APPLICATION OF RADIOACTIVE AND STABLE ISOTOPES TO TRACE ANTHROPOGENIC POLLUTION IN THE BALTIC SEA

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INTRODUCTION

The Baltic Sea is one of the seas most contaminated by various pollutants including the chemical munitions dumped after the Second World War.





Sanderson et al., 2010; CHEMSEA

Pu isotopes, Δ^{14} C and δ^{13} C of total or- to elucidate a possible leakage of CWA ganic carbon (TOC) as well as lipid and at the Gotland Deep dumpsite. sediments, to assess a possible effect to CWA leakage studies. of the petroleum hydrocarbon contamination on radiocarbon signatures and

phospholipid (PL) fractions of the sedi- CWA were produced before the Secments were applied to study sources of ond World War from petroleum, natupollutants including chemical warfare ral gas, petroleum distillates and from agents (CWA). The compound-specif- coal. For this reason the variations in ic $\delta^{13}C$ analysis, PL-derived fatty acid carbon isotope ratios have been exbiomarkers and an end-member (EM) pected. It has been supposed that apmixing model were used to estimate plications of carbon isotopes will ala relative contribution of the marine, low us to estimate the total amount of terrestrial and fossil as well as petro- CWA released into the environment. leum hydrocarbon (measured directly) This has been a first attempt to apply sources to the organic carbon in the stable and radioactive carbon isotopes





 Δ^{14} C of TOC and TLE extracted from sediments vs. water depth (A). δ^{13} C of TOC and TLE in sediments (B).







METHODS

Total lipid extracts (TLE) were extracted using methylene chloride and phosphate buffer mixture ($\delta^{13}C, \Delta^{14}C$).

Neutral lipid (NL), glycolipid (GL) and phospholipid (PL) fractions for $\delta^{13}C$ measurements were separated by SPE-SI column.

PLs were esterified and passed through a SPE-NH2 column to separate unsubstituted fatty acid methyl esters (FAME).

Humic substances were extracted using 1 mol/L NaOH and humic acids (HA) were separated with HCl at pH 1.0 and mineral fractions with 0.3 $mol/L K^+$ (HAMF).

Pu isotopes – TOPO/cyclohexane extraction and radiochemical purification using UTEVA, TRU (Lujaniene, 2013).

MEASUREMENTS

 δ^{13} C – Thermo Scientific Delta V Advantage MS, Flash EA 1112 EA

Spatial distribution of TOC, %; δ^{13} C of TOC, %; Δ^{14} C of TOC, %, THC, mg/ kg; DHC, mg/kg; MOHC, mg/kg in the Sediments in the studied area.

EM MIXING MODEL

EM mixing-model analysis for the three sources - continental, marine and fossil was applied. The EM for the three sources yields the following equations: $f_{\text{terrestrial}} + f_{\text{marine}} + f_{\text{fosill}} = 1$

 $\delta^{13}\mathbf{C}_{\text{sample}} = \mathbf{f}_{\text{terrestrial}} \delta^{13}\mathbf{C}_{\text{terrestrial}} + \mathbf{f}_{\text{marine}} \delta^{13}\mathbf{C}_{\text{marine}} + \mathbf{f}_{\text{fossil}} \delta^{13}\mathbf{C}_{\text{fossil}}$

 $\Delta^{14}\mathbf{C}_{\text{sample}} = \mathbf{f}_{\text{terrestrial}} \Delta^{14}\mathbf{C}_{\text{terrestrial}} + \mathbf{f}_{\text{marine}} \Delta^{14}\mathbf{C}_{\text{marine}} + \mathbf{f}_{\text{fossil}} \Delta^{14}\mathbf{C}_{\text{fossil}}$

where $f_{terrestrial}$, f_{marine} and f_{fossil} are the fractions of continental, marine and f_{fossil} OC contributions to the sediments.

