

C, N isotopic ratios in *P. oceanica* meadows of Alexandroupolis Gulf, NE Greece

Maria-Venetia Apostolopoulou
Analytical and Environmental Chemistry
Vrije Universiteit Brussel, Brussels

Patrick Roose
Management Unit of the North Sea Mathematical
Models and the Scheldt Estuary, Ostend

Pavlopoulos Kosmas
Geography, Harokopio University, Athens

Frank Dehairs
Analytical and Environmental Chemistry,
Vrije Universiteit, Brussel

We investigated the stable C, N isotopic composition of seagrass and sediments to track effects of pollution, as part of a study to assess 'base-line' conditions for seagrass meadows in Alexandroupolis Gulf (north-east Aegean Sea, Greece) where the construction of an oil-tanker terminal is being planned. *Posidonia oceanica* seagrasses and ambient sediment substrate were sampled at 4 different sites along the coast line during the summers of 2007, 2009, and 2010 and leaves, roots and rhizomes were analysed for C and N isotopic composition. Whole plant ^{15}N values increased over the years (2007: $+3.61 \pm 1.40\text{‰}$; 2009: $+5.99 \pm 2.32\text{‰}$; 2010: $+8.40 \pm 2.94\text{‰}$), while whole plant $\delta^{13}\text{C}$ values showed a slight depletion in ^{13}C for 2010 compared to 2007 and 2009 (2007: $-12.67 \pm 1.97\text{‰}$; 2009: $-12.65 \pm 1.27\text{‰}$; 2010: $-13.81 \pm 0.82\text{‰}$). Such trends possibly reflect increased impact of domestic and industrial wastes via river and groundwater inputs. This temporal trend is detected in leaves, roots and rhizomes alike. Overall, leaves, roots and rhizomes do not show a significant difference between their $\delta^{13}\text{C}$ values, while leaves were less ^{15}N enriched compared to roots and rhizomes. Comparing additional parameters and biomarkers such as 16 PAHs (EPA610) in the ambient sediment substrate, it appeared that these values also had significantly increased over the years, corroborating a possible pollution effect.

Address of corresponding author: M. V. Apostolopoulou: Pleinlaan 2, B-1050, Brussels, Belgium
e-mail: mapostol@vub.ac.be

Stable isotope distribution in deep-sea hydrothermal barnacle, Manus Basin, Papua New Guinea: a key in understanding their ecology

Ana-Voica Bojar

Department of Geology, Salzburg University, Salzburg

Department of Natural Sciences,
Universal Museum Joanneum, Graz

Hans-Peter Bojar, Werner Tufar

Department of Geology, Salzburg University,
Salzburg

One of the most extended and active hydrothermal fields of the Manus Spreading Center is the Hydrothermal field 1, Vienna Woods. In this study we present around 60 stable isotope data on carbonates and shell structure investigations of barnacles collected during the Olga 2 expedition. The heterogeneous faunal composition found at this site consists of gastropods, barnacles, bythograeid crabs, bresiliid shrimps, vestimentiferans, and sea anemones.

For this study, 5 specimens of a hydrothermal vent barnacle, *Eochionelasmus ohtai manusensis* were collected at depth of c. 2500 m.

Stable oxygen isotope data of *Eochionelasmus ohtai manusensis* were performed from the centre to the border of the calcitic shells, along profiles. Within one shell, the isotope values show variations of max. 0.6‰. The temperatures calculated from the stable isotope data consistently indicate that *Eochionelasmus* precipitated their shell carbonate at low temperature, up to a few °C. The calculated temperatures from the isotope data are also in agreement with the reported habitat from the North Fiji and Lau Basins, where temperatures of max. 6°C were measured at sites populated by *Eochionelasmus*. Both calculated and measured temperatures of a few degree °C indicate that at the sites where *Eochionelasmus* lives, hydrothermal fluid input is present, as ambient temperatures are around 1.5°C. Carbon stable isotope composition of *Eochionelasmus* show lower $\delta^{13}\text{C}$ values than for littoral barnacles, supporting the idea of input of a vent carbon source.

