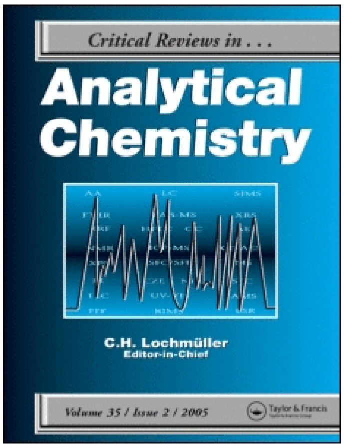
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

RESULTS OF STUDIES OF XENOBIOTIC CHEMICALS IN THE NEMUNAS RIVER BASIN

J. Jackson Ellington; Robert V. Thurston

Online publication date: 03 June 2010

To cite this Article Ellington, J. Jackson and Thurston, Robert V.(1998) 'RESULTS OF STUDIES OF XENOBIOTIC CHEMICALS IN THE NEMUNAS RIVER BASIN', Critical Reviews in Analytical Chemistry, 28: 2, 3 — 7

To link to this Article: DOI: 10.1080/10408349891194180

URL: http://dx.doi.org/10.1080/10408349891194180

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Critical Reviews in Analytical Chemistry, 28(2):[SI]3–[SI]7 (1998)

RESULTS OF STUDIES OF XENOBIOTIC CHEMICALS IN THE NEMUNAS RIVER BASIN

J. JACKSON ELLINGTON

Ecosystems Research Division, US Environmental Agency, Athens, Georgia, USA

and

ROBERT V. THURSTON

Department of Chemistry, Montana State University, Bozeman, Montana, USA

A study on the quality of surface waters in the Republic of Lithuania was initiated in 1989 under the sponsorship of the risk assessment program of the United States Environmental Protection Agency (U.S. EPA), Environmental Research Laboratory, Athens, Georgia (ERL-Athens). In 1990, 1991, and 1992 water samples were analyzed from 45 sites that spanned Lithuania (65,200 km^2) from Lake Drūkšiai on the eastern border with Belarus to Kuršių Lagoon (Kuršių Marios) on the coast of the Baltic Sea. Sample collection was conducted in cooperation with scientists from the Lithuania Environmental Protection Department, the Lithuania Academy of Sciences, and Vilnius University. The location of the sampling sites are designated by numbers in the figure. All sampling sites were in the Nemunas Basin, except the Kulpė River site in Siauliai (water flows north to Latvia), and Visaginas and Lake Drūkšiai on the Belarus border. The total area of the Nemunas Basin is 98,200 km^2. The basin area located in Lithuania is 46,600 km^2 (48%), with the remainder in Poland (2%), Belarus (46%) and Kaliningrad (4%).

Organic chemicals were extracted from the water samples by use of solid phase extraction (SPE) cartridges or disks, and these cartridges and disks were taken back to ERL-Athens for elution and analysis by means of gas chromatography and infrared/mass spectrometry. Water samples were filtered through borosilicate microfiber prefilters (Micro Filtration Systems), 47 mm diameter, to remove particles > 2.7 μ either during collection or within 24 hours thereafter, and then passed through SPE cartridges or disks to extract the organic chemicals. The SPE adsorption media were of three types: Bakerbond™ SPE cartridges (6 ml) that contained 500 mg of octylsilane (C-8) or octadecylsilane (C-18), Burdick and Jackson cartridges (6 ml) that contained 500 or 1000 mg of C-8 or C-18, and Empore™ extraction disks (47 mm) consisting of 500 mg of C-8 or C-18 suspended in a Teflon fibril network. The Bakerbond™ cartridges were precleaned at ERL-Athens by removing lettering on the cartridges with a tissue soaked in hexane and extracting the cartridges in a Soxhlet apparatus overnight with hexane:acetone (9:1). The Burdick and Jackson cartridges and the Empore™ disks were precleaned by applying vacuum and pulling through the sorbent bed, in sequence, two 5-ml portions of the final extraction solvent, methanol, and organic-free distilled, deionized water. All precleaned cartridges and disks were stored and transported in individual sealed containers.