EM δ^{13} C reference values:

 $\delta^{13}C_{\text{terrestrial}} = -28\%_0, \ \delta^{13}C_{\text{marine}} = -22\%_0 \text{ and } \delta^{13}C_{\text{fossil}} = -29\%_0$

EM Δ^{14} C reference values: Δ^{14} C_{terrestrial} (taking into account average sedimentation rates of 30, 6, 3, 2 and 1 mm y^1 during the period of 1984–2013) were as follows: 31‰, 37‰, 47‰, 57‰, 103‰, respectively; $\Delta^{14}C_{marine}$ (taking into account the local reservoir age offset in the study area of ~700 ¹⁴C years (Lougheed et al., 2013) were estimated as follows: -55‰, -49‰, -41‰, -32‰ and 10‰, respectively.





Fossil source

contribution

to OC in sedi-

ments assum

ing various

sedimenta-

 Δ^{14} C in TOC, THC, DHC and MOHC fractions in Sediments of the Curonian Lagoon (station CL10) and in the open Baltic Sea.

 δ^{13} C values of TOC, TLE, HA and HAMF extracted from Sediments.



Variations of δ^{13} C values in neutral lipid (NL), glycolipid (GL) and phospholipid fractions isolated from bottom sediments (A). Variations of δ^{13} C values in phospholipid-derived FAs: C14:0, C16:0, C16:1 ω 7c, **C18:1ω9c and C18:2 (B)**.

Spatial distribution of ¹³⁷Cs, ^{239,240}Pu, As, Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb in the surface sediments.



 δ^{13} C FAME – Finnigan Trace GC ultra gas chromatograph, Thermo Finnigan Delta plus Advantage SIS, Supelco SP[™]-2380 capillary column.

Measurements of Δ^{14} C in sediments were carried out using a **1.0MV HVE Tandetron AMS at the National Taiwan University.** Total petroleum hydrocarbons (THC) and their two fractions – diesel ($C_{10} - C_{20}$), hydrocarbon (DHC) and mineral oil ($C_{20} - C_{40}$) hydrocarbon (MOHC) – were measured using the GC-FID technique (Restek Rxi-1ms column).

¹³⁷Cs activities were measured with HPGe detectors (GEM40P4-76, efficiency 40%, resolution 1.85 keV (FWHM) at 1.33 MeV and GX4018, resolution 1.8 keV/1.33 Mev and efficiency 42 %). ^{239,240}Pu using alpha spectrometry (PIPS) detectors, 450 mm², ²⁴⁰Pu/²³⁹Pu ratio by ICPMS (ELEMENT-2, Thermo Fischer Scientific).

SAMPLING

Lagoon and the Baltic Sea.







PEARSON CORRELATION COEFFICIENTS OF METALS AND ORGANIC MATTER IN SURFACE SEDIMENTS IN THE CURONIAN LAGOON AND THE BALTIC SEA IN 2012–2014.

	δ ¹³ C	Corg	$\delta^{15}N$	Norg	Hg	Pb	Cu	Cd	Ni	Cr	As	Zn	Fe	AI	¹³⁷ Cs
C _{org}	-0.46*														
$\delta^{15}N$	-0.17*	-0.25*													
Norg	-0.45*	1.00	0.24*												
Hg	-0.53*	0.98	0.27*	0.98											
Pb	-0.40*	0.89	0.27*	0.88	0.92										
Cu	-0.52*	0.29*	0.23*	0.26*	0.45*	0.56									
Cd	-0.52*	0.95	0.11*	0.95	0.94	0.84	0.30*								
Ni	-0.56*	0.92	0.26*	0.92	0.97	0.93	0.60	0.89							
Cr	-0.51*	0.12*	0.10*	0.09*	0.29*	0.44*	0.96	0.17*	0.43*						
As	-0.39*	0.97	0.31*	0.96	0.97	0.93	0.40*	0.91	0.93	0.24*					
Zn	-0.41*	0.87	0.28*	0.86	0.91	0.44*	0.60	0.86	0.96	0.44*	0.88				
Fe	0.04*	0.65	-0.01*	0.63	0.26*	0.78	0.27*	0.71	0.65	0.68	0.87	0.77			
AI	-0.27	0.66	-0.04*	0.70	0.41	0.19	0.47	0.74	0.95	0.57	0.28*	0.78	0.69		
¹³⁷ Cs	0.17*	0.85**	0.10*	0.58	0.34	0.12*	0.19*	0.47	0.52	0.37	0.64	0.55	0.55	0.51	
^{239,240} Pu	0.16*	0.96**	0.03*	0.38	0.33*	0.81	0.70	0.92	0.72	0.83	0.84	0.79	0.88	0.88	0.69