Address of corresponding author: A.-V. Bojar: Hellbrunnerstrasse 34, A-5020, Salzburg, Austria
e-mail: Ana-Voica.Bojar@sbg.ac.at

Chemical and isotopic yearly seasonal observations of the ammonium and nitrate in Wrocław (SW Poland) precipitation

Monika Ciezka, Maciej Górka

Mariusz-Orion Jędrysek

*Laboratory of Isotope Geology and Geoecology,
Department Applied Geology and Geochemistry,
Institute of Geological Sciences,
University of Wrocław, Wrocław*

Magdalena Modelska

Stanisław Stacko

*Department of General Hydrogeology,
Institute of Geological Sciences,
University of Wrocław, Wrocław*

Major ion constituents and nitrogen isotopic ratios of ammonium ($\delta^{15}\text{N-NH}_4^+$) and nitrate ($\delta^{15}\text{N-NO}_3^-$) were measured in order to investigate the sources of NH_4^+ and NO_3^- in precipitation. Precipitation (41 samples) was collected from January 2010 to December 2010 in Wrocław (SW Poland) via a funnel in 5L plastic containers covered by plastic grid. Chemical analysis were carried out using Alliance Waters HPLC. For isotopic analyses nitrate and ammonium were absorbed by ion exchanging resins columns and isotopic ratios were measured using Delta V Advantage mass spectrometer.

The pH values ranged from 6.56 to 7.9 and electrical conductivity from $12\ \mu\text{S/cm}$ to $162\ \mu\text{S/cm}$. Concentrations of Ca^{2+} varied from 0.14 mg/L to 6.93 mg/L, Mg^{2+} from 0.05 mg/L to 0.97 mg/L, K^+ from 0.00 mg/L to 22.95 mg/L, Na^+ from 0.00 mg/L to 9.15 mg/L, SO_4^{2-} from 0.00 mg/L to 24.51 mg/L, Cl^- from 0.70 mg/L to 18.63 mg/L. Nitrate concentration ranged from 0.00 mg/L to 16.48 mg/L with average value 3.71 mg/L, ammonium from 0.00 mg/L to 7.92 mg/L with average value 2.46 mg/L.

Concentrations of ammonium and nitrate show weak positive correlation (0.57). There were no correlation observed between nitrogen forms and pH, Cl^- , Na^+ , K^+ , Mg^{2+} . Both ammonium and nitrate concentrations correlated positively with electrical conductivity, SO_4^{2-} and Ca^{2+} . Ammonium ions and atmospheric NO_x (analysed in Wrocław air in the same period of time) concentrations were negatively correlated (-0.36). The seasonal variations of ammonium and nitrate ions concentrations corresponded with each other. The concentrations of both compounds were higher in spring and summer – 19.42 mgNO_3^-/L and 7.92 mgNH_4^+/L than in autumn and winter – 3.88 mgNO_3^-/L and 0.39 mgNH_4^+/L .

The $\delta^{15}\text{N}$ values of ammonium oscillated from -11.5 to 2.2‰ in cold season and from -4.6 to 10.2‰ in warm season. Selected samples for $\delta^{15}\text{N}$ nitrate isotopic analyses show the values from -2.8‰ to 1.7‰. Ammonium $\delta^{15}\text{N}$ values show wide range of variations probably due to different origins of dissolved ions in precipitation. Conversely, we do not observe such significant variations in nitrate $\delta^{15}\text{N}$ values.

