed in laboratory conditions, had the aim to note the variation for Oxygen 18 and Deuterium content in the roots, stems and leaves of plants, in different stages of vegetation, depending on the different water used for irrigation (tap water, deuterium depleted water and deuterated water) and the different soil types (humus active and universal earth - moderate organic matter level) [1, 2]. Two varieties of salad, namely Lettuce Lollo Bionda and Lactuca sativa, were used as biological materials. Three different types of water have been considered for watering: tap water, with a stable isotope fingerprint of -9.13 ± 0.30‰ for $\delta^{18}O/^{16}O$ and 145 ± 1 ppm content in Deuterium, deuterium depleted water (DDW) having 26 ± 3 ppm Deuterium content and -125.16 ± 0.50‰ for $\delta^{18}O/^{16}O$, and deuterated water, with the isotopic fingerprint of +16.90 ± 0.40‰ for $\delta^{18}O/^{16}O$ and 173 ± 2 ppm content in Deuterium. Water extraction from the biological materials was made by lyophilisation. The Deuterium and Oxygen 18 isotope ratio analysis from water was performed after the isotope exchange of sample with equilibration mixture gas, using a Gas Bench II device coupled at a Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) Delta V Plus (Thermo Electron, Bremen-Germany) [3].

A significant enrichment in heavy isotopes of water was observed in plants growth with DDW water (3 to 4 times more than the stable isotopic fingerprint of DDW; the level of enrichment was higher in leaves than in roots and haulms) and small differences between the same plants growth in different type soil (more than 2 ÷ 3 ppm in Deuterium and 5 ÷ 7 ‰ Oxygen 18 in salad leaves grown in humus active soil than in universal earth). When tap water was used for watering, an insignificant influence of the growth substrate was observed. A 4 ÷ 5 ppm increased in Deuterium was registered in the water plants when universal earth was used as substrate and 2÷3 ppm increased in Deuterium for plants grown in humus active soil. When deuterated water was used for watering, a slightly different behaviour was registered: a light depletion in heavy isotopes than water used (3 ÷ 4 ppm Deuterium and 5 ÷ 7 ‰ Oxygen 18).

Both biological materials have been poorly developed in the presence of deuterated water but were positively influenced by the water with low concentration in Deuterium and Oxygen 18, stimulating faster and earlier formation of leaves and roots.

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P-12

THE ISOTOPIC COMPOSITION OF H AND O IN BODY WATER - COMPARISON OF THE RESULTS OBTAINED BY USE OF EQUILIBRATION AND HIGH TEMPERATURE CONVERSION IN CF-IRMS TECHNIQUES

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The isotopic studies of total body water were performed for several decades [1] [2] [3] [4]. Stable isotopes can be useful to determine the amount of water or other nutrients in the body and also to measure the ingested nutrient amount that is absorbed and metabolized or excreted. They can be also used to measure the rate of absorption, utilization or synthesis of proteins, fats or carbohydrates [5]. For isotopic analysis plasma, blood, saliva or urine can be used. Useful for studies could be water labelled with ^{2}H, ^{3}H or ^{18}O or doubly labelled water (DLW), contains both heavy isotopes, ^{2}H and ^{18}O [3][5].

Thanks to isotopic studies of δ^{2}H and δ^{18}O of TBW (total body water) we could i.e. determine the amount of fat in the human body; if a baby is exclusively breastfed or not, and how much human milk the baby consumes; DLW could be useful to estimate of total daily energy expenditure, which is used to determine a person's physical activity level [5].

Here we present and briefly discuss the results obtained for plasma, urine, blood and saliva H and O isotopic composition measurements. We compare the results for different pre-treatment techniques. The hydrogen and oxygen isotopic composition of studied samples were measured by two techniques: equilibration with CO_2 for δ^{18}O, and with H_2 for δ^{2}H measurements using CF-IRMS (GasBench II + MAT 253, Thermo Scientific) and high temperature conversion to H_2 and CO using CF-EA-IRMS (Flash 1112 HT EA + ConFloIV + Delta V Advantage, Thermo Scientific).

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P-13

PROCESSING OF LACTATE, BUTYRATE, PROPIONATE AND ACETATE BY METHANE-YIELDING MICROBIAL COMMUNITIES: INSIGHT FROM STABLE CARBON ISOTOPES

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Anaerobic digestion (AD), whose final products are CH_4 and CO_2, ensures energy flow and circulation of matter in ecosystems. The general scheme of AD is well known and comprises four major steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The final two steps, acetogenesis and methanogenesis, are closely linked. Acetogenesis is the stage of anaerobic digestion involves syntrophic oxidation of non-gaseous fermentation products (e.g. low-molecular weight organic acids and alcohols) to CO_2, H_2 and acetate, direct methanogenesis precursors. Our knowledge regarding the microbial ecology and physiology associated with AD is incomplete, because it is restricted to culture-dependent techniques. A good understanding of syntrophic cooperation between microorganisms in transformation of substrate to methane are crucial for attempts to recognize and describe poorly-recognized/unknown mechanisms of acetogenesis.

In this work series of laboratory experiments using carbon isotope labeling techniques were carried out to track metabolic transformation of lactate, butyrate, propionate and acetate by the CH_4-yielding communities. The carbon isotope signature ($\delta^{13}C$) of compounds used in the experiments and products of its processing ($\delta^{13}C(CH_4)$, $\delta^{13}C(CO_2)$, $\delta^{13}C(DIC)$) while AD from each experimental series were analysed. Based on the isotopic fractionation factor $\alpha^{13}C_{CO2-CH4}$ and isotopic mass balance calculations the methanogenic pathway and the main sources of CH_4 formation were determined.

Our study indicates that lactate [1] is oxidized mainly to acetate and this comprises the acetotrophic pathway of methanogenesis. In experimental series with lactate the dominant source of CH_4 formation was methyl group from acetate processing. Butyrate is processed to acetate (most likely dominant source of CH_4 and CO_2) and H_2, which may be utilized in syntrophic reaction by hydrogenotrophic methanogens to reduce CO_2 from acetate fermentation [2]. Propionate oxidation results in forming of acetate, H_2 and CO_2, which comprises both methanogenesis pathways – acetate fermentation and CO_2 reduction. Formation of CO_2 is connected mainly with processing of carboxylic group from acetate and direct processing of available organic compounds (e.g. lactate, propionate). Finally, these conclusions will be verified by culture-independent molecular biology techniques - metagenomics and metatranscriptomics.

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P-14

ASSESSMENT OF AUTHENTICITY OF PLUM SPIRITS IN SERBIA APPLYING CHEMOMETRIC TOOLS

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Regarding the quality and quantity of the produced fruit spirits, Serbia is one of the leading countries in the world. Serbian plum spirit, known as "Srpska Sljivovica" is the national, traditional alcoholic drink, which brings authenticity and distinctive feature of the region where it originates from and it is becoming the subject of forgery due to increasing success on the global market. Frauds in the production of fruit spirits are based on the use of sugar of non- fruit origin (made of sugar beet or cane sugar) during the fermentation in order to increase the yield of ethanol.

In the aspect of authenticity control, botanical and geographical origin of the fruit spirit, the most important analytical method is based on the determination of the stable isotopes of $\delta^{13}C$, $\delta^{2}H$, $\delta^{18}O$ (SIRA-Stable Isotope Ratio Analysis). The instrument for stable isotope analysis consists of Elemental Analyzer (FlashEA 1112 HT) and Isotope Ratio Mass Spectrometer (ThermoFinnigan DELTA V Advantage).

In SP Laboratorija, for the detection of the adulteration, we have made laboratory plum spirits from different geographical origin (South and North part of Serbia) and spirits from cane sugar and corn. At the same time, we have prepared plum spirit samples with different amount of added beet sugar (3%, 5%, 10% and 20% sugar was added on the weight of fruit during the fermentation). We have, also, collected plum spirits produced in Serbia in the period from 2013 until 2018.

Combined results of $\delta^{2}H$ and $\delta^{13}C$ values give us important information about botanical origin of ethanol and possibility of distinguishing between fruit spirits and spirits with non-fruit origin (made from beet sugar, maize, cane sugar). In the aim of geographical classification for spirit samples, originating from different locations in Serbia, spirits have been determined by isotope ratio $\delta^{2}H$ and $\delta^{18}O$.

Linear regression analysis were used in order to investigate the correlation between the amount of sugar and value of the stable isotope of hydrogen, and for the formulation of a mathematical model that describes the dependence. The value of percentage of added sugar was transformed in a negative logarithm of the molality (-log B) of added sugar to obtain a linear relationship between the variables. The practical application of these equations is reflected in the calculation of the approximate amount of added sugar, derived from beet sugar, in spirits during production, based on the values of δ^2H.

The application of the formed database and mathematical model enabled the classification of the commercial plum spirit based on the botanical and geographical origin.

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P-15

MONITORING OF FOOD ADULTERATION - QUALITY CONTROL OF BEE HONEYS

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Bee honey is officially defined as the natural sweet substance produced by honey bees from the nectar, which is collected, deposited in honeycombs and thickened by water evaporation. The problem of honey adulteration is well known and many branches of sciences are devoted to the quality control of honey. Besides the classical methods of quality control (pH and acidity, water content, the share of pollen etc.) carbon stable isotope ($\delta^{13}C$) analysis is an established and reliable method for detecting adulteration of honey with cheaper honey substitutes, such as corn syrup and cane sugar. The AOAC official method [1] is working well and solving the problem of honey adulteration with C4 plants sugar. For many Europe countries much more problematic is possibility of honey falsification with C3 plants sugar admixture. Unfortunately, complexity of the matrix and close-up isotopic composition of melliferous plants nectars and sugar syrups from C3 plants yield that common physio-chemical and isotopic analysis not providing unambiguous informations. Therefore, we hypothesised that coupled statistical interpretation of the stable isotope analysis with physio-chemical investigations will provide a new perspective monitoring tool.

Six honey samples (2 lime, 2 rape, 1 acacia and 1 pine honeydew) as well as glucose and fructose syrup (SGF) produced from wheat have been analysed [2]. The content of sugars (fructose, glucose, sucrose and maltose), proline content, diastase number as well as $\delta^{13}C$ of honey and proteins from honey were analysed. Additionally, the $\delta^{13}C$ of SGF and six mixture (10-80% wt. of SGF in honey) were measured. A combustion module (CM) coupled to Cavity Ring-Down Spectroscopy (CRDS) system (G2201-i Analyzer, Picarro Inc., USA) was used for $\delta^{13}C$ of honey, syrup and mixture analysis. The system was controlled by Picarro G2000-1.5.1.10 host software. Samples in tin capsules (Costech, USA) were loaded by an autosampler (Costech, USA) into the combustion module. After the burning at 980°C, purified CO_2 using nitrogen as a carrier gas was collected by Picarro Liaison™ A0301 interface and finally inputted into CRDS for carbon isotopic analysis. The earlier investigation e.g. [3] confirmed the relation between the C concentration and final $\delta^{13}C$ value. Due to varied C-concentration in honey/syrup mixture, the amount of sample necessary for C-isotope analysis in each run was tested experimentally to obtain c.a. 2000-4000 ppm of CO_2 signal. All $\delta^{13}C$ values were reported after multipoint normalisation [4,5] to the V-PDB scale based on international standards NBS-19, NBS-18, IAEA CO-8, USGS-24, USGS-40 and LSVEC. Additionally for larger spread and more precisely normalize $\delta^{13}C$ values the internal laboratory standard were prepared basing of 6-point international standard calibration curve. The $\delta^{13}C$ values of 5 new additionally calibrated laboratory standard (from most enriched in ^{13}C) were: xylitol -9.69±0.04‰; cane sugar -11.13±0.05‰; atropine -18.80±0.04‰; beet sugar -26.03±0.05‰ and caffeine -35.16±0.08‰. Therefore, for super precisely tested of CM-CRDS measurements and final normalization of measured honey/syrup/mixture samples the maximum 11-points calibration curve were used and analytical uncertainty was below or maximum 0.1‰ for $\delta^{13}C$. The $\delta^{13}C$ values of measured honeys varies from -25.97 to -28.26‰, whereas extracted proteins from honey shown $\delta^{13}C$ values between -25.82 and -27.13‰. Calculated possible C4 sugar addition [1] varies between -6.49 and +2.67% and indicate rather C3 than C4 addition. The $\delta^{13}C$ value of SGF was -26.50±0.08‰ and differ from our honeys c.a. ±0.15 to 1.76‰. Moreover, the $\delta^{13}C$ values of true SGF/honey mixture were measured as well as compared with mathematically calculated the $\delta^{13}C$ values and content based on isotopic mass balance. Finally, the coupled isotopic and physio-chemical data were tested for obtaining the comprehensive method that allows unambiguous identification of honey with C3 syrups.