Two blanks of each solid phase sorbent were left refrigerated at ERL-Athens during each sampling trip to Lithuania. Two more each were taken on the sampling trip and kept with the sampling solid phase sorbent containers. These were returned to ERL-Athens for extraction and analysis at the same time as the sample cartridges. The precleaned extraction cartridges and disks were activated with methanol according to supplier specifications prior to their use. The C-18 cartridges were used to concentrate nonpolar organic chemicals from the water samples. Carboxylic acids and phenols were extracted from the water samples by adjusting the pH of the samples ≤ 2 to protonate the anions before passage of the water through the prefilter and a C-8 cartridge or disk.

Low resolution electron-impact (EI) GC/MS was performed on either a Finnigan 4500 (Finnigan MAT, San Jose, California), or a Hewlett-Packard (Palo Alto, California) mass selective detector (MSD). Chemical ionization (CI) mass spectrometry was performed on the Finnigan 4500 system. High resolution EI GC/MS analyses of sample extracts were performed on a VG 70-SEQ high resolution hybrid mass spectrometer (VG Instruments, Manchester, United Kingdom). The GC/FT-IR/MS analyses were performed on a Hewlett-Packard system equipped with a 5965B infrared detector and a 5971 series mass selective detector.

GC/MS analysis of the 1990 surface water extracts identified the major peaks as several dialkyl phthalates, silica-containing components, saturated hydrocarbons, and some unidentified peaks with the same mass fragmentation pattern that appeared in every extract. Dialkyl phthalates are commonly found in environmental samples and stringent precautions are necessary to assure that their presence in the collected sample is not due to accidental contamination. Hydrocarbons, phthalates, and fatty acids were found in a few of the method and field blanks but at lower levels than in the samples; the presence of phthalates in the samples may have been real. Absence of man-made chemicals, other than possibly the phthalates, in the surface water samples was surprising, but could have been caused by the low ambient water temperature (4°C) and the high levels and flows of the surface water due to recent heavy rainfall. Both of these conditions would lower the concentration of organic chemicals in the surface water, possibly below the level of detection for the volume of water we sampled. Organic chemicals identified in surface water samples collected during this and subsequent expeditions are listed in the table.

In July 1991 three unknown tetrachlorinated isomers were found in samples from the Neris River (31) and Kaunas Reservoir (20). Surface water samples collected at Kaunas Reservoir and the Neris River at Grigiškės also contained 2,4-dichlorobenzoic acid in addition to the three tetrachlorinated unknowns. The observed fatty acids, identified in the Kaunas Reservoir and Grigiškės samples as their methyl esters, could be an indication of contamination by municipal sewage.