Address of corresponding author: M. Cieżka: Cybulskiego 30, 50-205 Wrocław, Poland
e-mail: monika.ciezka@wp.pl

Apportionment of carbon dioxide over central Europe: insights from combined measurements of atmospheric CO₂ mixing ratios and carbon isotope composition

Michał Galkowski, Dorota Jelen, Mirosław Zimnoch, Tadeusz Kuc, Jarosław Necki, Łukasz Chmura, Zbigniew Gorczyca, Alina Jasek, Kazimierz Rozanski
AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Kraków

Carbon isotope composition of atmospheric CO₂ constitutes an important source of information on circulation of carbon between the atmosphere, biosphere and the ocean. It also helps to quantify anthropogenic disturbances of the carbon cycle. The European continent, with high population density and numerous sources of anthropogenic CO₂ emissions, plays an important role in the global carbon budget. Observations of atmospheric CO₂ mixing ratios alone cannot provide information on apportionment of biogenic and fossil-fuel related contributions to the overall CO₂ burden of the regional atmosphere. In order to perform such apportionment, additional information is required. Such information can be obtained from measurements of carbon isotope signatures (¹⁴C/¹²C and ¹³C/¹²C ratios) of atmospheric carbon dioxide.

Regular observations of carbon isotope composition of atmospheric CO₂ are performed in Krakow, southern Poland (19°55'E, 50°04'N, 220 m asl) since 1983. Analogous data are available for the past decade also for Kasprowy Wierch (High Tatra Mountains, at 19°56'E, 49°14'N, 1987 m asl), a regional reference site relatively free of local anthropogenic influences. The available data on atmospheric mixing ratios and carbon isotope composition of atmospheric CO₂ at both sites for the period 2005–2009 (and monthly composite samples) were used to quantify biogenic and fossil-fuel related contributions to the overall CO₂ load of the regional atmosphere using isotope and mass balance approach. In addition, the ¹³C signature of fossil-fuel component at both sites has been evaluated and used for assessing long-term trends and changes in the internal structure of fossil CO₂ emissions. The results of this apportionment clearly indicate distinct seasonal changes in the local CO₂ budget at both locations as well as large differences between them in terms of impact of anthropogenic CO₂ emissions. The average load of urban atmosphere of Krakow with fossil-fuel derived CO₂ is approximately five times larger than that derived or Kasprowy Wierch site.

Address of corresponding author: M. Galkowski: al. Mickiewicza 30, 30-059 Kraków, Poland
e-mail: galek1@poczta.onet.pl

5-year (2004–2009) isotopic seasonal observations of the sulphates in Wrocław (SW Poland) precipitation

Maciej Górka

*Laboratory of Isotope Geology and Geoecology,
Institute of Geological Sciences,
University of Wrocław, Wrocław*

Stanisław Halas

*Department of Mass Spectrometry, Marie Curie-
Sklódowska University, Lublin*

Dariusz Strapoc

*Department of Geological Sciences,
Indiana University, Bloomington*

Dominika Kufka, Mariusz-Orion Jędrysek

*Laboratory of Isotope Geology and Geoecology,
Institute of Geological Sciences
University of Wrocław, Wrocław*

The aim of this study was to observe the seasonal variations in concentration and isotopic composition of sulphates in precipitation in relation to other parameters (air temperature, air SO₂ concentration, etc.). The field studies taking place in Wrocław (SW Poland) started from 25th May 2004 and finished on 25th May 2009. The precipitation samples were collected after each rain episode. The sulphates were precipitated from filtered water using barium chloride method. The concentration of sulphates was calculated from weight of sulphates samples and water amounts.

The concentration of sulphates vary between 0.93 mg·dm⁻³ (1st August 2005) and 98.39 mg·dm⁻³ (12th April 2007) with average 12.79±13.10 mg·dm⁻³. The $\delta^{34}\text{S}_{\text{SO}_4}$ values vary between 0.3‰ (13th June 2005) and 5.4‰ (16th May 2007) with average 2.8±0.9‰. The $\delta^{18}\text{O}_{\text{SO}_4}$ values vary between 4.7‰ (12th December 2005) and 19.1‰ (18th March 2008) with average 13.5±2.0‰. Statistically significant positive correlations have been noted between: (i) SO₄²⁻ concentration and air SO₂ (R=0.22, p=0.008); (ii) SO₄²⁻ concentration and $\delta^{18}\text{O}_{\text{SO}_4}$ (R=0.24, p=0.002); (iii) $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (R=0.27, p=0.000), while statistically significant negative correlations have been observed between: (i) SO₄²⁻ concentration and air temperature (R=-0.21, p=0.005); (ii) SO₄²⁻ concentration and $\delta^{34}\text{S}_{\text{SO}_4}$ (R=-0.21, p=0.007); (iii) $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ (R=-0.27, p=0.001).