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P-16

THE INFLUENCE OF TEMPERATURE ON CARBON ISOTOPE COMPOSITION AND ORGANIC GEOCHEMISTRY OF COAL FROM UPPER SILESIAN COAL BASIN: AN EXPERIMENTAL STUDY

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Carboniferous age coal of Upper Silesian Coal Basin (S Poland) in the south-western part of formation show reduced the thickness of the rock sequence. The strongly altered rocks are characterized by varied in colour breccia and heavily cracked grey-black coal without a banded structure. It is a well known fact that thermally transformed coal-bearing rocks are characterized by increased fracturing, porosity and reduction of physical and mechanical properties as well as petrological and geochemical indicators. Recently several possible explanations have been proposed for altered coal such as weathering or igneous intrusion but the most probable reason seems thermal changes resulting from intra-deposit coal fires that affected several square kilometres. The main goal of the research is to explain the possible geological process that affected the investigated coal formation. We hypothesize that thermally changed coal saved the influence of temperature (supposed fire) in various conditions on their $\delta^{13}C$ signature as well as organic matter characteristics.

Fifteen samples of bituminous coal and coal shales characterized by different rank and petrographic properties from underground coal mines: (i) Jankowice, (ii) Marcel; (iii) Ziemowit; (iv) Wujek; (v) Piekary and (vi) core Gołkowice IV were investigated. Samples from Marcel coal mine and Gołkowice IV core are mainly altered coals, whereas other locations shown little or negligible changes. Raw coal/ coal shale samples and samples heated in the laboratory to 400°C in an open system (24 hours, pre-heated oven) and in a closed system for 2 hours (heating rate 20°C/min) have been petrologically and geochemically investigated and their isotope composition was determined. Spatial interpretation of raw samples from coal basin indicated that coalification increases with depth (the average vitrinite random reflectance R_r ranges from 0.56 to 2% with the gradient 0.2%/km) and towards the western part of the investigated basin. Moreover, enrichment in ^{13}C with increasing rank in the raw coal have been observed.

A laboratory open-system heating experiment, with free access of oxygen and free evaporation of organic compounds, led to almost total destruction of bitumen either free or bound with a macromolecule. Such compositional changes are shown by depletion of the bituminous fraction in lighter *n*-alkanes in the range of n-C_{11}-n-C_{18} ca in 15-20% rel. In these conditions, light-weight compounds have been evaporated or oxidized. Very small amounts of residual bitumen were composed mostly of heavy PAHs and their oxidized products. A closed-system heating experiment with oxygen depletion increased extract yields comparing to that of raw coals and coal shales. The extracts have been enriched in bitumen from closed pores and possibly partial pyrolysis of organic matter. However, typical pyrolytic products such as *n*-alkenes were not found in the extracts indicating that temperature was too low or time too short to cause advanced macromolecule cracking. Most of lighter compounds are still present in these extracts preserving initial distributions and ratios of compounds. The increase in *n*-alkane concentrations over Pr, Ph, and aromatic hydrocarbons is the most significant change in composition in these samples.

The $\delta^{13}C$ values of raw coals and the samples heated in the closed system varies between 0.01-0.45‰, whereas the $\delta^{13}C$ values of raw coals and the samples heated in the open system varies in wide from 0.18-9.79‰. In the second case, probably some extracted/desorbed carbon species (methane/carbon dioxide/hydrocarbons) depleted in ^{13}C in comparison to raw coal material escaped during the heating procedure and ended up enriching residual thermally changed coals in ^{13}C.

Our $\delta^{13}C$ values and GC-MS data of raw samples experimentally heated in laboratory led us to conclusion that probably main process influenced petro-geochemical characteristics of the heavily cracked grey-black coal (mainly from Marcel coal mine) from Upper Silesian Coal Basin was the thermal transformation of fresh/raw coals in anoxic almost closed conditions.

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CARBON ISOTOPES AS AN INDICATOR OF AIR POLLUTION BY SULFUR – CASE STUDY FOR SUDETEN AND SUWAŁKI REGION IN POLAND

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Human activities have altered atmospheric composition. Trees are interactive monitor of environment and therefore anthropogenic impact has implications for plants physiology and physical response. Since the beginning of industrial revolution, the $\delta^{13}C$ of the atmospheric CO_2 has decreased due to emission of ^{13}C-depleted CO_2 from human activities such as fossil fuels burning and land clearing. The so called Suess effect is reflected in tree rings $\delta^{13}C$.

Freyer [1], who compared the values of $\delta^{13}C$ in annual rings of trees from the control area with less pollution, and from the more polluted area, suggested that the $\delta^{13}C$ values in rings are affected not only by the $\delta^{13}C$ value of atmospheric CO_2, but also other pollutants present in the atmosphere (especially SO_2) that modify the differentiation of the isotopic composition by changing the ratio of intercellular (c_i) to ambient (c_a) CO_2 concentrations during photosynthesis. In particular, the increase of the atmospheric CO_2 concentration may cause the closure of the stomata due to the rise in the CO_2 concentration in the intercellular spaces of a leaf, leading to a smaller differentiation of the isotopes, and thus resulting in an increase of the $\delta^{13}C$ values in the rings. Furthermore, it may, to a certain extent, obscure the effect related to the collection by the plants of carbon dioxide with lowered $\delta^{13}C$ values, caused by the combustion of fossil fuels. Numerous studies conducted later have shown the effect of the pollutants such as SO_2, NO_x, or O_3 on $\delta^{13}C$ values in annual rings of trees. Although the physiological mechanisms of the influence of these pollutants on the photosynthesis process are varied, the increase in their concentrations leads to the rise of the $\delta^{13}C$ values by reducing the conductivity of the stomata or increasing the rate of carboxylation. Meanwhile, acid rains may lead to the reduction of $\delta^{13}C$ by the inhibition of the carboxylation process, caused by chlorophyll degradation [2]. Therefore, it is clearly visible that air pollutants may alter the $\delta^{13}C$ values by influencing the discrimination of carbon isotopes [3].

Carbon isotopic composition ($\delta^{13}C$) in tree rings has been widely used to estimate temporal and spatial variations in intrinsic water use efficiency (iWUE), which is defined as the ratio of photosynthetic carbon assimilation (A) to stomatal conductance (g). The $^{13}C/^{12}C$ ratio in trees is controlled at the leaf level by the ratio of intercellular (c_i) to ambient (c_a)

CO_2 concentrations. If c_i is high relative to c_a, strong discrimination against ^{13}C yields isotopically light biomass. Conversely, if c_i is low - discrimination against ^{13}C results in higher $\delta^{13}C$ values. Therefore, any change in carboxylation and/or stomatal conductance that altered ratio c_i/c_a is recorded as a change in $\delta^{13}C$ and *i*WUE is driven by changes in atmospheric CO_2 and pollutions [4, 5].

Presented results concern measurements of $\delta^{13}C$ (Fig.1) on α-cellulose extracted from tree rings of spruce and pine for Sudety and Suwałki region respectively. The selected research areas: Sudeten and Suwałki represent regions with various intensification of anthropopression. The forest of the Sudeten mountains located on the east of "black triangle" and outside coal mining and industrial regions experienced massive tree death in the 1970s and 1980s. A time span for investigations region is rather long and covers years 1850-2010 in case of Sudeten and 1850 -2003 for Suwałki.

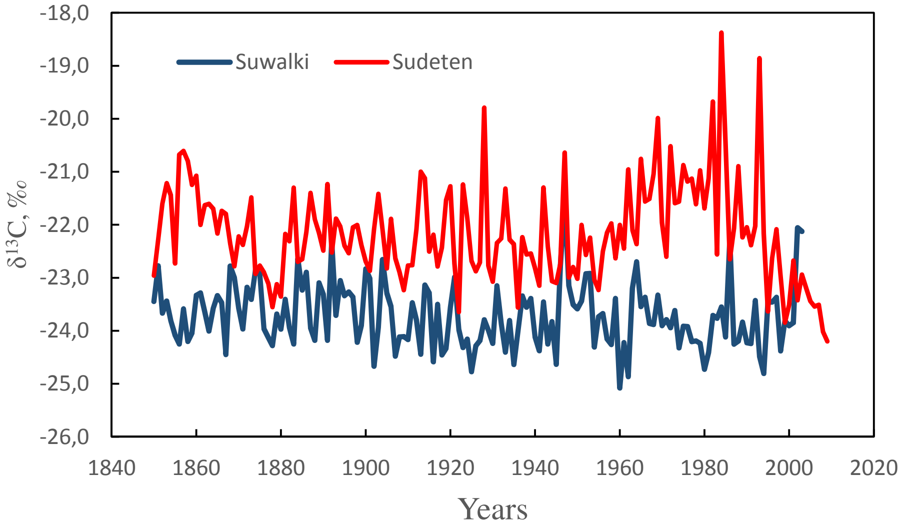

Figure 1: *Comparison of $\delta^{13}C$ for Sudeten and Suwałki region.*

Samples of α-cellulose were isotopically analysed in Gliwice Mass Spectrometry Laboratory using an EuroVector elemental analyser coupled to a continuous flow IsoPrime mass spectrometer. $\delta^{13}C$ results are reported in per mil (‰) relative to VPDB standards. Each sample was run in triplicate, with analytical errors of 0.1‰ and for $\delta^{13}C$. Values of $\delta^{13}C$ in tree rings were used for assessing changes in iWUE.

In the case of $\delta^{13}C$ increasing trend is observed in the years 1960 - 1985 for Sudeten due to SO_2 emission. For Suwałki region this increasing trend is observed only for 1980-1986. Numerous studies have reported widespread increases in iWUE coinciding with rising atmospheric CO_2

concentration over the past century. Investigations for Sudeten and Suwałki regions confirm that the intrinsic water use efficiency of trees (the ratio between carbon uptake and water loss through transpiration) increases as stomatal conductance decreases in response to elevated CO_2. Differences in iWUE, calculated from data sets include not only trend of CO_2 concentration changes but also trend of SO_2 concentration changes.

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P-18

RADIOCARBON AMS DATING AND STABLE CN ISOTOPE COMPOSITION OF MESOLITHIC HUMAN REMAINS FROM POLAND

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Biological studies on Mesolithic human remains from the Polish region are a rare subject of scientific research due to the limited number of these relics and their poor state of preservation. From the project titled "Old material with new methods: Using the latest bio-chemical analysis in studies of Mesolithic human remains from the Polish areas", the radiocarbon dating of bones using accelerator mass spectrometry (AMS) has been performed (Piotrowska *et al*. 2019). For these experiments, the gelatin was extracted from bones, and its quality evaluated by the carbon and nitrogen content, and C/N atomic ratio. The stable isotope composition of both carbon and nitrogen was also determined.