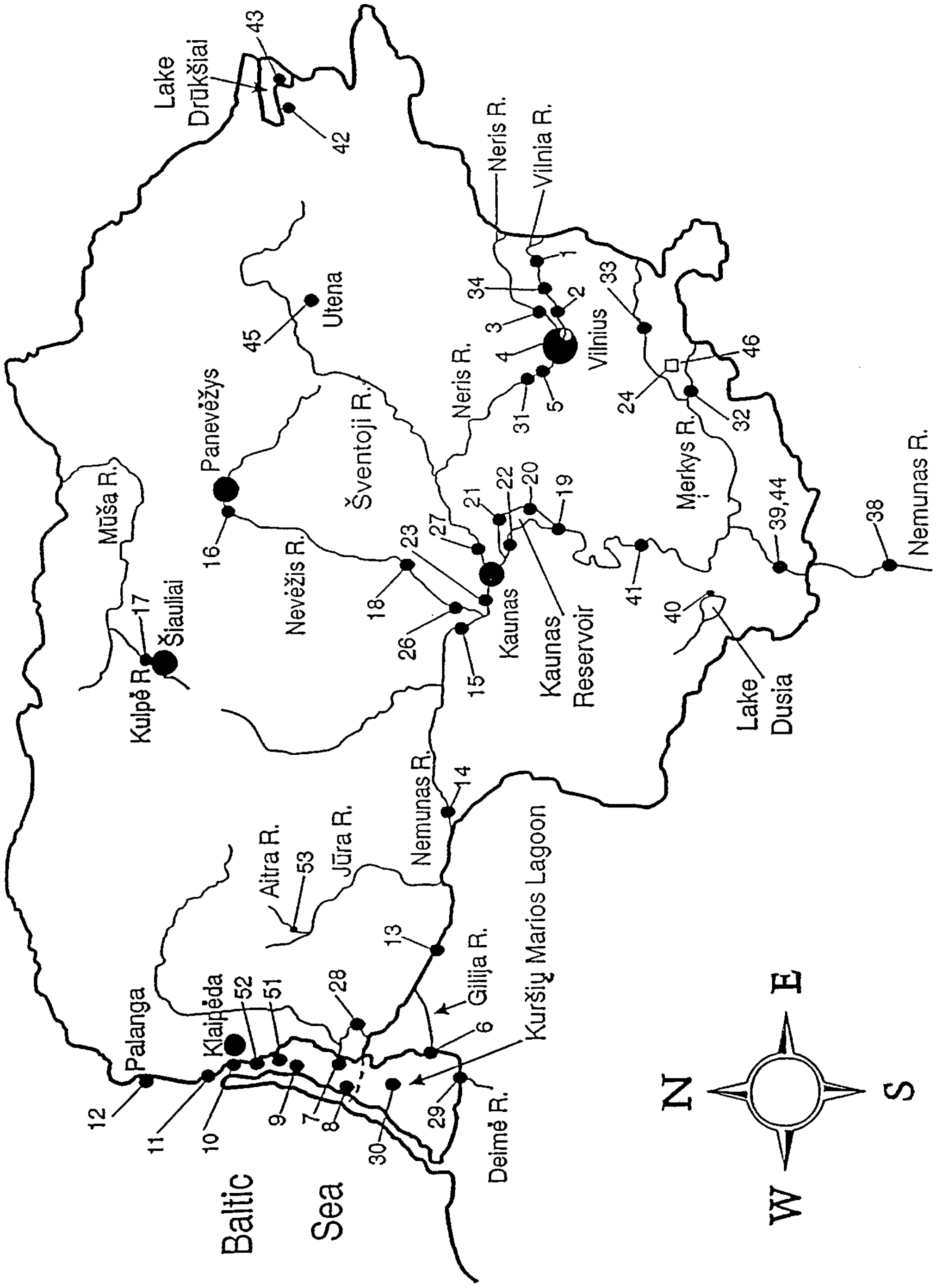
The LR-EI/GC/MS of two of the tetrachlorinated peaks had identical major mass ions (m/z 348, 317, 254, 184) in almost the same relative abundances. The third tetrachlorinated peak lacked the m/z 348 molecular ion but had an intense ion at m/z 313 that could result from loss of a very labile chlorine. The ratios of the isotopic cluster ions in the three tetrachlorinated peaks indicated that each unknown peak contained four chlorine atoms. The m/z 317 ion in two of the three could result from loss of a methoxy group OCH_3 from the molecular ion. High resolution GC/EI-MS yielded best fit empirical formulae of either $C_7H_{13}Cl_4O_5P$ or $C_{14}H_8Cl_4O_2$. A tetrachlorinated trialkyl phosphate fits the former formula, whereas tetrachlorinated aromatic esters or other structures containing both carbonyl and methoxy groups can be drawn for the latter. Both formulae are similar to those of compounds commonly used as electrical insulators and flame retardants. Compounds containing phosphorus were eliminated, however, by further

GC analysis of the sample using nitrogen-phosphorus specific detectors. The presence of a carbonyl functional group in the three isomers was confirmed by GC/FT-IR as each of the three unknowns exhibited strong absorption peaks centered around 1749 cm^{-1}. The presence of the carbonyl group together with a methoxy group (loss of the m/z 31 ion) would normally indicate a methyl ester. This is also consistent with the detection of these unknowns only after treatment of the pH 2 SPE eluates with diazomethane. A biphenyl ring system can be drawn for the m/z 254 fragment ion ($C_{12}H_5Cl_3$) formed in all three isomers by the consecutive loss of the methyl ester functionality $C_2O_2H_3$ (m/z 59) and Cl (m/z 35). This information together with the empirical formula $C_{14}H_8Cl_4O_2$ was strong evidence that the unknown isomers were tetrachlorinated biphenyl esters. However, the absence of a strong peak in the 1100-1300 cm^{-1} region of the GC/FT-R spectra which occurs in all esters due to the C-O stretch argued strongly against the methyl ester functionality.