Moreover, the dominant sulphate sources have been identified based on the samples showing the highest sulphate concentration. These sources show the isotopic signature of sulphur ca. 2.7‰ and oxygen ca. 17.3‰.

Probably for lower concentrations of sulphate the dominant signal has been masked by the multiple sources of sulphur and oxygen.

Finally, we conclude that in 5-year observation period the fluctuation of isotopic signals in sulphates are distinct for S and O, which is probably caused by different sources and processes influencing the final isotopic composition of sulphates in precipitation.

Address of corresponding author: M. Górka: ul. Cybulskiego 30, 50-205 Wrocław, Poland
e-mail: maciej.gorka@ing.uni.wroc.pl

Triple oxygen isotope composition as a potential tracer for mixing ratios of carbon dioxide sources in urban air

Balázs Horváth, Magdalena E. G. Hofmann, Andreas Pack
Georg-August-University, Geoscience Centre, Isotope Geology Section, Göttingen

Urban air investigations are important, as urban regions are the main sources of anthropogenic CO₂. The ¹³C/¹²C and ¹⁸O/¹⁶O ratios are traditionally used to distinguish between CO₂ sources. However, the number and variability of sources are large, thus unambiguous determination of different fluxes need further tracers. The ratio ¹⁷O/¹⁶O to ¹⁸O/¹⁶O is a potential new tracer. Atmospheric O₂ has an anomaly in its triple oxygen isotope ratio. During combustion, O is transferred from O₂ to CO₂. Hence, CO₂ from combustion should carry the isotope anomaly of air O₂. In this study, we present the triple oxygen isotope data of CO₂ with different anthropogenic (combustion) provenance and we compare the results to local atmospheric CO₂.

Carbon dioxide from laboratory combustion experiments and air CO₂ were isolated cryogenically. The triple oxygen isotope composition of CO₂ was determined by equilibration with CeO₂, and subsequent analysis of Δ¹⁷O and ¹⁸O of CeO₂ by means of IR laser fluorination GC-CF-irmMS. The oxygen isotope anomalies are reported as Δ¹⁷O relative to the terrestrial fractionation line. The CO₂ concentrations were measured by gas chromatography.

High temperature combustion (>900 °C) resulted in CO₂, which inherited the isotope signature of tropospheric O₂. Combustion at lower temperatures (biomass) was accompanied by kinetic fractionation between the starting material (O₂) and the product (CO₂). As result of the kinetic fractionation, δ¹⁸O values of CO₂ decreased and Δ¹⁷O values increased. The CO₂ from car exhaust pipe line was also significantly different from atmospheric O₂, which we interpret by partial equilibration with water in the exhaust fume. These results suggest that each combustion process yields CO₂ with a characteristic triple oxygen isotope signature.

Atmospheric CO₂ samples were collected on the campus of the University of Göttingen (NW Germany), between June 2010 and March 2011. The Δ¹⁷O shows variations of 0.045‰ (SD) without correlation between Δ¹⁷O and 1/[CO₂]. Variance analysis suggests a small difference in Δ¹⁷O (0.07‰) between summer and winter. The small variation could be due to differences in the mixing ratio of anomalous anthropogenic and isotopically normal natural CO₂.

Address of corresponding author: B. Horváth: Goldschmidtstrasse 3, D-37077 Göttingen, Germany
e-mail: bhorvat@gwdg.de

Sulphur and oxygen isotopes in dissolved sulphates as tracers of sea and river water mixing in the Szczecin Lagoon (Poland)

Piotr Jezierski, Adriana Trojanowska
*Laboratory of Isotope Geology and Geoecology,
University of Wrocław, Wrocław*

Artur Skowronek
*Department of Geology and Paleography, University
of Szczecin, Szczecin*