The results have been obtained for 11 bone samples from 5 sites, and throughout this work the results of two preparation methods were compared. Only 7 of the investigated bone samples yielded ages within Mesolithic period, and the most reliable dates range from 5800 to 6800 cal BC. One sample was not datable, and two were shown to be much younger than expected.

Gelatin subsamples were subjected to graphite preparation using an AGE-3 system equipped with a VarioMicroCube by Elementar elemental analyzer, calibrated to obtain the %C, %N and C/N atomic ratios, connected to an automated graphitization unit. Another subsample was assigned for stable isotope analysis of the carbon and nitrogen ($\delta^{13}C$, $\delta^{15}N$), %C, %N and C/N_{at} quantities by using a CF-EA-IRMS system. The equipment comprises of an EuroVector elemental analyzer and continuous-flow IsoPrime mass spectrometer. The results for two independent analysis C/N_{at} values do not differ by more than 0.2.

The first batch of gelatin, prepared without a NaOH wash (Treatment A), yielded unsatisfactory results, in terms of the elevated C/N_{at} ratios (3.5-10.3) and depleted %C and %N for almost all the samples. The average gelatin yield was 14.6%. Therefore, additional sample material was collected, and the preparation procedure was repeated with an alkali treatment step (Treatment B). Most of the Treatment B samples yielded less gelatin (6.5% on average) than the previous ones. Quality indicators fell within acceptable ranges, with C/N_{at} values ranging from 3.2 to 3.5 and the expected carbon and nitrogen content.

Additionally, analysis on bones from Fifth and Sixth International Radiocarbon Intercomparison (VIRI/SIRI) were conducted. Despite the disputable result for the VIRI E sample, which proved to be problematic for many laboratories, the demonstrated reasonable ^{14}C background level allows to expect our results to be accurate.

Five of the radiocarbon ages obtained for the archaeological samples, from the Treatment B, are older than the ^{14}C ages for the Treatment A by 250 to 1400 ^{14}C years. This indicates the presence of a contaminant which is younger than the age of bones. Adding this to elevated C/N_{at} ratios for the Treatment A gelatin, the most probable contaminant is a substance rich in carbon, which was removed by the alkali treatment in the Treatment B. The difference between ages for the same samples subjected to Treatments A and B is proportional to the difference in C/N_{at} ratios for the same samples. Also, the $\delta^{13}C$ was shifted towards values more common for human bone collagen: increased for four of them (Giżycko and Janisławice sites) and decreased for Warsaw-Grochów sample. For Giżycko and Janisławice, the contamination by the humic substances of high carbon content and $\delta^{13}C$ around −25‰ is the most probable explanation for the rejuvenated ages obtained by Treatment A. In the light of the obtained results the most reliable age of Janisławice hunter skeleton is connected with sample from femur bone, prepared with alkali wash, which is 6885±30 BP, and 5840-5715 cal BC. In case of Warsaw-Grochów, the preservative(s) which may have been used are the suspected cause of the discrepancy in the results. The skull of the "little girl from Grochów" was dated to 1415-1260 cal BC, thus it is not of Mesolithic age.

In the case of the Woźna Wieś sample, the new date is 320 years younger. This sample is also characterized by a significant C/N_{at} shift from 10.3 to 3.5 between the Treatments A and B, and a huge difference in %C and %N. In this case the contaminant had a carbon content much higher than collagen, and was older than the bone sample. The significant improvement in a quality of dated material is seen also in $\delta^{13}C$ (shift from −25‰ to −19.4‰) and $\delta^{15}N$ (from 5.4‰ to 13.7‰). We conclude, that the dated material was contaminated by a component much older than the actual age of this sample. The glue, which had been used to reconstruct the skull, must have been present in the material despite physical cleaning before preparation, but the alkali treatment was sufficient enough to remove it. Similarly to Warsaw-Grochów, the bone from Woźna Wieś was dated to an age much younger than Mesolithic: 1640-1880 cal AD.

Freshwater food consumption by humans from Giżycko-Pierkunowo site is likely, as the location of the site is in a close vicinity to Lake Kisajno. Therefore, the freshwater reservoir effect (FRE), causing the ages to appear older than the actual age, was suspected, and was discussed in the light of stable isotope data (Piotrowska *et al*. 2019). A more detailed study on the isotope-based diet reconstructions may provide a prospect to re-evaluate the dates from the Giżycko site, until then the dates should be regarded as maximal.

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BIO-MONITORING OF THE INDUSTRIAL FOREST AREA NEARBY ŁAZISKA POWER STATION (POLAND): DISTRIBUTION OF THE CONTAMINATION ON THE SURFACE OF THE SCOTS PINE NEEDLES

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Abstract

We present the results of the quantitative scanning electron microscopic analysis of pine growing in the industrial forest area in the south part of Poland. The samples of the needles collected from conifers investigated in this study covered the time span 2012-2013. Dendrochemical analysis for trace metal pollution is based on the assumption that element concentrations in the tree represent element availability in the environment in which the tree was grown. The analysis show the impact of the pollution emitted inter alia by one of the most burdensome factory in this area - Łaziska Power Station and also householders and traffic on the elements concentration in trees. The observed presence of different elements and chemical compounds such as ^{11}Na, ^{12}Mg, ^{13}Al, ^{14}Si, ^{15}P, ^{16}S, ^{17}Cl, ^{19}K, ^{22}Ti, ^{20}Ca, ^{26}Fe, ^{30}Zn, ^{33}As, on the surface of the needles, has insular character.

Introduction

Anthropogenic effects affect the physiological processes that control tree growth. Trace elements are removed from the atmosphere by wet and dry deposition, diffusion and retention on solid surfaces. The contamination of the air and rain and soil can be a source of the foliar injury. Most of the trace elements (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) are derived from mining, metal smelting, coal and petroleum combustion, oil burning, incineration of waste, cement production and other industrial activities. Additionally, Pb, Cd, Zn and Ni are found in petrol and motor oil; therefore, motor vehicles are an important source of these contaminants [1, 2]. In the last few decades, the scientists have studied spatio-temporal distribution of contamination by conducting a dendrochemical analysis of different species to establish the impact of soil, air and water pollution.

The determination of properties of tree-rings and foliage is crucial for many applications in the investigation of local and global environmental changes. The aim of research conducted, within various projects since 2011, in the areas located near different industrial factories in Silesia is to assess the impact of anthropogenic contamination on pine tree stands. Dendrochronological and mass spectrometric studies (using different mass spectrometers such as LA-ICPMS, IR-MS, AMS) allowed to determine the effect of contamination on light element stable isotopic composition (C, O, N) and radiocarbon concentration in annual tree-rings width and foliage of Scots Pine [3-6]. In this article, we present the results the elemental analysis of the young pine needle.

Material and methods

The needles of young annual pine shoots were collected in three cities/commune (Fig.1. Table 1) located at different distances from industrial plants Łaziska Power Station (50°8'4,30"N, 18°50'39,79"E): Wyry (ca 5 km far from factory), Mikołów (ca 7 km far from factory) and Podlesie (ca 12 km far from factory) in January 2013 (shoots of pine created in 2012) and in September 2013 (shoots of pine created in 2013).

In our research we used young pine needles for monitoring of trace elements and particulate matter deposited on the pine needles surface. It is known, that rain can remove a considerable proportion of particles accumulated on the foliage, that is why the sampling sites were located in close neighborhood and the samples were collected in the same day to remove the effect of different weather conditions.

Table 1. Main characteristics of the sampling sites

Lab. code	Sampling site and geographical coordinates	Year of creation of the pine needles	Season and year of sample collection
LW_2012	Wyry 50º08'N, 18º56'E	2012	Winter, 2013
LW_2013		2013	Summer, 2013
LM_2012	Mikołów, 50º09'N, 18º57'E	2012	Winter, 2013
LM_2013		2013	Summer, 2013
LP_2012	Podlesie 50º10'N, 18º59'E	2012	Winter, 2013
LP_2013		2013	Summer, 2013

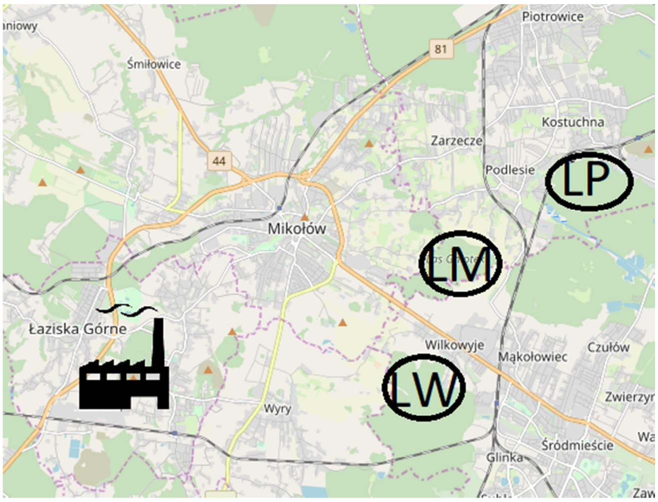


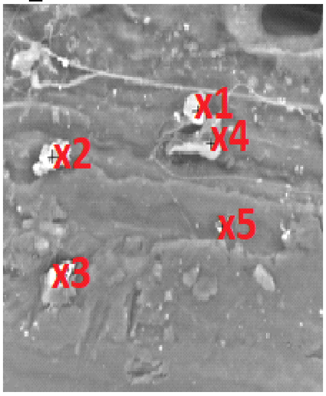
Figure 1: *Localization of the sampling sites at different distances from industrial plants Łaziska Power Station (50°8'4.30"N, 18°50'39.79"E): Wyry (~5 km far from factory), Mikołów (~7 km far from factory) and Podlesie (~12 km far from factory)*

The analysis of the elemental composition of pine needles was done using the PhenomWorld ProX scanning electron microscope equipped with an EDS (X-ray energy dispersion spectrometer). The voltage accelerating the electrons used during the measurements was 15 kV. Micrographs of the surface of selected pine needles are shown in Figures 2 and 3. The points of the surface in which the chemical composition was determined were marked in the picture using crosses. The chemical composition is determined from an area of 2.5 μm ^{2}. Chemical composition of samples determined based on the analysis of the X-ray energy spectrum. The analysis of the surface area of annual pine shoots allows us to compare the image of the needles surface and to determine which elements are currently deposited on the surface of needles [7-10].

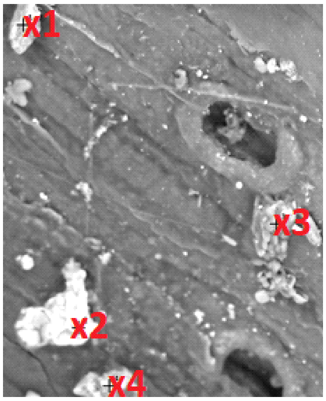
Results

The observed presence of different elements and chemical compounds of ^{11}Na, ^{12}Mg, ^{13}Al, ^{14}Si, ^{15}P, ^{16}S, ^{17}Cl, ^{19}K,^{22}Ti, ^{20}Ca, ^{26}Fe, ^{30}Zn, ^{33}As, (Figure 2 and 3), on the surface of the needles, that has insular character.