The remote possibility that the ester functionality could be present and the C-O peak not observed due to high background interference during acquisition of the GC/FT-IR spectra or steric and/or electronic interactions within the molecular framework of the isomers was pursued by carrying out a reaction reported by Choudhry et al. Choudhry showed that irradiating a water/acetonitrile (9:1) solution of pentachlorobenzene and benzoic acid with UV light centered at 300 nm yielded photoincorporation of the UV-generated polychlorobenzene radicals into benzoic acid, thus forming polychlorinated biphenyl carboxylic acids. Accordingly we reacted pentachlorobenzene with benzoic acid using UV light at 300 nm as described by Choudhry. At the completion of irradiation, the reaction mixture was adjusted to pH ≤ 2, extracted with diethyl ether, and the ether volume reduced to 1 ml before treatment with diazomethane.

The mass and infrared spectra of the early eluting peaks of the GC/FT-IR-MS chromatogram exhibited mass fragmentation patterns that were consistent for mono-, di-, tri-, and tetrachlorinated biphenyls. Several di- and trichlorinated compounds also contained a carbonyl functional group as shown by the IR spectra. In order to check for coelution of the three unknowns and the three compounds produced in the synthesis, the derivatized extract of the Choudhry reaction mixture and the extract that contained the original three unknown isomers were first injected separately on the GC/ECD to determine the compounds' relative retention times versus that of the methyl ester of 2,4-dichlorobenzoic acid. They were then coinjected to check for coelution. The six peaks of interest had six distinctly separate retention times within a 2 minute window, proving that they were not the same compounds.

The IR spectra of three late eluting compounds in the Choudhry synthesis extract were consistent for aromatic methyl esters in that each contained a sharp peak centered around 1747 cm^{-1} and an even more intense peak centered around 1274 cm^{-1}. We concluded from these data that if the unknown tetrachlorinated compounds were methyl esters and were similar in structure to the Choudhry synthesis esters, a C-O stretch peak would be observed in the unknown infrared spectra. The mass spectra of the three synthesis peaks were identical and had the major ions m/z 348/350, 317/319, 254/256, 184 in essentially the same intensities as the unknown isomers. Therefore, although the mass spectra of the three unknowns were consistent with methyl esters of tetrachlorinated biphenyls, we concluded, based on the lack of C-O stretch in the infrared, that this was not the correct structure. The tetrachlorinated isomer peaks remain unidentified, but the evidence suggests a structure very closely related to the Choudhry reaction products. Tetrachlorinated aromatic ring systems containing a carbonyl group and a methoxy group of unknown chlorine substitution patterns are the most likely structures for the three unknown isomers.


Baltic Sea
Palanga
12
11
10
Klaipėda
52
51
9
7
8
30
28
29
Deimė R.
6
Gilija R.
Kuršių Marios Lagoon
13
Aitra R.
53
Jūra R.
Nemunas R.
14
Kulpė R.
17
Šiauliai
Mūša R.
16
Panevėžys
Nevėžis R.
18
26
23
15
Kaunas
27
21
22
20
19
Kaunas Reservoir
Šventoji R.
Neris R.
45
Utena
42
43
Lake Drūkšiai
Neris R.
Vilnia R.
1
34
2
3
4
Vilnius
31
5
33
24
46
32
Merkys R.
39,44
41
40
Lake Dusia
38
Nemunas R.
N
E
S
W

Hazardous chemicals identified in surface water samples.

Chemical	**Grigiškės (LT-31)**	**Kaunas Reservoir (LT-19-22)**	**Green Harbor (LT-52)**
Alachlor[1]			x
Alkyl hydrocarbons[2]	x	x	
Aromatic hydrocarbons[2]	x		
Dialkylthiophene[2]	x		
2,4-Dichlorobenzoic acid[1]	x	x	
Fatty acids[2]	x	x	x
2-(Methylthio) benzothiazole[2]	x		
Phenanthrene carboxylic acid[2]	x	x	
Phthalates[1,3]	x	x	x
Silicon organics[2]	x	x	x
Tetrachlorinated unknowns[2]	x	x	

[1] Identified by GC/FT-IR/MS and confirmed with a standard
[2] Identified by GC/FT-IR/MS but not confirmed with standards
[3] Diisooctyl-, Butylbenzyl-, Di-n-octyl-, and Di-n-butylphthalates were observed the most frequently