Sulphur and oxygen isotope ratios ($\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$) in dissolved SO_4^{2-} ions and concentration of sulphates in water were analyzed in the Szczecin Lagoon (SW Baltic Sea) – an area of inland and coastal water mixing. This reservoir receives from the south the Odra River water, whereas, in its northern part, the lagoon connects via straits with the Baltic Sea. Therefore, mixing of marine and riverine waters is an important feature of the lagoon hydrodynamics and its hydrochemistry as well. Frequent storms in this shallow lagoon promote oxygenation of waters and the redox stability of SO_4^{2-} ions, which is the important property of the good geochemical tracer. The proportion of sea and river waters in the lagoon depends on several hydrological and weather factors that determine the direction and distribution of water current (wind direction and strength, the relationship of sea level to the level of water in the lagoon, etc.).

Interpretation of the chemical and isotope data allowed to recognize two main sources of SO_4^{2-} ions: riverine (the Odra River) and marine (Baltic Sea). Marine sulphates were characterized by distinctly higher concentration and higher values of $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ than riverine ones. Concentration of SO_4^{2-} ions varied from 202 to 571 mg/l, values of $\delta^{18}\text{O}_{\text{SO}_4}$ from 3.6 to 8.9‰ and $\delta^{34}\text{S}_{\text{SO}_4}$ from 2.9 to 14.9‰. It was found that the concentration of sulphate ions and $\delta^{34}\text{S}_{\text{SO}_4}$ values were increasing from south to north. The significant correlations between SO_4^{2-} conc. ($r=0.893$, $p=0.000$) and $\delta^{34}\text{S}_{\text{SO}_4}$ ($r=0.537$, $p=0.039$) versus sample points latitude were noted.

The results showed that sulphur and oxygen isotopes in dissolved sulphates are good tracers of sea and river water mixing in the Szczecin Lagoon. It seems that studies of similar scope may be helpful for simple and quick quantitative estimation of inland and marine waters contribution in other coastal reservoirs as well.

Address of corresponding author: P. Jezierski: Ul. Cybulskiego 30, 50-205 Wrocław, Poland
e-mail: piotr.jezierski@ing.uni.wroc.pl

Methanogenesis in the Pliocene Velenje Coal Basin, Slovenia, inferred from stable carbon isotopes

Tjaša Kanduč

*Department of Environmental Sciences,
Jožef Stefan Institute, Ljubljana*

Miloš Markič

Geological Survey of Slovenia, Ljubljana

Simon Zavšek

Velenje Coal Mine, Velenje

Jennifer McIntosh

*Department of Hydrology and Water Resources,
University of Arizona, Tucson*

In this study, stable isotopes of carbon were used to trace organic and inorganic carbon cycles and biogeochemical processes, especially methanogenesis within different geological media of the Pliocene lignite-bearing Velenje Basin in northern Slovenia. The study is based on investigations of carbon isotopic composition of the following geological media: 1.) lithotypes of lignite, 2.) coalbed gases, 3.) calcified woods (xylites) and carbonate-rich sediments, and 4.) groundwaters in various aquifers. For different lignite lithotypes it was found that $\delta^{13}\text{C}$ values ranged from -28.1 to -23.0‰ , the variability is being a consequence of original isotopic heterogeneity of the source plant ingredients and of biogeochemical processes (gelification, fusinitization, mineralization of organic matter) at the early stage of biomass accumulation and its early diagenesis. In the lignite seam the major gas components were found to be CO_2 and CH_4 with small amounts of N_2 . The carbon isotope compositions of carbon in CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$) and CH_4 ($\delta^{13}\text{C}_{\text{CH}_4}$) were very variable and ranged from -9.7 to 0.6‰ and from -70.5 to -34.2‰ , respectively. The presence of thermogenic gases is unlikely due to the low rank of the coal and lack of higher chain hydrocarbons. Calcified xylite enriched with ^{13}C ($\delta^{13}\text{C}$ values up to 17.1‰) indicated that CO_2 reduction process was present at the time of formation of the basin. The $\delta^{13}\text{C}_{\text{DIC}}$ values (from -17.4 to -3.2‰) of groundwaters recharging the basin from the Triassic aquifer were consistent with degradation of organic matter and dissolution of dolomite. Groundwaters from the Pliocene sandy and Lithotamnium carbonate aquifers had $\delta^{13}\text{C}_{\text{DIC}}$ values (from -9.1 to 0.2‰) suggestive of degradation of organic matter and biogenic CO_2 reduction.