* correlations are not significant, p > 0.05 **¹³⁷Cs and ^{239,240}Pu data for 1997–2014

THE CHERNOBYL DERIVED PU IN THE SUSPENDED PARTICULATE MATTER IN THE KLAIPĖDA STRAIT



A significant decrease in the ²³⁸Pu/^{239,240}Pu activity ratio in the surface soil samples was found in 2011–2012 as compared to that reported after the Chernobyl accident. In addition, ²³⁸Pu/^{239,240}Pu activity and ²⁴⁰Pu/²³⁹Pu atom ratios indicated different contributions of the Chernobyl-originated Pu to the suspended particulate matter and bottom sediments. The largest amount of the Chernobyl-derived Pu was found in the smallest suspended matter particles of 0.2–1 µm in size collected in the Klaipeda Strait in 2011–2012. The obtained data showed the possible application of the Chernobyl-derived Pu to trace the pollutants of terrestrial origin. Contrary to Pu isotope data on activity concentrations of ¹³⁷Cs in the bottom sediments indicated its redistribution in the Curonian Lagoon – the Baltic Sea system that points to certain limitations in the application of ¹³⁷Cs in the tracer studies.

The lowest concentrations were found for Hg while the highest ones were observed for Pb and its spatial distribution showed a different pattern as compared with the other heavy metals with the maximum concentration in the accumulation zone of the Nemunas river crease of the Baltic Sea.

Spatial distribution of ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios in surface bottom sediments showed small variations.

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Data obtained in this study have indicated wide OC variations in the coastal and open Baltic Sea. The spatial distribution of $\delta^{13}C_{TOC}$ in coastal sediments showed strong impacts of terrestrial and fresh waters on OC. Similar values of $\delta^{13}C_{TOC}$ and $\delta^{13}C_{HA}$ revealed that HA (due to their high abundance) determine the $\delta^{13}C$ distribution in sediments. However, $\Delta^{14}C_{TLE}$ and $\delta^{13}C_{TLE}$ variations have shown mixed (relict and modern) sources of lipids in the coastal area. The most depleted values were detected for $\Delta^{14}C_{TOC}$ (-453%) and $\Delta^{14}C_{TLE}$ (-812.4 %) at the CWA dumping site in the Gotland Deep. The contribution of petroleum to the fossil fractions was estimated from measurements of THC in sediments. It was found that THC accounted for 0.81% of TOC, d.w. (from 0.02 to 5%). To understand a reason for high contribution of fossil sources (causing low Δ^{14} C values of TOC and TLE), as well as to distinguish between the methane oxidizing bacteria and CWA sources at the dumpsite, the δ^{13} C compound-specific analyses were applied. The δ^{13} C analyzed in PDFAs – C14:0, C16:0, C16:1 ω 7c, C18:1 ω 9c and C18:2 showed the most depleted δ^{13} C values for C¹⁴:0 biomarker collected at sampling stations ChS2 (-37.6%), ChS5 (-36%) and ChS1 (-33.4%) at the CWA dumpsite. Application of the EM mixing-model-analysis allowed estimating sources (continental, marine and fossil) of OC in the sediments of the Baltic Sea. On the average, terrestrial, marine and fossil sources accounted for 26%, 52%, and 22% of OC, respectively. The high contribution of fossil sources at the CWA dumpsite (on the average 32% with the maximum value of 38% at ChS5 station) as compared to other stations (on the average 14%) in the Baltic Sea might indicate a leakage from CWA.

Data on the spatial distribution of As, Zn, Ni, Cr, Hg, Cd, Cu and Pb concentrations as well as ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios in the surface sediments indicated the highest concentrations of Pb with their different pattern of distribution. The values of ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios in the recent surface sediments revealed "natural" non-anthropogenic sources.

The obtained data revealed the possible application of the Chernobyl-derived Pu to trace the pollutants of the terrestrial origin.