LP_2012



LM_2012



LW_2012

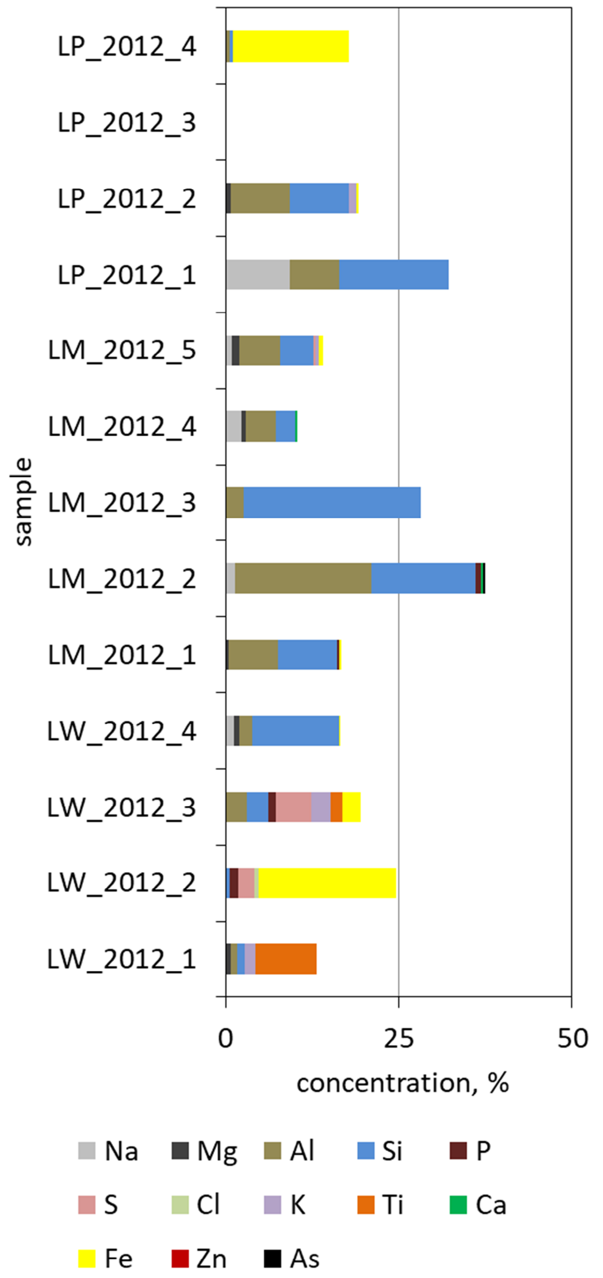


Figure 2: *Micrographs of the surface of the needles and the elements and chemical compounds deposited on the needles in 3 cities: Wyry (LW), Mikołów (LM) and Podlesie (LP) in the area located nearby industrial factory Łaziska Power Station. The samples were created in 2012 (collected in January 2013). "x" mark the points of the surface in which the chemical composition was determined by SEM.*

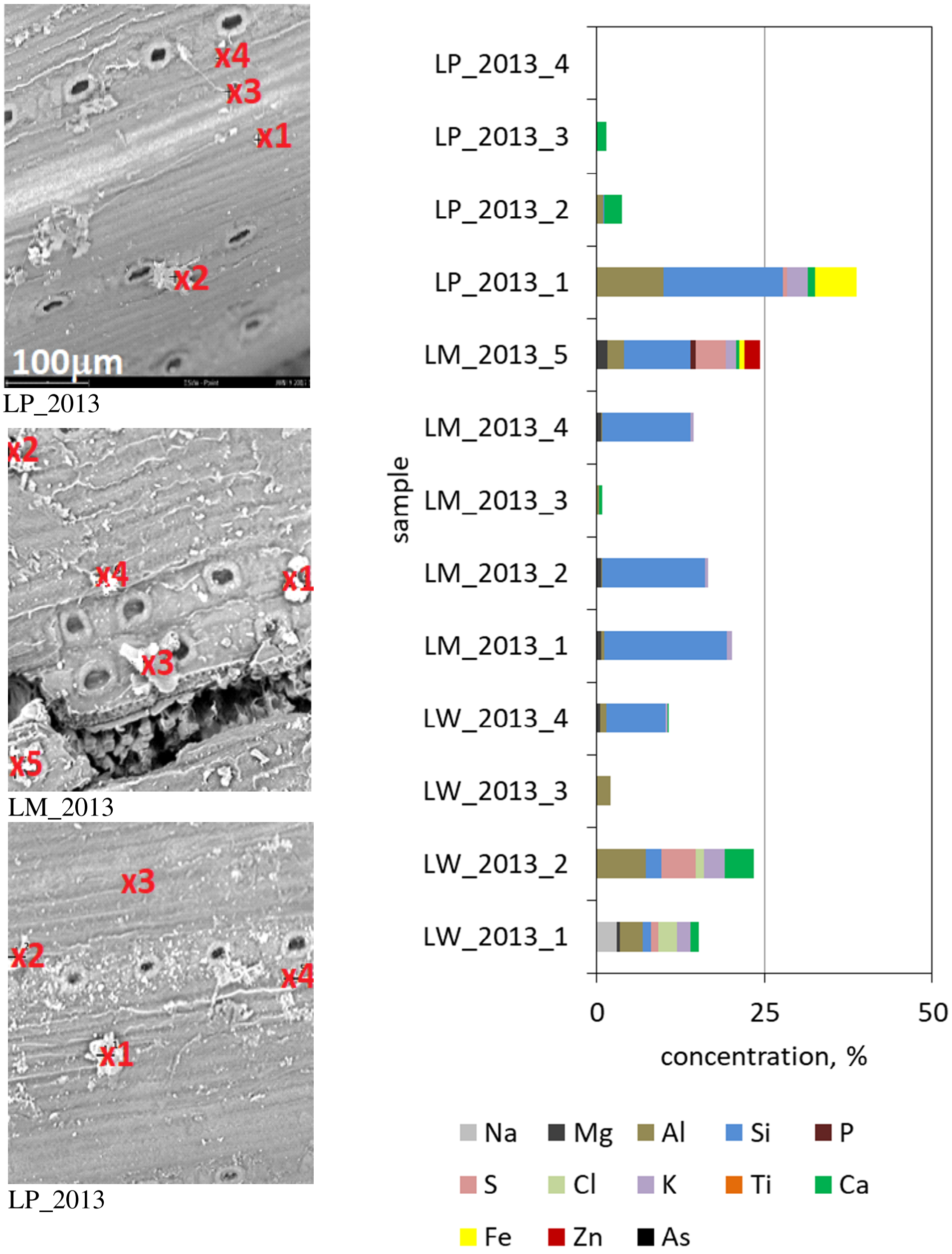


Figure 3: Micrographs of the surface of the needles and the elements and chemical compounds deposited on the needles in 3 cities: Wyry (LW), Mikołów (LM) and Podlesie (LP) in the area located nearby industrial factory Łaziska Power Station. The samples were created in 2013 (collected in September 2013). "x" mark the points of the surface in which the chemical composition was determined by SEM.

The analysis, that have been made since 2011 at the Institute of Physics-CSE of the Silesian University of Technology in cooperation with the Faculty of Agricultural Sciences of the University of Silesia, Faculty of Geoscience of the University of Silesia and the Department of Geology Université de Liège, allow a comprehensive analysis of the impact of ecosystem change and analysis of the impact of the variation in the industrial activities from the first decades of the twentieth century to the present day. The pressure of industrial pollution has been reflected in the short and medium-term incremental reactions of pines.

On the surface of the needles, collected from each sapling site, a presence of aluminium and silicum has been noted. The components deposited on the needles surface contain also magnesium, phosphorus, sulfur, chlorine, potassium, titanium, calcium, iron. Generally, the samples collected in the winter are characteristic by higher deposition of sodium, aluminium, silicon, phosphorus, sulphur and iron in compare to the sampels collected in the summer. We have noted also the presence of titanium on the samples collected in the winter in LW. Relatively high concentration of sulphur have been detected in Mikołów (LM) and Wyry (LW), two cities located nearest Laziska Power Plant. Additionally, in one case (LM_2012) arsenic and in one case zinc (LM_2013) has been detected on the surface. Chlorium have been deposited only on the surface of the needles collected in LW (in both years, in 2012 and in 2013). The degree of air pollution is associated with the amount and type of the substance in the atmosphere. There have been several studies that successfully monitored the trace elements in different tree components such as bark, leaf, needle, and leaf litter [11-14]. Vegetation intercepts the aerosol and the concentrations of some of these elements are high in samples of plants from urban and industrial areas [14].Most of the elements deposited on the foliage are essential for the functioning of many enzymes, responsible for metabolism, nut some of the elements do no play any physiological function, and high concentration can be toxic to the plant [15]. Particulate matter can be harmful also to human life. The plants can be used as a filter, because they can accumulate different contamination on their foliage [16]. To analyze total effect of vegetation in pollutant remediation, a variations in dynamic of deposition and precipitation should be taken into account.

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CLIMATE SIGNAL IN THE RING WIDTH AND STABLE ISOTOPIC COMPOSITION OF SCOTS PINE IN SILESIA

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Scots pine (*Pinus sylvestris* L.) is a very useful archive of changes in ecosystems, because it has a specific sensitivity to local environmental conditions, including climate.

In our research the light element stable isotopic composition in Scots pine growing in three industrial regions in Poland (nearby Dąbrowa Górcznicza, Kędzierzyn Koźle and Łaziska) was analyzed.

Prior to mass spectrometric analysis, the dendroclimatological analysis has been done in 16 pine sites in three regions: Dąbrowa Górnicza near Huta Katowice (HK), Kędzierzyn-Koźle (KK), and Łaziska (LA) [1-3]. The sampling sites were located at different distances from industrial factories. At each site, 20 pine trees were sampled by taking one increment core per tree at a height of 1.3 m above ground. All 320 tree samples were dominant and co-dominant individuals without damage. The examined pine stands, aged between 80 and 100 years, were located in similar habitat conditions around the industrial factories. Thus, one site form each region was chosen for stable isotopic analysis. The absolute-dated annual tree rings were manually separated as thin slivers and then, pooled (equally weighted per tree) and homogenized. The isotopic chronologies were based on a pooled-ring approach with 10 trees per each 3 sites. The α-cellulose samples were extracted using Green's method [4] with further modifications [3,5] in the Silesian University of Technology, Poland.

The carbon and oxygen stable isotope compositions were measured by IRMS (Isoprime, GV Instruments, Manchester, UK) in the Institute of Physics, Silesian University of Technology, Poland. We reported the isotope values in the delta notation as follows:

$$\delta = (R_{sample}/R_{standard} - 1)*1000, ‰ \quad (1)$$

for carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) with respect to the international standard, which was Vienna Pee Dee Belemnite (VPDB) for carbon and Vienna Standard Mean Ocean Water (VSMOW) for oxygen. R_{sample} and

$R_{standard}$ is the molar fractions of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ for the sample and the standard, respectively. The calibration was done using the measurement of International Atomic Energy Agency (IAEA).

The climate–radial growth relationships were analyzed for the period 1951–2012, whereas the climate–stable isotopic relationships were analyzed for the period 1975–2012. The software programs *Statistica 12* (Statsoft Inc. 2014, Kraków, Polska) were used for the statistical analyses.

Meteorological data were provided by the Polish Institute of Meteorology and Water Management (IMiGW). The temperature, humidity, and precipitation data were obtained from the meteorological stations in Katowice and Opole.

To describe the variation of the carbon and oxygen isotope composition of cellulose in annual tree rings of pine caused by climate changes, we used the following model based on multiple regression (Fig. 1):

$$\delta = b_a + \sum_{M=Apr}^{Sept} b_{MT} T_M + \sum_{M=Apr}^{Sept} b_{MP} P_M + \sum_{M=Apr}^{Sept} b_{MS} S_M + \sum_{M=Apr}^{Sept} b_{MH} H_M \qquad (2)$$

where M denotes the month (from April to September) and b represents the regression coefficient for the following variables: T (mean of the monthly temperatures), P (total monthly precipitation), S (monthly hours of sunshine), and H (mean of the monthly relative humidity). Further, ba corresponds to the interdependences between the monthly climate factors and the other environmental changes. In Poland, it is possible to observe that different climatic factors can be linked together, for example: higher number of sunshine hours is linked to higher temperature, also higher total precipitation is linked to higher air humidity during hot summer.

The weather conditions of the current growing season have been reflected in variation of the isotopic ratio. A positive relationship was noted between $\delta^{13}C$ and temperature and $\delta^{13}C$ and sunshine relationships. A negative relationship has been observed between $\delta^{13}C$ and precipitation and $\delta^{13}C$ and humidity. Whereas, a positive relationship was noted between $\delta^{18}O$ and sunshine and $\delta^{18}O$ and temperature, and negative between $\delta^{18}O$ and humidity. Climate signal recorded in stable isotope composition was temporally unstable and only for a few of the climatic parameters we found temporally stable climate signals, however the variability in the strength and direction of relationship between variables has been observed. In general, the weather in July and August is important for determining the $\delta^{13}C$ and $\delta^{18}O$ signals. The instability can reflect the physiological adaptation of the plants to changes in ecosystem.

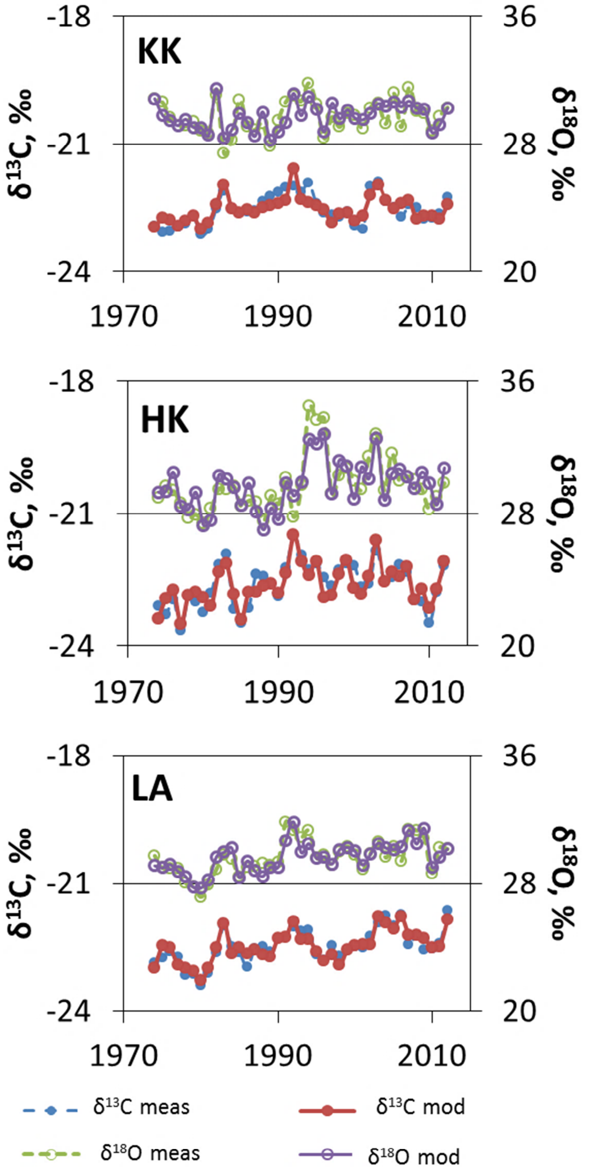

Figure 1. *Variation of the carbon and oxygen isotope composition of cellulose in annual tree rings of pine caused by climate changes based on multiple regressions (mod) and measured $\delta^{13}C$ and $\delta^{18}O$ value (meas).*

According to [6] under most conditions several factors control variability in δ^{13}C, so correlations with a single climatic parameter are oversimplifications. They observed, for example, that stable carbon isotopes record the balance between stomatal conductance and photosynthetic rate, dominated at dry sites by relative humidity and soil water status and at moist sites by summer irradiance and temperature. Whereas, stable oxygen isotopic ratios record source water, which contains a temperature signal, and leaf transpiration, controlled dominantly by vapour pressure deficit. Variable exchange with xylem (source) water during wood synthesis determines the relative strength of the source water and leaf enrichment signals [6]. However, at least part of this signal may be indirect, due to correlation between different factors. For example, hot summers, tend also to be dry, so that temperature is correlated with air humidity and soil moisture status, both of which directly control stomatal conductance and therefore $\delta^{13}C$. Summer temperature and sunshine are strongly correlated, and irradiance exerts a strong control on photosynthetic rate, and therefore $\delta^{13}C$. Although temperature is one of the factors influencing photosynthetic rate, and therefore $\delta^{13}C$, in C3 plants at atmospheric concentrations of CO_2 the direct effect may be weaker than is often implicitly assumed [6, 7].

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P-21

RECONSTRUCTION OF THE CLIMATE AND VEGETATION IN KUZNETSKI ALATAU MOUNTAINS (NORTHERN ALTAI) IN LATE GLACIAL AND HOLOCENCE ACCORDING TO ISOTOPE δ^{18}O AND POLLEN DATA FROM HIGH-MOUNTAIN MIRE CHUDNOE

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For palaeogeographic aim, the content of a stable oxygen isotope δ^{18}O in sediments of the Chudnoe mire located on the Kuznetski Alatau ridge of the northern Altai at an altitude of about 1400 m. (54°12’N, 8910'E) was measured. Pollen analysis was performed for the same sediment core. In addition, in order to identify the possible influence of local mire meso-relief on the accumulation of the δ^{18}O isotope in peat-forming plants, the content of stable isotope was measured in surface samples taken from different elements of meso-relief - from over-wetted hollows and from relatively dry ridges both in mire located in high-altitude zone (1400 m asl) and in mire from low mountain zone (273 m asl) in the mountains of the Kuznetski Alatau.

It was found that the plants and peat of the low-mountain mire contain more heavy oxygen isotope δ^{18}O than in the highland mire (+16.3‰ and +14.5‰, respectively). In addition, the study showed that both in the low-mountain mire and in the high-mountain mire the plant and peat in the wet hollows contain less heavy oxygen isotope δ^{18}O than plants and peat from elevated mesorelief elements. If the first dependence reflects the influence of the temperature regime, then the second, most likely - the influence of moisture regime. Thus, change in δ^{18}O may have a dual nature. Ratio of differences in average annual temperatures and average July temperatures in the highlands and in the lowlands (ie, -2.9°C – -1.0°C = 1.9°C) (+14.9°C – +13.2°C = + 1.7°C) °C to the average isotopic composition of samples of high-mountain and low-mountain mires (ie + 16.3‰ - + 14.5‰ = 1.8‰), shows that an increase in the oxygen isotopic composition by one ppm corresponds to the increase in the average annual temperature by 1°C and average July temperature by 0.9°C. This ratio reflects the regional ISOTOPIC TEMPERATURE EFFECT of the oxygen isotope (‰/°C) or Parameter Fo, similar to the parameter Fq calculated for the carbon isotope [1].

Using the δ^{18}O isotope content and the spore-pollen data from the core of lake-peat sediments of the Chudnoe mire, we reconstructed the temperature regime and the type of vegetation that existed in the mountains of the Kuznetski Alatau in the last 12800 cal yr BP. In general, the $\delta^{18}O$ isotope content varies in the section of the Chudnoe mire over the entire period of sedimentation from + 7‰ to + 14.8‰, which corresponds to a change in average annual temperature by 7.8°C. Since the peat-forming plants photosynthesize and assimilate oxygen only during the growing season, we believe that the temperature of the growing season, and especially the average July temperature, (as most favorable month for growing of plants in Siberia), should be reflected most correctly in isotopic signature of $\delta^{18}O$.

The content of $\delta^{18}O$ in the sediments of Lake Chudnoe in general corresponds quite well to the allocated spore-pollen zones.

The pollen zone Ch-1 (12800-11200 cal yr BP) corresponds to the cooling of the Younger Dryas. The sediments of this zone have the lowest content of heavy oxygen isotope $\delta^{18}O$, around 8.4‰. The landscapes of the Kuznetski Alatau mountains were dominated by spruce-larch forest-tundra-steppe in this period. The climate was probably cold. The average July temperature calculated from the content of the oxygen isotope $\delta^{18}O$ was + 7.5°C, which currently corresponds to the average July temperature of the tundra zone in West Siberia. End of Younger Dryas about 11,500 cal yr BP is marked by increasing the content of the oxygen isotope $\delta^{18}O$ to 11.3‰. Pollen zone Ch-2 corresponding to this time, reflects the rapid spread of Siberian cedar (*Pinus sibirica*) forests.

Then after 9600 cal yr BP in the pollen zone Ch-3 the oxygen isotope $\delta^{18}O$ content decreases and fluctuates throughout the Ch-3 pollen zone at relatively low levels from +8.4 to + 10.6‰ (averaging + 9.7‰). During this period, in the vegetation cover of the Kuznetski Alatau Mts, Siberian cedar forests change to Siberian fir (*Abies sibirica*) forests. Relatively low content of a stable oxygen isotope gives relatively low average July temperatures during this period of fir forests in the Kuznetski Alatau Mts (+7.6 - +9.54°C). Most possibly this contradiction between vegetation change and low content of oxygen isotope was caused by an increase in the amount of precipitation carried to Kuznetski Alatau Mts by Atlantic cyclones from north-west Atlantic during this period from 9,500 to 7,554 cal yr BP. Recent data show that these atmospheric precipitations are poor in oxygen isotope $\delta^{18}O$ content [1]. In addition, high humidity reduced the effect of isotope fractionation.

From 6300 to 4000 cal yr BP the peat deposits of Chudnoe mire contain maximum amount (up to 15.1‰) of $\delta^{18}O$ (on average +14.3‰). The calculated average July temperature was 12.87°C. Two factors could cause this increase in the isotopic composition of oxygen. First, the sediment substrate changed – a lake sapropel changed to swamp peat. Thus, the contribution of aquatic organisms to the isotopic composition of the sediment decreased. The second factor is the climate. It is known that during this period the Holocene optimum occurred in Western Siberia [2]. The corresponding pollen zone CH-4a reflects a sharp reduction in the participation of fir in mountain forests and increase of birch. It means climate became less humid.

After 4000 cal yr BP the content of $\delta^{18}O$ in the peat of Chudnoe mire decreased almost in 1.4 ‰ and varied within the range of +12.3‰ to +13.96‰ (average +12.9‰) till to 200 cal yr BP. This corresponds to the pollen zones Ch-4b and Ch-5a. During this period, the role of birch in the vegetation cover decreases and the role of Scots pine, Siberian cedar and fir somewhat increases. In general, the climate of this period is characterized by a great instability of moisture. The decrease in the oxygen isotope content by 4‰ to in the period from 4000 to 200 cal yr BP was due to the cooling of the climate, and its increase from 200 cal yr BP to present time reflects the beginning of modern climate warming. Thus, according to isotopic data, the Little Ice Age cooling is part of the general cooling trend of Siberian climate, which began 4,000 years ago.

Thus, the pollen and stable oxygen isotope $\delta^{18}O$ studies of lake-peat sediments of the high-mountain Chudnoe mire in the Kuznetski Alatau Mts allowed to reconstruct for the first time the dynamics of vegetation and climate during the last 12,800 cal yr BP. Five periods in the vegetation development were revealed. The isotopic data reflect both local features of the lake-peat sedimentation, and global change of climate. They reflect clearly pronounced warming of the Early Holocene 11000-10000 cal yr BP and the thermal optimum of Holocene in Siberia 6500-4000 cal ye BP. At the same time, we found that early-middle Holocene 9500-6500 cal yr BP in the mountains of the Kuznetski Alatau was marked by very humid climate, probably due to the intense influence of the North Atlantic air currents brought rains with low content of oxygen isotope $\delta^{18}O$ far in the middle of Eurasian continent.

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STABLE ISOTOPE AND GEOCHEMISTRY STUDY ON THE MURMANSK-OLENIEGORSK GNEISSES, AS A POSSIBILITIES OF DETERMINING THE CONTRIBUTION OF COSMIC MATERIAL - PRELIMINARY STUDY

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Kola Peninsula, located entirely outside the Arctic Circle, is the northern part of the Fennoscandian Shield. It is an area built of several blocks: Murmask, Kola and Belamoryian, among which there are archaic igneous and metamorphic rocks [1,3,5,6]. In the Kola Block, in the area of Murmansk city, granitogneisses are revealed, they are visible both in the city center, in the area of the Kola Gulf of the Barents Sea and in the region of the city highway. These rocks usually form a compact complex of parametamorphites, which have undergone multiple transformations and are cut by numerous vein-shaped works associated with various stages of geological processes development in the region [4]. The oldest rocks of this complex have zircons, whose age was determined at 3.75 Ga (U-Pb), [2], being at present also one of the oldest rocks in Europe [7-11]. The petrographic analyzes allowed to determine that the discussed gneisses from Murmansk are mica-garnets rocks with plagioclases, quartz sometimes also sillimanite and a series of accessory and ore minerals. These minerals are accompanied by zircons, often with diversified internal structure and apatite (rich in fluorine, less in chlorine). On the other hand, in the Banded Iron Formations quarcite from the Olengorsk region, the occurrence of quartz and magnetite was found, which is accompanied by orthopiroxenes sometimes covered with clinopiroxenes. They are accompanied by cummingtonite, garnets, epidote and chlorites. None of them have a cataclase character. In the samples from Murmansk and Oleniegorsk, numerous secondary processes are of particular interest. The current numerous phases, such as garnets, amphiboles, and mica, indicate the processes of replacing mafic minerals as a result of various stages of rock metamorphism. In these rocks one can also find individual carbonate crystals. Especially interesting are the accessory minerals in which it can distinguish numerous types of sulphides, including pyrite, galena, and barite, as well as several generations of apatites, also accompanied by small minerals of graphite. In the rocks there is also gold, silver, bismuth and tellur phases. Isotopic analysis of graphite showed that it comes from the aquatic environment, where it was formed as a result of the interaction of carbonaceous substances with sea water. Micro-ramman research has shown that besides graphite there are also numerous admixtures that are relic forms of compounds preserved in the rock (Fig. 1). Isotopic analyzes of sulphides separated from the gneiss showed values corresponding to the contamination of organic sulfur in sulphides. The occurrence of polymetallic sulphide mineralization may be the result of the abrasion of older rocks, whose products were found in the original ocean and were processed by bacteria. However, the origin of the sulphides and graphite can also be correlated with small meteorites, which after impacting into the basement was weathering under water condition. Behind this hypothesis is the occurring tellurium and bismuth as well as the nature of graphite. Currently, the authors carry out further analyzes aimed at finding diamonds in discussed graphite and further research on sulphides

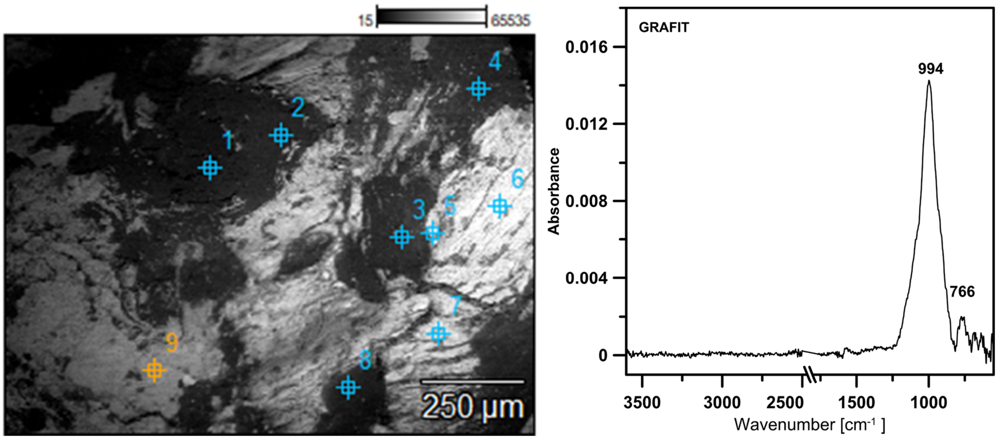

Figure 1. *Back scattering electron microphotographs (in left) and Micro-Raman spectra (in right) of graphite from studied rocks.*

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EVOLUTION OF PALEOPROTEROZOIC PGE LAYERED INTRUSION ON THE NE FENNOSCANDIAN SHIELD - STABLE ISOTOPE AND GEOCHEMISTRY STUDY

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Paleoproterozoic PGE Layered Intrusions formed in a period of about 2.4-2.5 Ga [10,12,13] in the area between the Kola and Belamoryian paleorift blocks, constituting intrusions related to the hotspots, which contributed to magmatism in these region, thus also separating Fennoscandia from the Kenorland continent (Fig. 1), [1, 3, 4]. These intrusions also extend in the region of Finland and Karelia. Particularly interesting is the intrusion Monchepluton, which is located in the region of paleorift, rebuilt in laid-Aug 2.2-1.8 and younger periods forming part of the active-Lapland-Kola Mobile Belt [6].

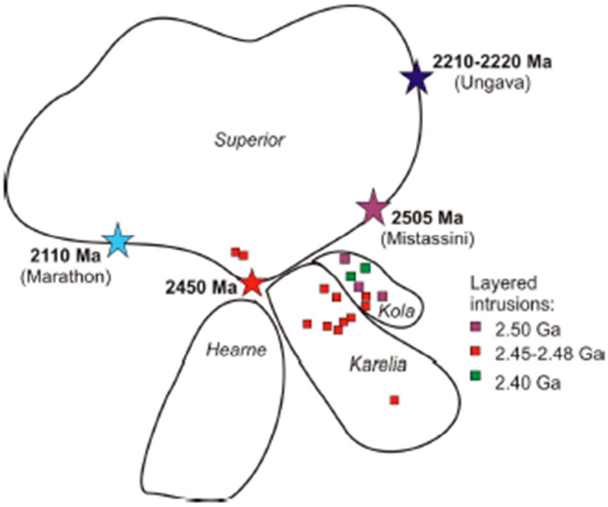

Figure 1. *Paleogeographical situation sketch of the Kenorland system in the time of destruction after [4].*

In the all discussed intrusions, there are ultrabasic and basic rocks in various proportions, often overlapping each other, creating critical horizons in which there is also enrichment in sulphides and PGE mineralization. This is the case Monchegorsk, Monchetundra, Imandra, Fedoro-Pana intrusions, and many also present in the region of Karelia (Burakovsky) and Finland (Tornio-Narankavaara, Penikat, Koilismaa, Kemi) [2,3,7,9]. During the injection-magma was going to their contamination by melting the ingredients of the archaic surrounding rocks, causing polymetallic ore mineralization also contribute to the diversification of the isotope $\delta^{34}S$ [5,8]. The research on sulphides with SIMS showed that they are heterogeneous which means the multistadiality of their crystallization. The isotope origin of the intrusion is also confirmed by isotope studies of helium. The hotspot hypothesis is also suggested by a number of other geochemical studies, including εNd analysis [3,8,11].

In subsequent stages, the metamorphism of the discussed units occurred to varying degrees and their blocking and tectonic revival. The last episode is the impact of hot spots in Paleozoic that contributed to the creation of anomalies strontium, cerium, after getting-carbonate-prehnite veins in these rocks as well as in the whole region wheel [9].

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SURFACE WATER FROM SELECTED REGIONS OF THE KOLA PENINSULA AS AN INDICATOR OF THE ARCTIC ENVIRONMENT - PRELIMINARY STUDY

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The Kola Peninsula is the northern part of Scandinavia and is almost entirely located above the North Arctic Circle. Water samples were collected in 2012, field observations were made and in 1999, along with photo documentation and phytology research (conducted in 2000-2004). The water sampling idea was guided by the principle that relatively widely compare water around the Khibina (due to acting of processing plants) and take the sample of other parts of the Kola Peninsula. In order to determine the content of selected metals in the analyzed samples a high resolution absorption spectrometer with flame spray (F-AAS) was used in the Department of Analytical Chemistry, Department of Chemistry, Medical University of Lublin. In the first stage of the study calibration curves for metal ions was prepared determining and tested samples. Absorbance was measured parameter. Its quantity value changed during the measurement, a signal as a peak. Result analyses were held in a specialized program Cs Aspect, wherein the measured absorbance values were read out as the concentration [mg/l], in relation to a calibration curve. The results are shown as the arithmetic mean of obtained values. In the Department of Soil Science additional experiments, concerning isotopic studies, were undertaken. Preliminary study of pre-processing the results are as promising. The preliminary analysis of the highest chemical components contents were found lowest of the lake Bolshoi and Mayli Vudiawar lakes, surveyed Belaya and Zhemchuzhnaya rivers, Siemianowski Lake in Murmansk, in recognition of the city in Apatytes, snow in Ramzaya Pass in Khibina mountain and Kola Gulf of Murmansk respectively. More studies are planned this year, the statement will be extended by a few more elements to analysis the physical and chemical conditions. Therefore the Kola Peninsula has quite a lot of rainfalls, temperatures normally reach 10ºC in July, and -3ºC in January. Therefore rarely frosts below 30ºC, there are rare rainless days as well. Snow is ageing from September to May (especially in the mountains). This has an impact on growing season, which are very short, however very intense. It also contributes to other environmental conditions, resulting in a much smaller distribution of pollutants. The preliminary analyses of water samples from the Kola Peninsula area to solve the problem of the influence of anthropogenic factors which are of anthropogenic origin in the study area [4]. The goal of this study was to resolve the problem concerning the impact of geogenic and anthropogenic factors and to mention their origin. Samples were collected from surface waters during the summer. The current chemical components necessary for proper functioning of organisms and those that interfere with the life processes were identified and analyzed [2]. Selected components were tested, necessary for the functioning of living, among others: zinc, copper and iron, calcium, magnesium, etc., and on the other hand toxic for organisms. These were cadmium, lead, nickel, etc.[1,3,5]. The sampling place has been determined on the basis of observations of possible exposition to pollutants. Attempts to come from melting snow, with water flowing from stagnant water and water supply intake. The greatest wealth of the analyzed chemical components in the preliminary studies were obtained from White River, with snow in the Zhemchuzhnaya River near Anof, Siemonowski Lake and of the tap water from Murmansk. The highest concentrations of chemical constituents carries White River, except chemical compounds such as sodium, potassium, magnesium, calcium there are rubidium, strontium, cadmium rather rare. The concentration was in the tenths of a milligram per cubic decimeters. The content of these components suggests the occurrence of anthropogenic pollution. Lower concentrations of the above-mentioned chemical components were also found in the Siemonowski Lake, in snow, and the river of Anof area. For samples analyzed in 2013, flood waters of the Barents Sea are relatively largest contents of Sr, (also contain ions of Mg, Ca, K, and HCO_3). Perhaps Sr ions are associated with flushing of the metal from the mainland rivers, where there are old crystalline rocks. A relatively large Sr also appears in the waters of the rivers of Khibina. In Khibina is present apatite, which can be a source of Sr. The enrichment of the water in the alkali elements can be explained by alkaline rocks occurring in the area. Apatite as carrier ions supplied to the waters of the river enriches the PO_4 ions and F. With sulphates are relatively rich the water from Monchegorsk, where present in the substrate sulfide ore. This analysis have a preliminary character.

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STABLE CARBON ISOTOPE AND BIOMARKER ANALYSES OF CH_4 IN MIOCENE LIGNITES, POLAND

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Coal is one of the most popular energy sources in the world, covering 1/3 of the power consumption demand. Unfortunately, its extraction and combustion have a very negative impact on the natural environment. Due to the dynamic development of renewable sources, the coal industry must look for more environmentally friendly opportunities to use the energy stored in coalified organic matter (OM). One such technology is exploitation of coalbed (CBM)/coalseam (CSM) methane. CH_4 is released from OM during both biogenic and thermal cracking.

The aim of this work was to identify possible biological "hot spots" within coal beds and ongoing methane production process with the use of stable isotope and biomarker methods.

Four lignite samples were obtained (courtesy of the PGE GiEK S.A.) from Miocene lignite-bearing formations exploited by "Bełchatów" (51°15′46.4″N 19°18′49.2″E) (BCB) and "Turów" (50.9124°N 14.9031°E) (TCB) mines. In each case samples derived from two locations, representing the upper- and lower- most parts of the exploited coal beds.

The stable carbon isotopic analysis of CH_4 and CO_2 in coal beds was performed with an isotope ratio mass spectrometer Thermo Delta V Advantage coupled with gas pre-concentrator Thermo Precon.

The GDGTs analysis was performed using a high-performance liquid chromatography–mass spectrometry (HPLC-APCI-MS) with a Shimadzu 8030 system at IEECAS with Inertsil CN-3 column (250mm×4.6 mm, 3 µm; GL Sciences Inc.).

Carbon isotope ratios of the desorbed gas exhibited a wide range of $\delta^{13}C$ values of CH_4 (−28‰ to −93‰) whereas $\delta^{13}C$ of CO_2 was much less variable (−15‰ to −20‰). In Bełchatów, $\delta^{13}C_{CH4}$ values in samples derived from the vicinity of the upper margin of the seam (BCB-W1), were-57‰ whereas $\delta^{13}C_{CH4}$ values in lower (BCB-W2) margins of the seam were-87‰. In Turów $\delta^{13}C_{CH4}$ values were -29‰ and -53‰ for lower (TCB-W1) and upper (TCB-W2) margins, respectively.

The acyclic isoprenoid GDGT-0 was a dominant lipid among the detected iGDGTs and in all lignite samples with maximum 66% found in BCB-W1. The GDGT-0/crenarchaeol ratio was >42, with the highest value (142) found in the sample BCB-W1, whereas the other three samples had similar values.

brGDGT distribution in the lignites investigated, were represented by predominant Ia followed by IIa, Ib, and IIIa, with minor concentrations of the remaining branched tetraether forms.

Enhancing the process of methane production within coal beds and the biological "hot spots" identification are a matter of great interest worldwide. Here we provide evidence for the present-day microbial degradation of lignite occurring in the uppermost layers of the lignite seam at the BCB (BCB-W1) which is confirmed by both isotopic and biomarker methods. This shows that these methods can be used to determine the potential suitability of a deposit for biogasification.

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For more information see:

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P-26

REPEATABILITY EVALUATION OF ON-LINE SET OF PYROLYSER, GAS CHROMATOGRAPH AND ISOTOPE RATIO MASS SPECTROMETER (PY-GC-IRMS)

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Pyrolyzer allows to perform a pyrolysis process under defined conditions. Coupled on-line with GC-IRMS gives possibility to determine the isotopic composition of the pyrolysis product (the individual chemical compounds of the pyrolysis product). Obtained chemical compounds are: methane, ethene, ethane, propylene, propane, 1-butene, n-butane and carbon dioxide. The Py-GC-IRMS used is a Thermo Scientific Delta V Advantage mass spectrometer with a Trace GC Ultra chromatograph (HP-PLOT / Q capillary column, 30 m) and Pyroprobe 6150 pyrolyzer. Details of methodology and its partial validation are described in "Pyrolysis Py-GC-IRMS – partial validation…"[1].

The repeatability test was performed by analyzing the shale sample six times. The smallest values, the largest values, range, arithmetic averages, standard deviations and the relative standard deviations for individual compounds are presented in Table 1. Statistical parameters indicate that the most reliable are $\delta^{13}C$ for methane and carbon dioxide, for the remaining hydrocarbons, the unsaturated are more reproducible than the corresponding saturated hydrocarbons.

The lowest standard deviation was 0,11 ‰ for carbon dioxide and the highest 1,03 ‰ for n-butane. The lowest relative standard deviation is 0,6% for methane. All values of relative standard deviations are below five percent, which is a satisfactory and confirming that the method is reproducible.

Table 1. *Statistical parameters of repeatability test*

	Minimum value [‰]	Maximum value [‰]	Range [‰]	Arithmetic mean [‰]	Standard deviation [‰]	Relative standard deviation [%]
CO_2	-7,79	-7,55	0,24	-7,66	0,11	1,4
Methane	-31,36	-30,91	0,45	-31,20	0,17	0,6
Ethene	-29,57	-28,55	1,02	-29,04	0,42	1,5
Ethane	-29,60	-27,20	2,41	-28,21	0,79	2,8
Propylene	-27,52	-25,58	1,94	-26,14	0,72	2,7
Propane	-26,54	-24,01	2,53	-25,13	0,98	3,9
1-Butene	-25,88	-24,01	1,87	-24,76	0,64	2,6
n-Butane	-25,51	-22,66	2,85	-23,85	1,03	4,3

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The abstract is based on a statutory works to the order of the Ministry of Science and Higher Education, archive number: DK-4100-45/18, INiG-PIB order: 45/SG/18 and archive number: DK-4100-17/19, INiG-PIB order: 27/SG/19

P-27

PRELIMINARY RESULTS OF THE ANALYSIS OF STABLE SULPHUR ISOTOPE IN SO_2 GAS BY NEGATIVE ION MASS SPECTROMETRY

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The SO_2 gas prepared from the studied sulphide or sulphate samples is frequently used in the stable sulphur isotope analysis. In commonly used methods of SO_2 isotope analysis the positive ionization of SO_2 is applied. The resulting ions of SO_2^+ or SO^+ are then analyzed mass spectrometrically and respective (for isotope ^{32}S and ^{34}S) ion currents for the ion beams are measured.

In our studies we employed negative ionization method for the isotope analysis in SO_2 gas. For this purpose we used the constructed in our lab mass spectrometer with the negative ion source previously built for the chlorine isotope analysis [1,2]. As the efficiency of negative ionization of SO_2 is relatively low, the new detecting system was assembled and used in the studies. This allowed us to detect several types of negative ions which are generated by the electron attachment to the SO_2 molecules. In measurements we were able to detect of intense ion signal of S^-, SO^- SO_2^- with their isotope representation. This gives us possibility to determine not only standard $^{34}S/^{32}S$ ratio but also $^{33}S/^{32}S$ and $^{33}S/^{34}S$ ratios. In the presentation more detailed data will be presented on this achievement.

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STUDIES OF THE CHLORINE STABLE ISOTOPE RATIO IN THE WATER SAMPLES

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The most common method used in the chlorine isotope ratio analysis employs the conversion of a chlorine sample to chloromethane (CH_3Cl) prior to the mass spectrometric analysis.

For CH_3Cl preparation the exchange reaction between the iodomethane (CH_3I) and silver chloride (AgCl) is applied. We followed the procedure described by Eggenkamp [1] with the following modifications: (i) the aliquot of iodomethane is added to the preparation line by using the pipette connected to a container with pure liquid CH_3I, thereby the injection of iodomethene throught a septum is eliminated, (ii) the conversion of AgCl to CH_3Cl is performed in glass ampoules with Teflon stopcocks sealed with elastomer O-rings, thereby cracking tubes are eliminated, (iii) the obtained chloromethane is cryogenically separated from iodomethane using three traps (one with butyl acetate and two with trimethylpentane) connected in series.

The obtained chloromethane is then analysed by the isotope ratio mass spectrometry (IRMS). For this purpose we have devised a negative ion mass spectrometer which retains all the best features of IRMS, including dual inlet system with changeover valve, dual collector assembly and CH_3Cl gas as analyte. In the modified ion source we have replaced the ionization chamber with electron beam by a metal tube with a hot metal filament inside. Within this tube the $^{35}Cl^-$ and $^{37}Cl^-$ ions are generated. No other ionic species were found in the mass spectrum except of traces of CN^- and CO^-. The method's precision is better than 0.01‰ (1σ) [2,3]. In the presentation, both, the methodology as well as recent results on chlorine isotope analysis in water samples will be presented.

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P-29

NEW CONCEPT OF TRIPLE FILAMENT ION SOURCE FOR TIMS

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An improved version of well-known three filaments ion source for Thermal Ionization Mass Spectrometry (TIMS) is described.

The filaments are located along the longitudinal axis of the extraction slit, all being perpendicular to the slit plane (Fig. 1). Internal (ionizer filament) is wider and longer than the external ones (evaporators filaments) and fulfill the role of screen separating them. Under high vacuum conditions internal filament effectively precludes the migration of vaporized molecules between separate evaporators, preventing cross-contamination of isotopically different samples loaded on two separate evaporators. In the classic version of the triple filament ion source, the ionizer filament is parallel to the plane of the extraction slit, hence does not serve as a separator.

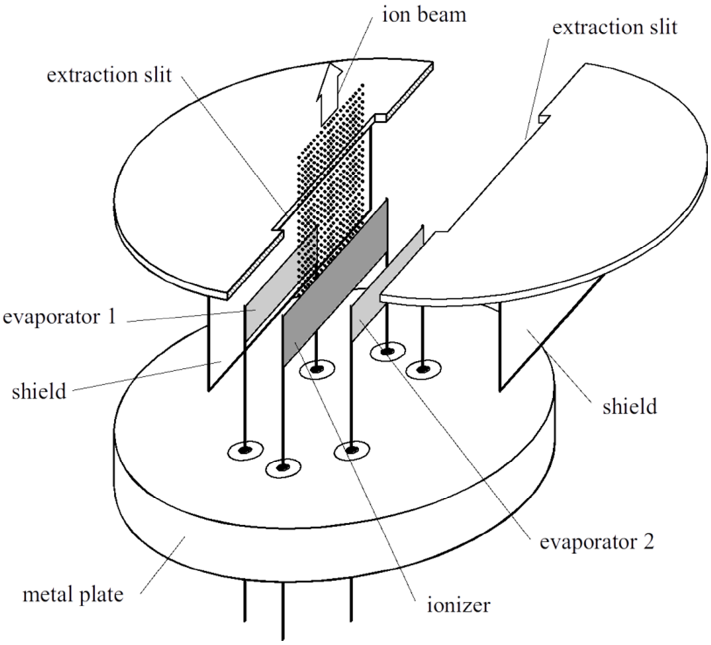

Figure 1. *Simplified schematic diagram of the improved triple filament ion source for TIMS.*

Such a slight modification of ionizer filament configuration significantly improves the functionality of the source i.e. enables to perform independent isotopic analysis of different samples (e.g. a studied sample and a standard) from each evaporator alternately one after another without venting the mass spectrometer chamber.

The lack of cross-contamination during such a measurements has been demonstrated by alternating analyses of a natural potassium sample ($^{39}K/^{41}K = 13.78$) versus a spike ($^{39}K/^{41}K = 1.57$) and the isotopic lithium standard L-SVEC ($^{7}Li/^{6}Li = 12.21$) versus a seawater sample ($^{7}Li/^{6}Li = 12.56$). The results of measurements for potassium and lithium obtained using improved ion source are shown on figures 2 and 3 respectively. Each marker on the figures below represents the weighted average of a series of 12 acts of measuring the isotopic ratio. The series were measured with peak-jumping method. The duration of each series was about 3 minutes. The analyses were conducted alternately (left/right evaporator) for over one hour each time, however no symptoms of cross contamination were noticed until the sample had totally run out. The replacement of evaporators, or application of the samples on evaporators inversely, did not affect the measurements results significantly, neither in case of potassium nor of lithium.

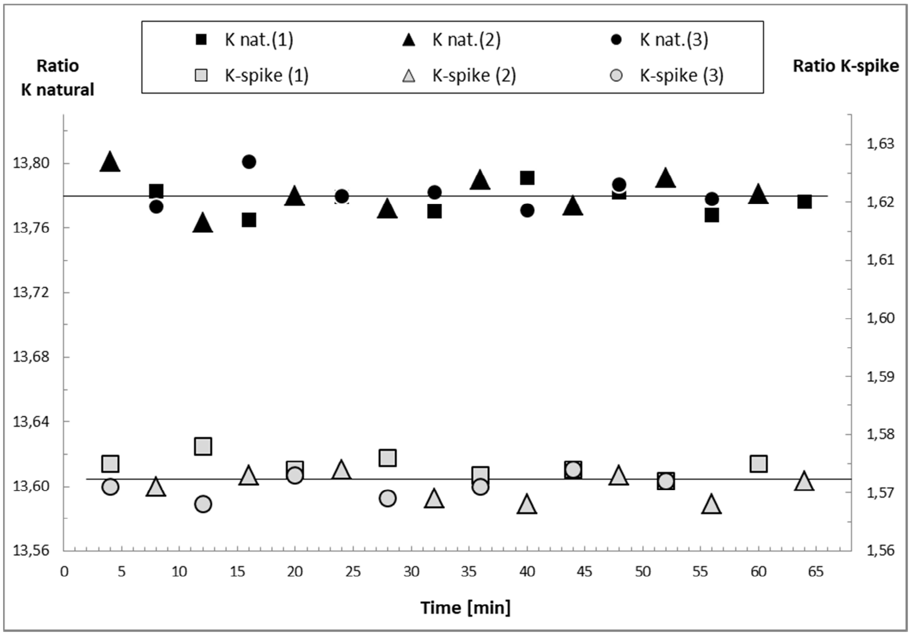

Figure 2. *The Results of the isotopic ratio measurements of two extremely different potassium samples (K natural and K-spike) loaded at the same time on different evaporators. The figure shows the measurement results for three separate applications of both samples. The analyses were conducted alternately (left/right evaporator) without venting spectrometer chamber.*

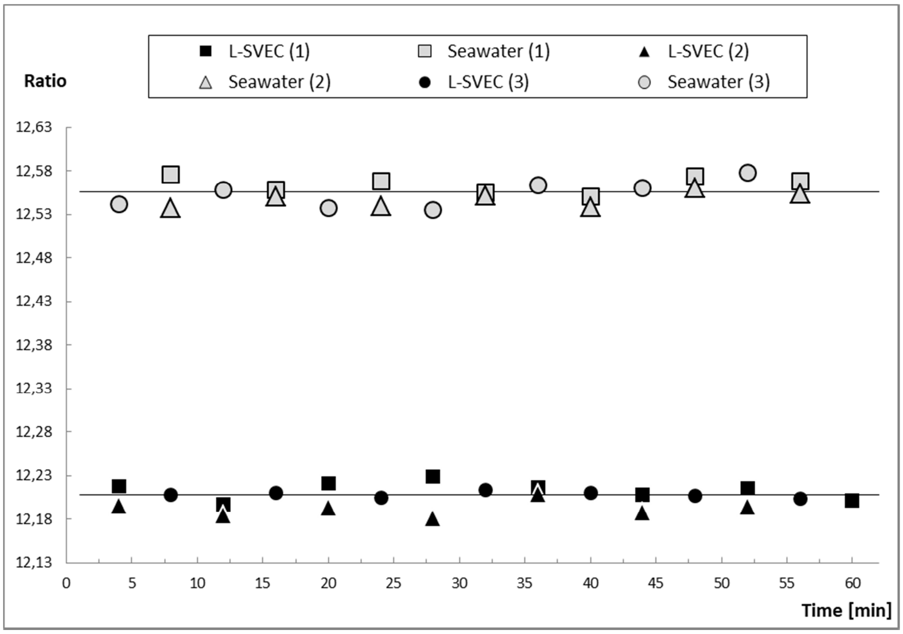

Figure 3. *Results of the isotopic ratio measurements of two different lithium samples (seawater and isotopic lithium standard L-SVEC) loaded at the same time on different evaporators. The figure shows the measurements results for three separate applications. The analyses were conducted alternately (left/right evaporator) without venting spectrometer chamber.*

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P-30

AN EXAMPLE OF THE IMPACT OF FISH FOOD PREFERENCES ON THE DIVERSITY OF THE ISOTOPIC COMPOSITION OF FISH SCALES

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Isotope analyses are useful to ecology studies and to understand relations between food and animal tissues. The study of trophic dependencies are easier on the example of a particular water environment.

The isotopic composition of sulphur contained in scales of two species of fish: roach and silver crucian carp was examined. Both species of fish were caught in the same environment, a small 200 m section of the Bystrzyca river above the dam. The examined individuals did not differ significantly in size, so it can be assumed that they have the same age. The results are presented in the table.

The differentiation of $\delta^{34}S$ between each of individuals is significant, despite the same environmental conditions and identical possibilities of using food resources. Comparing the mean values of $\delta^{34}S$ we may see that the $\delta^{34}S$ values in the carassius scales are shifted in plus compared to the roaches. This is probably due to a different preference of the diet of both species despite the same food availability.

The fish diet was probably consisted of small invertebrates occurring on this section of the river: gammarus, larvae of caddis flies, larvae of mayfly, larvae of the lobster. The values of $\delta^{34}S$ invertebrates found in the Bystrzyca river are diverse. Examples of average values of $\delta^{34}S$ for common aquatic invertebrates from the Bystrzyca river are: -6.7 ‰ mayfly, -6.5 ‰ caddisworm, -3,8 ‰ gammarus shrimp (Trembaczowski, Kot, Pieńkos, in preparation). These large variation is caused by different food of these organisms, (eg gammarus feed on decaying plant and animal remains, while caddisflies and collarflies prefer vegetable food). The values of $\delta^{34}S$ of water plants (Canadian waterwort *Elodea canadensis*) on this section of the Bystrzyca river are close to -4.6 ‰ (Trembaczowski, Kot and Pieńkos, in preparation). The larvae of the Chironomus which live in the mood have not been tested, however, their tissues can be assumed to contain heavier isotope sulfur.

Thus, despite the similar availability of roach and carassius diet, food preferences of fish play a significant role. Carassius prefer invertebrates from the bottom of river, like gammarus, lobsters and others, while roaches choose food that floats in the river like mayfly, caddisworm, also gammarus and other.

It may be noticed that the value of $\delta^{34}S$ in the scales of the roach is similar to the value of $\delta^{34}S$ of grayling living in the Bystrzyca river (Trembaczowski, Niezgoda 2011). Both these species prefer food that floats in the river.

Food preferences can also affect the variability of the isotopic composition of tissues of individual individuals of the same species.

Tab. 1 Sulphur isotopic composition of fish scales

Fish	Length, weight and data of catching	$\delta^{34}S$ VCDT (‰)
Roach (*Rutilus rutilus)*		
	26 cm, 27 dkg, 31.08.2012	-6,55
	21 cm, 11 dkg, 31.08.2012	-6,71
	22 cm, 12 dkg, 31.08.2012	-7,51
	27 cm, 28.08.2012	-7,55
	24 cm, 18 dkg, 31.08.2012	-7,77
	26 cm, 24 dkg, 31.08.2012	-6,51
	26 cm, 22 dkg, 31.08.2012	-6,71
	23 cm, 17 dkg, 18.09.2012	-7,89
	22 cm, 13 dkg, 18.09.2012	-6,46
	25 cm, 21 dkg, 18.09.2012	-6,71
	mean value	**-7,04 (10)**
Silver Crucian Carp (*Carassius auratus gibelio)*		
	23 cm, 27 dkg, 31.08.2012	+1,34
	22 cm, 23 dkg, 18.09.2012	-7,24
	27 cm, 37 dkg, 18.09.2012	-5,80
	mean value	**-6,52 (2), -3,9 (3)**

Within bracket amount of individuals

Acknowledgements: The author would like to thank to Piotr Lubiarz, fly fisherman, for delivering the samples of fish.

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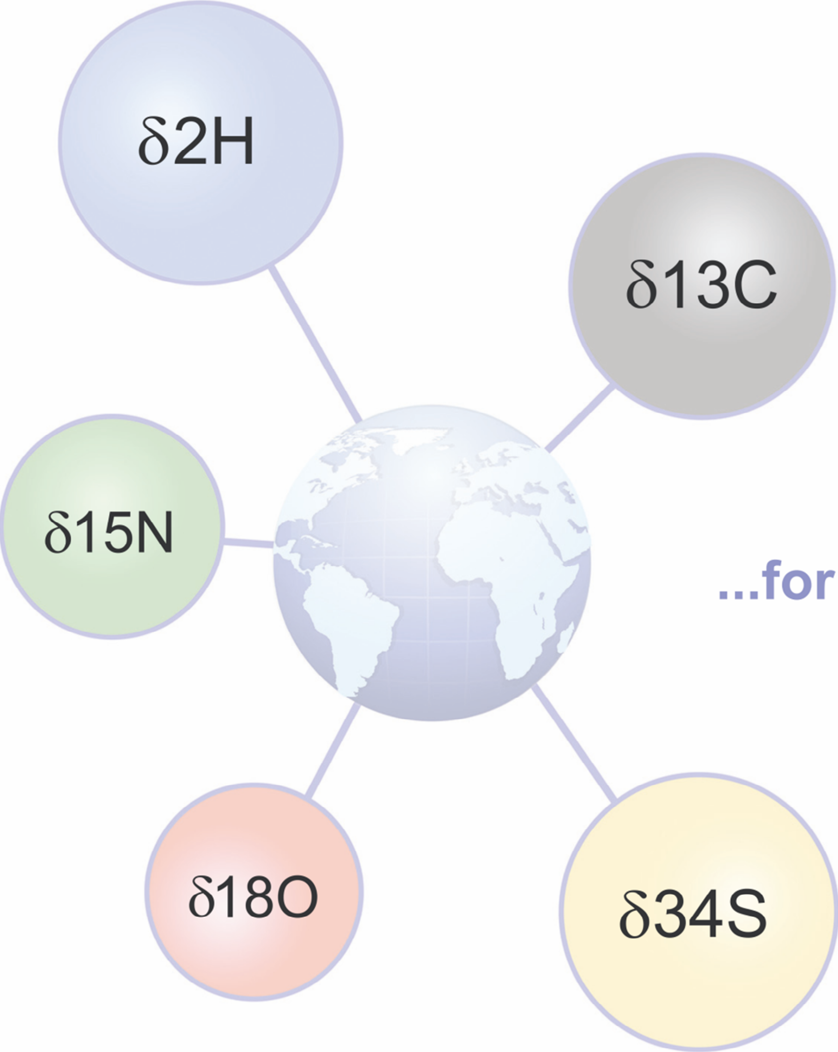

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