Address of corresponding author: T. Kanduč: Jamova 39, 1000 Ljubljana, Slovenia
e-mail: tjas.kanduc@ijs.si

Carbon isotopic variation in $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ during early anaerobic decomposition of organic agriculture wastes

Dominika Kufka, Beata Biega, Mariusz Orion Jędrysek
*Laboratory of Isotope Geology and Geoecology Institute of Geological Sciences,
University of Wrocław, Wrocław*

This abstract reports carbon isotopic variation in $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ formed during anaerobic decomposition of grass and corn silage. This study is an initial part of a larger experiment regarding methanogenic processes in incubated conditions. Decomposed biomass was incubated in batch approach (closed system) at temperature 32 °C. Experiments were started at 14th February 2011. Fermented biomass has been located in a half litter bottle with rubber septum. In the first bottle (B1) 40 g of biomass was placed and filled up with distilled water up to 350 ml – the remaining volume was air. Another bottle (B 2) has been filled with 10 g of biomass, and 350 ml of distilled water – the remaining volume was completed with gaseous nitrogen.

DIC (10 ml of water) and CO_2 (7 ml gas) has been sampled daily since 23rd March 2011 to 1st April 2011. Five samples of gaseous CO_2 and five samples of DIC from the B1 have been sampled. Four respective samples have been collected from the B2. The sampled volume has been substituted with distilled water each time. Additionally the analyses of $\delta^{13}\text{C}$ from unfermented organic matter (prior to the experiment) have been carried out. The method of DIC and CO_2 analyses was based on conversion all of DIC forms to gaseous CO_2 under acidic condition. The analyses of concentrations of gaseous and dissolved CO_2 were not carried out. However, visual judgement shows that the production of carbon dioxide decreased along experiment. Measurements of carbon isotope composition have been made using a mass spectrometer Finnigan Mat Delta E.

In the B1 $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ varied from 9.05 to 12.90‰ and 8.82 to 9.72‰, respectively. In the B2 $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ varied from 7.55 to 10.54‰ and 1.90 to 8.69‰, respectively. The $\delta^{13}\text{C}$ value of the initial organic load was –12.65‰. In the B1 $\delta^{13}\text{C}_{\text{CO}_2}$ increased with time while in the B2 $\delta^{13}\text{C}_{\text{CO}_2}$ and both in B1 and B2 $\delta^{13}\text{C}_{\text{DIC}}$ values have shown chaotic variations. These suggest the experiment was too short to observe isotopic effect in anaerobic conditions, but selective oxidation of C isotopes took place when atmospheric O_2 was available.

Address of corresponding author: D. Kufka: Cybulskiego 30 Str; 50-205 Wrocław; Poland
e-mail: ominika.kufka@ing.uni.wroc.pl

Recent paleolimnological changes in small carbonate rich hypertrophic lake

Annika Mikomägi

Institute of Ecology, Tallinn University, Tallinn

Tonu Martma

*Institute of Geology, Tallinn University of
Technology, Tallinn*

Agata Marzecova

*Institute of Mathematics and Natural Sciences,
Tallinn University, Tallinn*

In paleolimnological studies oxygen and carbon isotopes have been used for reconstructions of climate changes and productivity within the lake. This study presents the use of stable isotopes from lacustrine carbonates in a multi-proxy approach to track environmental changes and associated anthropogenic impacts in lake. The main objective was to combine different indicators and to detect how they correspond to the documented history of the lake. Sedimentary pigments were used because they are known as good indicators of changes in lake primary production. Geochemical composition of lake sediment is influenced by processes taking place in lake and also by the surrounding catchment therefore XRF analysis can be used as a supportive tool to understand how human activities affect the natural ecosystem. For this study, two short sediment cores from Lake Verevi littoral zone were collected. The study site L. Verevi is small, hard-water and intermittently open/closed lake. Lake is situated in town Elva (Estonia) and during the last 100 years it has been highly popular recreation area. Town located in the vicinity of the lake contaminates the lake from various sources (discharge of urban wastewater, infiltrated water from farms, swimming pool). Carbon and oxygen stable isotopes in carbonates ($\delta^{13}\text{C}_{\text{Carb}}$ and $\delta^{18}\text{O}_{\text{Carb}}$) were analysed, sediment pigment markers were identified using high-performance liquid chromatography (HPLC) and bulk geochemistry determined by XRF spectroscopy. The sediment record covers last 150 years (based on ^{210}Pb dating). XRF chemistry reflects increase of the pollution and significant changes in the lithology of the sediment which changes from organic-rich to mineral sediment. Changes in sediment pigment markers show strong eutrophication. Isotopic values at the same time show increase in the amount of heavier isotopes. We were able to link these results with collected historical and monitoring data which confirmed that at the beginning of 20th century the lake was moderately eutrophic and during 1970s and 1980s the distinctive changes in lake productivity occurred and lake became hypertrophic. In addition, the results of our multi-proxy analysis show drastic changes in lake carbonate precipitation processes after extensive human impact has started. Based on shift in carbon isotope values we conclude that a change in lake sediment has been caused by excessive eutrophication.

Address of corresponding author: A. Mikomägi: Uus-Sadama 5, 10120 Tallinn, Estonia
e-mail: annikam@tlu.ee

Use of light stable isotopes, dissolved gas constituents, and microbial community abundances to characterize biodegradation of chlorinated ethenes in a fractured-rock aquifer

Kinga Révész
U.S. Geological Survey, USA

Barbara Sherwood Lollar
University of Toronto, Canada

Allen M. Shapiro, Julie Kirshtein, Mary Voytek, Thomas E. Imbrigiotta,
Eurybiades Busenberg, Claire R. Tiedeman, Daniel J. Goode
U.S. Geological Survey, USA

The $\delta^{13}\text{C}_{\text{VPDB}}$ and concentration results of TCE are qualitatively consistent with kinetic isotope fractionation by natural microbial TCE dehalogenation and indicate clearly that TCE microbial dehalogenation has occurred in a fracture rock aquifer at the former Naval Air Warfare Center (NAWC) site in West Trenton, New Jersey. The estimated value of the isotope fractionation factor (α) obtained from the borehole interval with the lowest transmissivity was 0.99345, which is in the range of published values. With the knowledge of the site-specific α the original TCE concentration that degraded microbiologically can be calculated in the various monitored intervals. The data from the same low-transmissivity well also could be used to determine the site-specific, first-order reaction kinetic constant. It is also close to published values.

Bioaugmentation was used to accelerate the dechlorination of TCE in groundwater at NAWC site. Water enriched in deuterium was used as a tracer. The $\delta^2\text{H}$ of water and the concentration of H_2 gas were more sensitive indicators of bioremediation than the $\delta^{13}\text{C}$ of the chlorinated hydrocarbons and the abundance of the microbial communities. The combined evidence suggests that the effects of bioaugmentation were detectable up to 15 m from the injection well, and that the effect of it might have occurred to a lesser extent up to 26 m. Data also showed that the sum of the molar chlorinated hydrocarbon concentrations was higher than the sum of the background molar concentration in those wells where the bioaugmentation was intensive. The concentration ratios of TCE/(cDCE+VC) and the carbon isotope mass balance calculation of these compounds indicated that the additional concentration may be from a less degraded TCE, that could be desorbed from the rock matrix due to the sudden concentration gradient change caused by the bioaugmentation.

Address of corresponding author: K. Révész: MS 431, Reston, VA 20192, USA
e-mail: krevesz@usgs.gov

Distribution and origin of organic matter in the Baltic sediments based on $\delta^{13}\text{C}$ profiles in sediment cores dated with ^{210}Pb and ^{137}Cs

Aleksandra Szczepanska, Anna Maciejewska, Karol Kulinski,
Janusz Pempkowiak
Institute of Oceanology, Sopot, Poland

Organic carbon in marine sediments is an important part of the global carbon cycle. Knowledge concerning the role of shelf seas (including the Baltic Sea) in the carbon cycle is inadequate. Accumulation of carbon in marine sediments, in general, and in the Baltic sediments, in particular, still requires clarification. The study demonstrates methods used and the obtained results for assessing organic carbon sedimentation rates and provenience in the Baltic contemporary sediments.

The experimental work is based on sediment cores covering sediment accumulation areas in the Baltic Sea. Mass sediment accumulation rates (230–570 $\text{gm}^{-2}\text{yr}^{-1}$) are based on ^{210}Pb method validated with ^{137}Cs measurements. The provenience of organic matter (autochthonous vs allochthonous) is assessed by $\delta^{13}\text{C}$ data (range from -23.2‰ to -26.4‰).

Marine (autochthonous) organic matter constitutes some 45% of the total in the surface (0–10 cm below sediment-water interface), and 30% in the subsurface (20–30 cm) sediment layers. The organic carbon accumulation rates in contemporary Baltic sediments ranging from 18 to 75 $\text{g C m}^{-2}\text{yr}^{-1}$ were established.

The obtained results indicate that the Baltic Sea sediments are an important sink for organic carbon originating, mostly, from terrestrial areas.

Address of corresponding author: J. Pempkowiak: PO Box 197, Sopot, Poland
e-mail: pempa@iopan.gda.pl

Carbon and nitrogen isotopic analysis coupled with palynological data of PM10 dust in Wrocław city (SW Poland) – assessment of anthropogenic impact

Elzbieta Zwolińska, Maciej Górka
Dominika Lewicka-Szczebak
Mariusz-Orion Jędrysek
*Laboratory of Isotope Geology and Geoecology,
Department Applied Geology and Geochemistry,
Institute of Geological Sciences,
University of Wrocław, Wrocław*

Malgorzata Malkiewicz
*Department of Paleobotany,
Institute of Geological Sciences,
University of Wrocław, Wrocław*

The purpose of this study was to assess the anthropogenic impact on the urban air quality in the city of Wrocław (SW Poland) based on carbon and nitrogen isotopic analyses and palynological analysis of PM10 samples. The 23 samples (about two per month) were chosen for isotopic analysis.

The PM10 concentrations vary from $10.5 \mu\text{g}/\text{m}^3$ (5th June 2007) to $98 \mu\text{g}/\text{m}^3$ (21st November 2007), showing higher values in heating season when compared to vegetative season. The $\delta^{13}\text{C}(\text{PM10})$ values vary from -26.9‰ (24th April 2007) to -25.1‰ (21st November 2007), with the average of -26.1‰ . The $\delta^{15}\text{N}(\text{PM10})$ values vary from 5.0‰ (9th September 2007) to 13.7‰ (5th June 2007), with the average of 9.9‰ . The palynological analysis determined eight taxons of pollen and six types of spores of mildew fungus. Furthermore, in the analyzed samples insect fragments, hair and plant tissues were noted.

The results obtained show that carbon isotopic delta values differ dependently on the season – the lower values are observed in the summer (vegetative season), and the higher in winter (heating season). During the heating season the main source of carbon in PM10 are products of coal combustion, while in the vegetative season, two generations of carbon in PM10 can be distinguished: (i) originating from the coal combustion, (ii) a mixture of organic molecules and pollution from transport. Seasonal variations in nitrogen isotopic values in PM10 were not clearly observed. However, it is possible to determine isotopic composition of the dominant nitrogen source, which is about 10‰ in summer and about 9‰ in winter. These values do not allow us to discriminate precisely between various sources of atmospheric dust.

Address of corresponding author: E. Zwolińska: Cybulskiego 30, 50-205 Wrocław, Poland
e-mail: elzbieta.zwolinska@ing.uni.wroc.pl: