



# **The exposure assessment of the residues of pharmaceuticals in SGD area in the Bay of Puck, southern Baltic Sea**



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# PHARMACEUTICALS IN THE ENVIRONMENT



Pharmaceuticals (PCs) as '*new emerging pollutants*'

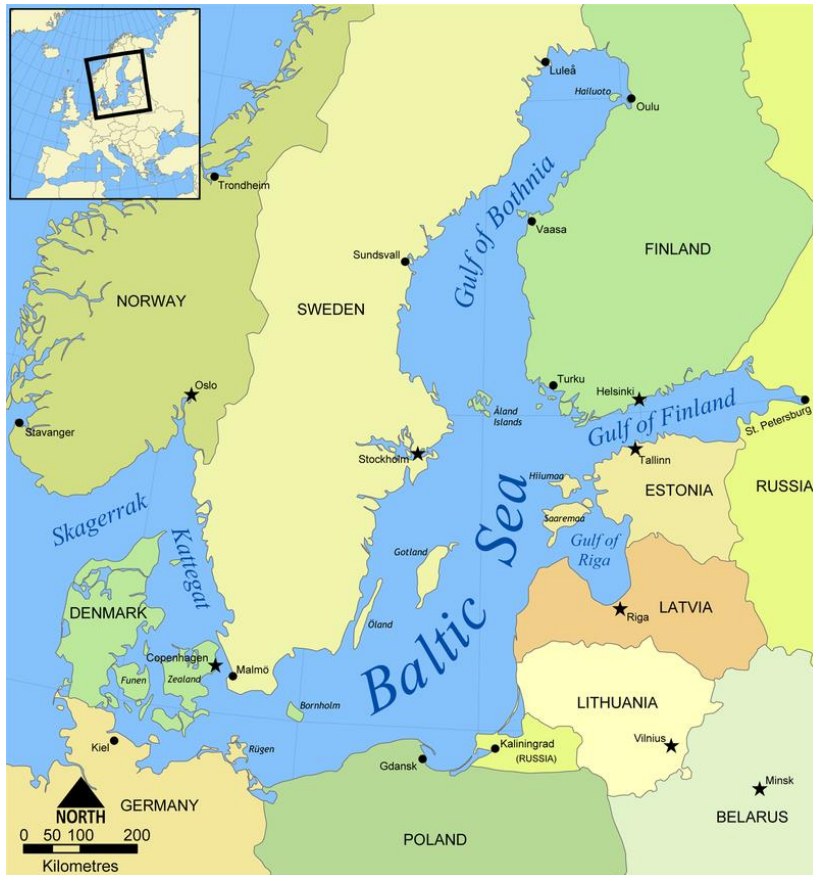
Biologically active compounds designed to have an specific effect at a very low doses

Widely used for different purposes (human medicine, veterinary, livestock production)

Excreted in the parent forms and as metabolites

They can persist in the environment or undergo different processes creating a new and emerging problem

# BRIEF CHARACTERIZATION OF THE BALTIC SEA



[https://en.wikipedia.org/wiki/Baltic\\_Sea](https://en.wikipedia.org/wiki/Baltic_Sea)

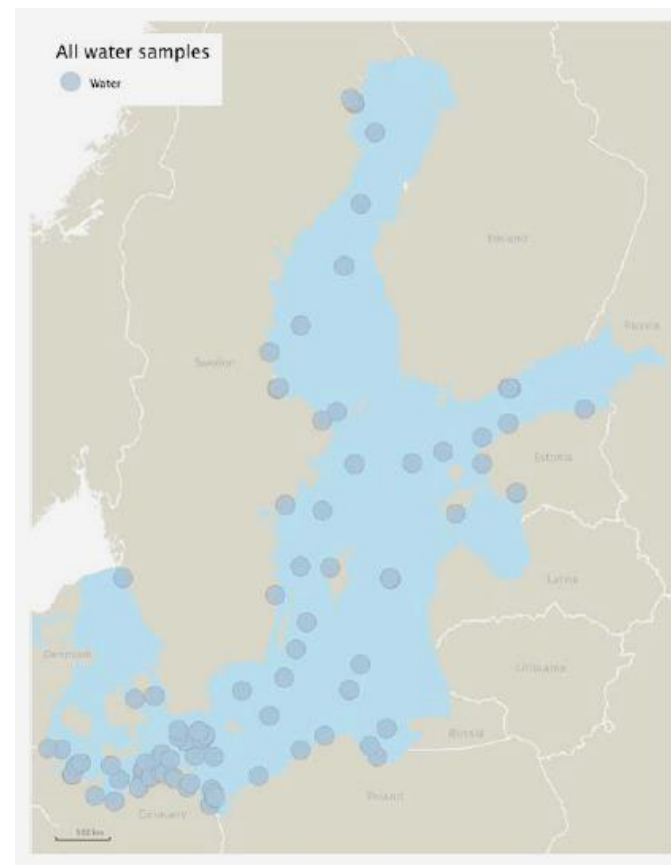
- ❑ average salinity – 7 PSU
- ❑ a large semi-enclosed sea
- ❑ various branches of drugs industry, intensive farming and animal husbandry in surrounding countries
- ❑ small depth
- ❑ low water exchange with the North Sea
- ❑ risk of chemical accumulation

# Pharmaceuticals in the aquatic environment of the Baltic Sea region – A status report

The report presents data for the period from 2003 to 2014. In total, 4,600 observations in water, sediments and biota were reported. Presence of pharmaceuticals was detected in 640 of these samples. One hundred and sixty-seven different pharmaceuticals were measured.

## Overview of all 3647 samples in the compiled data set

Source: Data submitted by Denmark, Estonia, Finland, Germany, Poland and Sweden



## International Initiative on Water Quality



United Nations  
Educational, Scientific and  
Cultural Organization



International  
Hydrological  
Programme

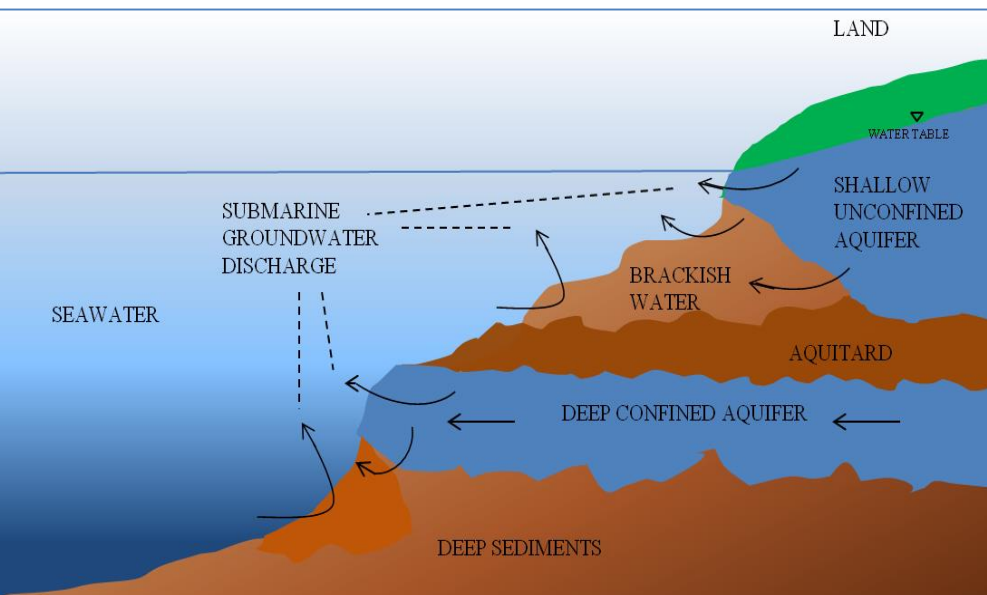


POLICY AREA 'HAZARDS'

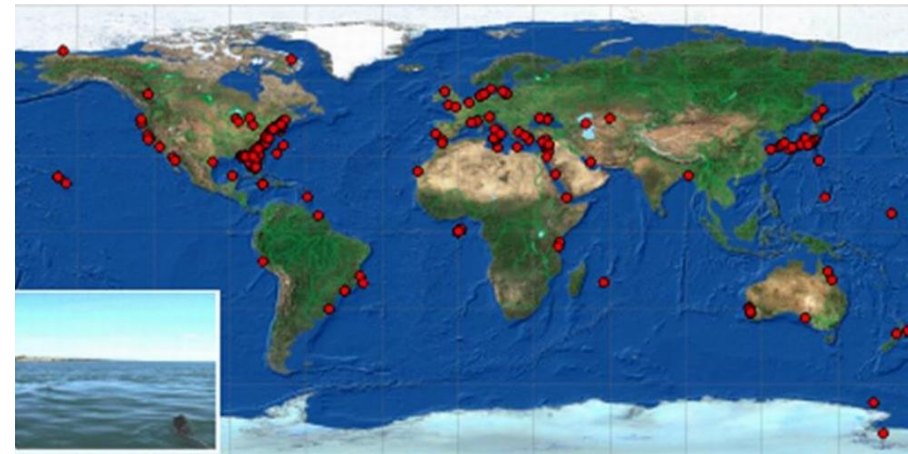


# SUBMARINE GROUNDWATER DISCHARGE

- **SGD** – direct groundwater outflow across ocean-land interface into the sea (Burnett et al., 2003)

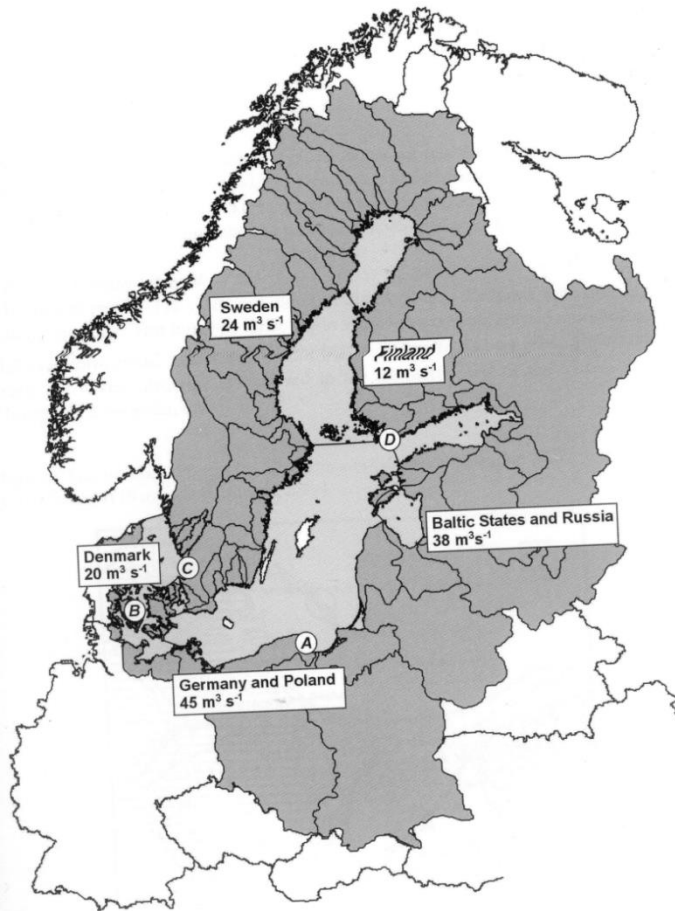


Modified after Burnett, 2006



[www.iaea.org](http://www.iaea.org)

# SUBMARINE GROUNDWATER DISCHARGE



Peltonen, 2002

Approximate groundwater discharge to the Baltic Sea Sub-basins and the Baltic Sea	m <sup>3</sup> /s	m <sup>3</sup> /h	km <sup>3</sup> /yr
Puck Bay <sup>1</sup>	0.97	3500	0.03
Germany and Poland <sup>2</sup>	45	162000	1.4
Baltic states and Russia <sup>2</sup>	38	136800	1.2
Finland <sup>2</sup>	12	43200	0.4
Gulf of Finland <sup>2</sup>	19	75000	0.6
Sweden <sup>2</sup>	24	86400	0.8
Denmark <sup>2</sup>	20	72000	0.6
The Baltic Sea <sup>2</sup>	139	50040055	4.4

<sup>1</sup>Piekarek-Jankowska, 1994

<sup>2</sup> Peltonen, 2002

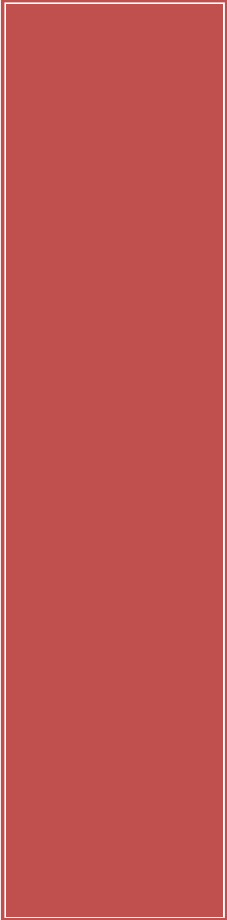
<sup>3</sup>Viventsova and Voronow, 2003

# AIM OF THE WORK



- ❑ Determination of pharmaceuticals residues and caffeine concentrations in piezometers and in the coastal groundwater discharged to the Bay of Puck.

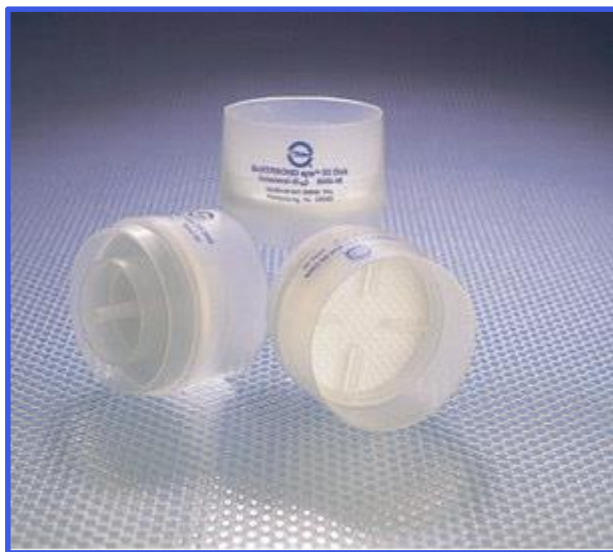
# SELECTED COMPOUNDS

- 
- ☐ Ibuprofen
  - ☐ Naproxen
  - ☐ Diclofenac
  - ☐ Ketoprofen
  - ☐ Carbamazepine
  - ☐ Trimethoprim
  - ☐ Enrofloxacin
  - ☐ Tetracycline
  - ☐ Oxytetracycline
  - ☐ Sulfapyridine
  - ☐ Sulfadiazine
  - ☐ Sulfamethoxazole
  - ☐ Sulfamerazine
  - ☐ Sulfamethazine
  - ☐ Acetyl-sulfamethoxazole
  - ☐ Sulfadimethoxine
  - ☐ Caffeine



# METHODOLOGY

## SOLID PHASE EXTRACTION



**SPE-speed disks**

## ANALYSIS WITH LC-MS/MS

- Identification → multiple reaction monitoring mode (MRM)
- Quantification → the use of isotopically labeled internal standards

# VALIDATION PARAMETERS OF THE DEVELOPED SPE-LC-MS/MS METHOD

Compound	MDL [ng L <sup>-1</sup> ]	[MQL (ng L <sup>-1</sup> )]	R <sup>2</sup>	Precision (%)	Accuracy (%)
Caffeine	0.8	2.5	0.9997	4.9 – 6.8	93.8 – 104.2
Ibuprofen	1.7	5.0	0.9983	1.2 – 7.9	95.5 – 116.2
Naproxen	3.3	10.0	0.9990	3.7 – 9.5	99.7 – 115.0
Carbamazepine	0.3	1.0	0.9985	2.1 – 7.2	84.5 – 113.0
Sulfapyridine	1.7	5.0	0.9989	2.4 – 9.3	88.1 – 105.4
Sulfadiazine	1.7	5.0	0.9993	2.3 – 6.9	92.5 – 106.3
Sulfamethoxazole	1.7	5.0	0.9999	1.6 – 6.0	98.0 – 107.7
Ketoprofen	3.3	10.0	0.9981	2.0 – 9.2	98.4 – 101.4
Sulfamerazine	0.2	0.5	0.9991	4.3 – 9.6	99.3 – 114.8
Sulfamethazine	0.2	0.5	0.9989	3.9 – 9.8	83.5 – 108.7
Trimethoprim	1.7	5.0	0.9985	1.1 – 7.1	99.5 – 104.2
Dicofenac	0.2	0.5	0.9994	2.2 – 9.4	96.2 – 103.6
Acetyl-sulfamethoxazole	1.7	5.0	0.9990	3.7 – 8.3	91.3 – 103.4
Sulfadimethoxine	0.2	0.5	0.9989	1.9 – 8.8	96.2 – 116.9
Enrofloxacin	3.3	10.0	0.9977	0.7 – 6.6	93.1 – 111.3
Tetracycline	3.3	10.0	0.9998	4.1 – 8.8	89.3 – 102.1
Oxytetracycline	3.3	10.0	0.9996	3.5 – 8.9	82.5 – 106.2

MDL: method detection limit; MQL: method quantification limit

# SUBMARINE GROUNDWATER DISCHARGE IN BAY OF PUCK

## The influence of SGD at coastal sites of the Bay of Puck



Observations of presumable groundwater seepage occurrence in Puck Bay (the Baltic Sea)

by

Maciej Matciak<sup>1,\*</sup>, Sylwia Bieleninik<sup>2</sup>, Aleksandra Botur<sup>2</sup>, Michał Podgórski<sup>2</sup>, Karolina Trzcńska<sup>2</sup>, Katarzyna Dragańska<sup>2</sup>, Damian Jaśniewicz<sup>2</sup>, Anna Kurszewska<sup>2</sup>, Marta Wenta<sup>2</sup>

**Abstract**  
We report the results of recent field measurements of seawater thermohaline structure and transparency carried out in early summer 2014 in Puck Bay. Near-bottom, less saline waters occurred almost in the entire study area. Their occurrence in the shallow part of Puck Bay was accompanied by an increase in the seawater transparency. The most likely explanation of these observations is a submarine fresh groundwater discharge.

Journal of Marine Systems xxx (2013) xxx–xxx



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Submarine groundwater discharge to the Baltic coastal zone: Impacts on the meiofaunal community

L. Kotwicki<sup>a,\*</sup>, K. Grzelak<sup>a</sup>, M. Czub<sup>b</sup>, O. Dellwig<sup>c</sup>, T. Gentz<sup>d</sup>, B. Szymczycha<sup>a</sup>, M.E. Böttcher<sup>c</sup>

Science of the Total Environment 438 (2012) 86–93



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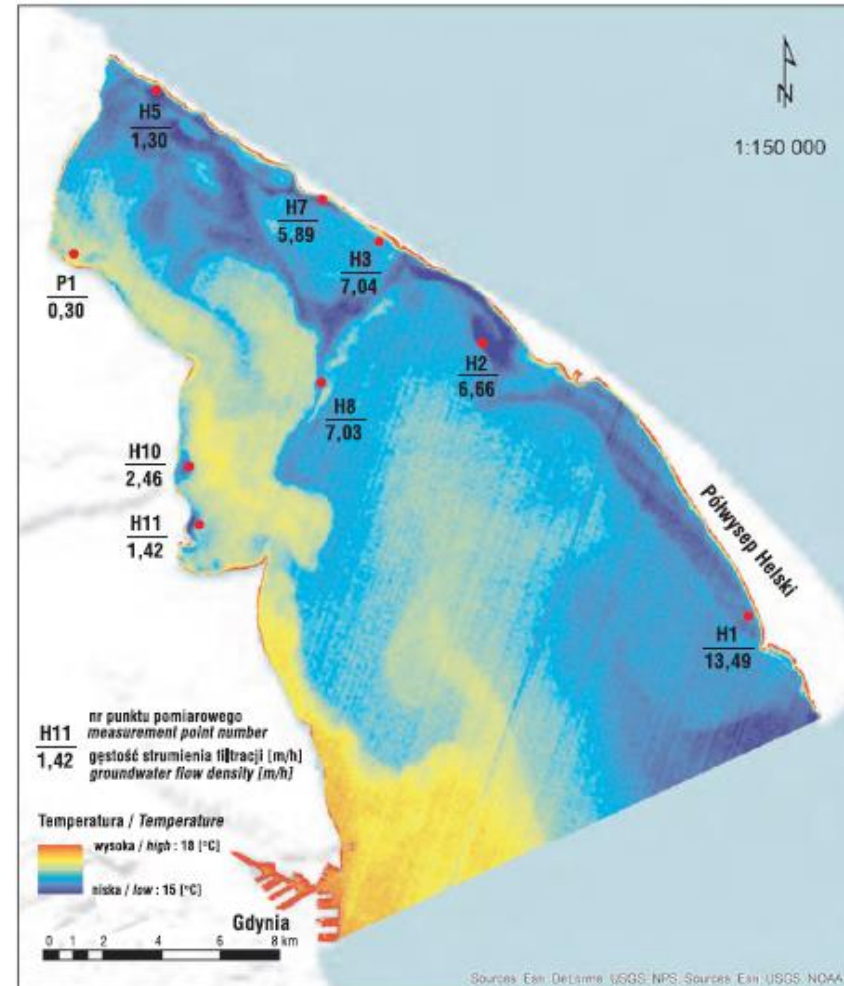
Nutrient fluxes via submarine groundwater discharge to the Bay of Puck, southern Baltic Sea

Beata Szymczycha<sup>a</sup>, Susanna Vogler<sup>b</sup>, Janusz Pempkowiak<sup>a,c,\*</sup>

doi:10.5697/oc.56-1  
OCEANOLOGIA, 56 (2),  
pp. 327

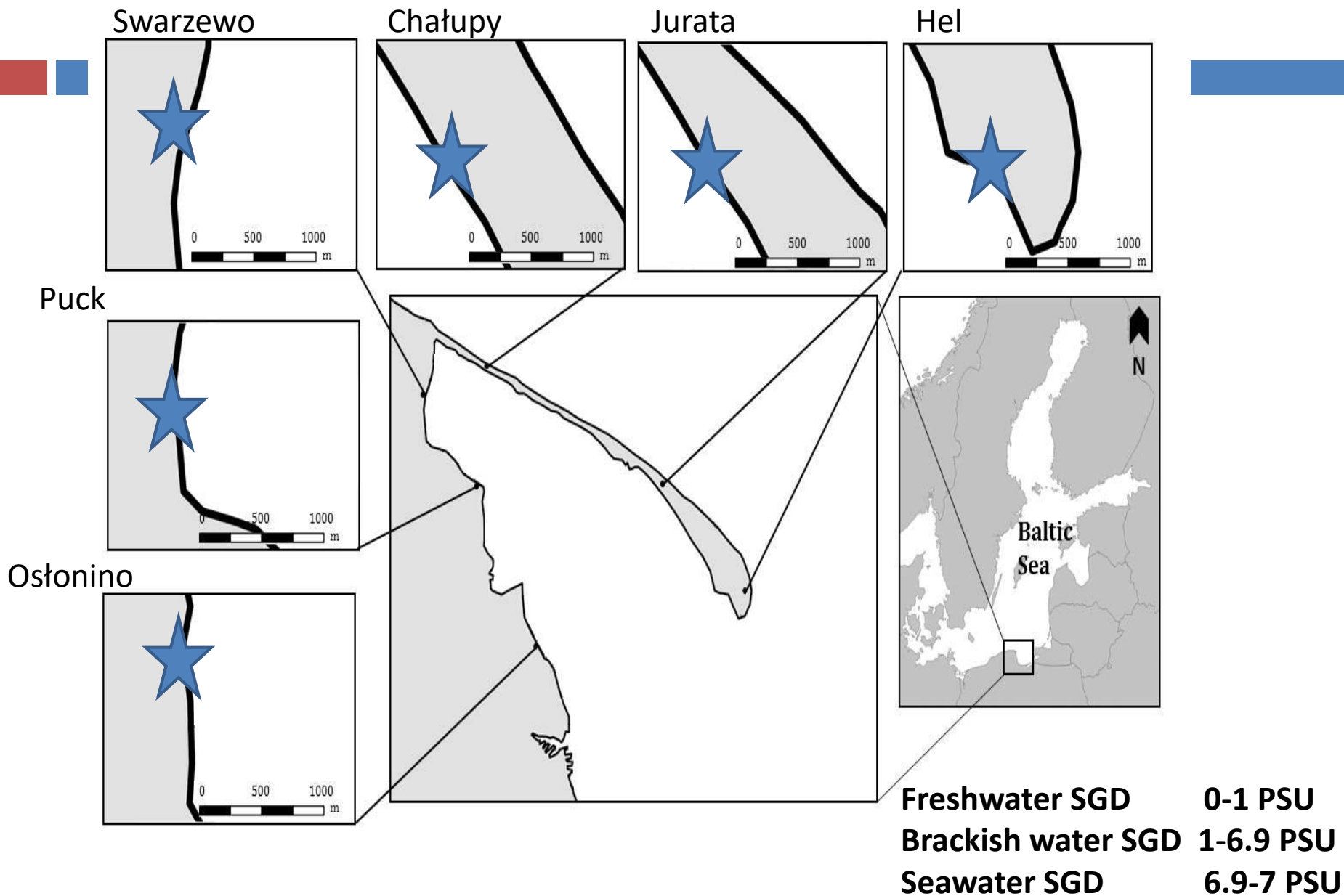
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**KEYWORDS**  
Bay of Puck  
Seepage  
Dissolved organic carbon  
Dissolved inorganic carbon  
Carbon budget  
Baltic Sea  
World Ocean

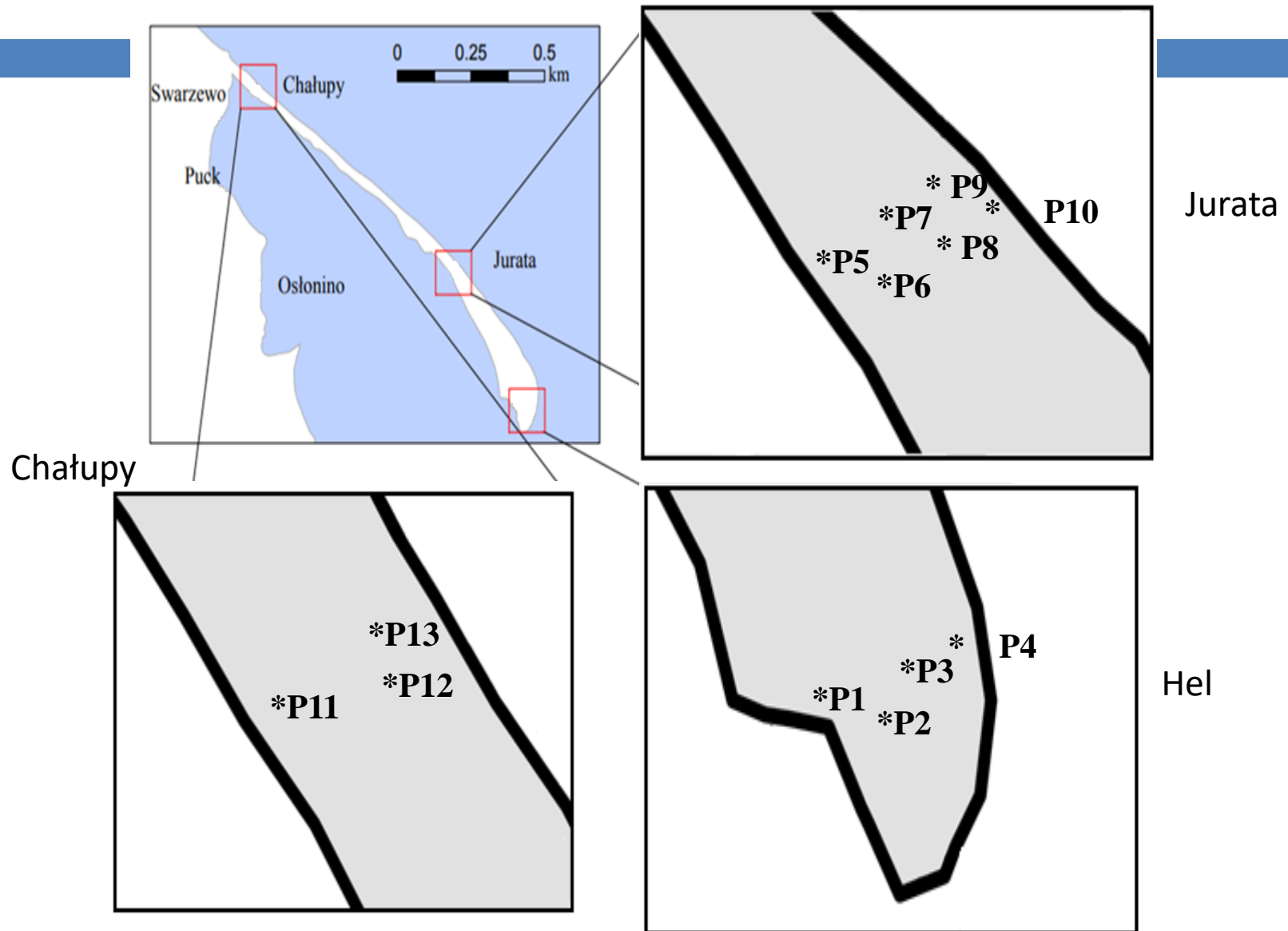


Bubliwska et. al 2017

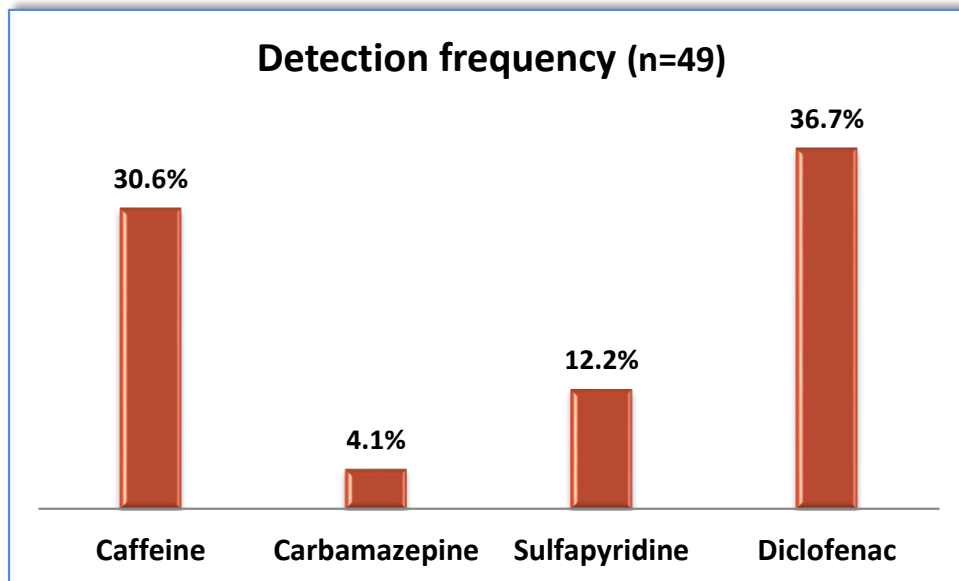
# STUDY AREA: COAST CAMPAINGS



# STUDY AREA: LOCATIONS OF PIEZOMETERS



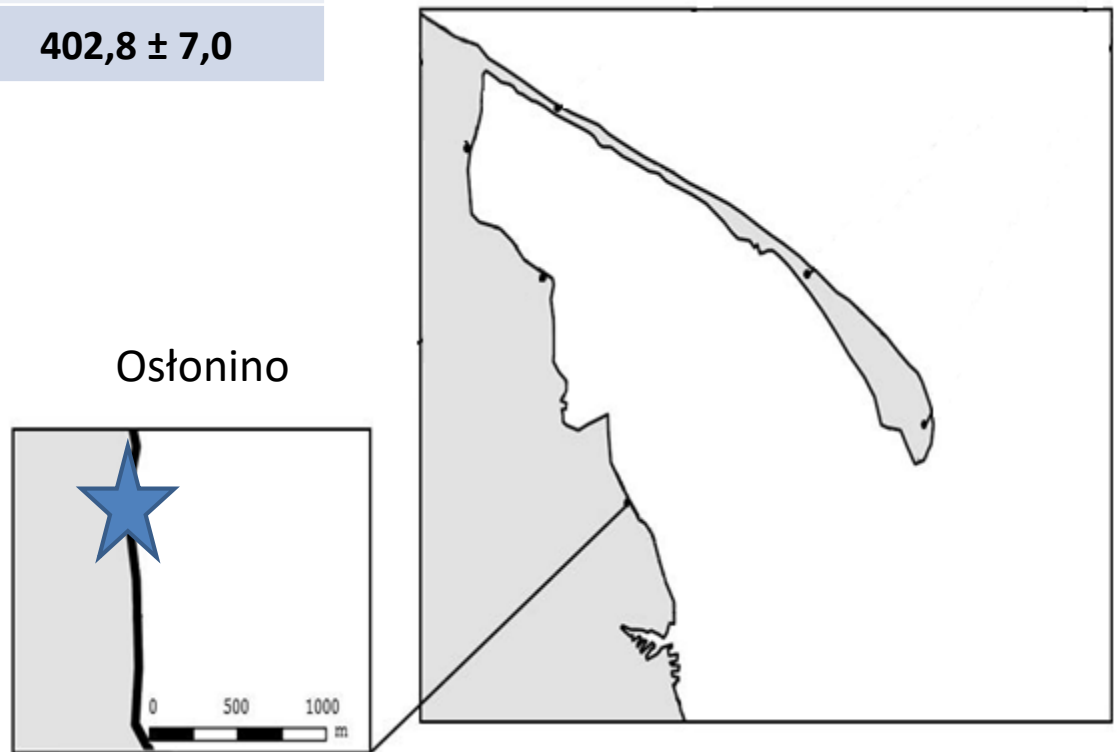
# RESULTS



	min. conc. [ng L <sup>-1</sup> ]	max. conc. [ng L <sup>-1</sup> ]
Caffeine	58,1 ± 4,6	1528,2 ± 57,5
Carbamazepine	3,5 ± 0,1	41,0 ± 2,8
Sulfapyridine	27,5 ± 1,4	186,1 ± 13,2
Diclofenac	13,3 ± 3,3	552,4 ± 31,0

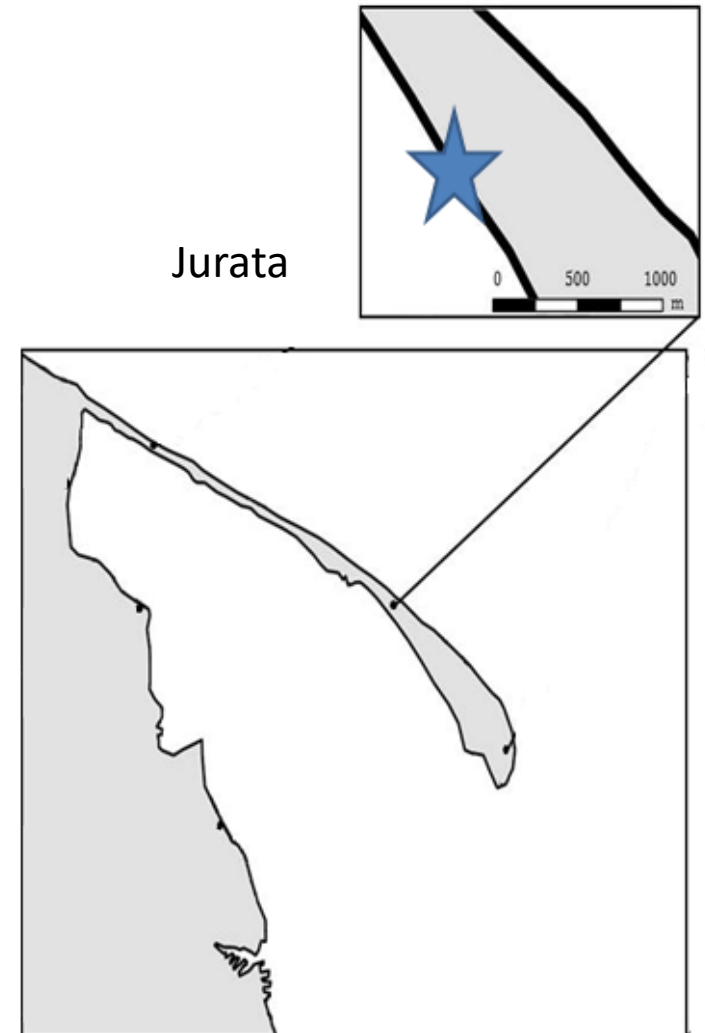
# RESULTS: COAST CAMPAINGS

	Freshwater SGD	Brakish SGD
	Concentration [ng L <sup>-1</sup> ]	
Caffeine	208,9 ± 11,7	1205,6 ± 11,4
Diclofenac	-	402,8 ± 7,0



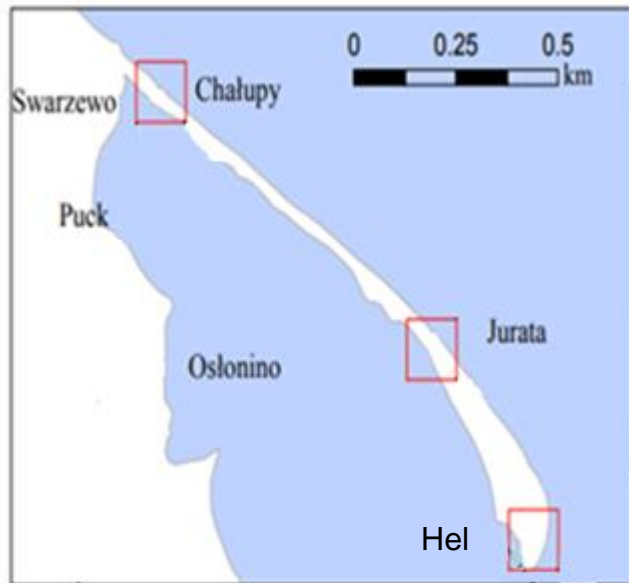
# RESULTS: COAST CAMPAINGS

	Brakish SGD	Seawater SGD
	Concentration [ng L <sup>-1</sup> ]	
Caffeine	1029,8 ± 58,0	-
Sulfapyridine	186,1 ± 13,2	-
Diclofenac	291,3 ± 12,6	369,8 ± 16,5





# RESULTS: PIEZOMETERS



	Caffeine	Sulfapyridine	Diclofenac
	Concentration [ng L <sup>-1</sup> ]		
P 1	58,1 ± 4,6	127,2 ± 3,4	320,3 ± 10,5
P 2	76,2 ± 5,0	-	383,0 ± 21,5
P 3	110,7 ± 9,1	141,9 ± 8,3	552,4 ± 31,0
P 4	-	-	-
P 5	-	-	-
P 7	-	-	-
P 8	114,7 ± 3,6	-	-
P 11	-	-	-
P 12	-	-	-
P 13	-	-	-
P 14	-	-	13,3 ± 3,3

# CONCLUSIONS

- ❑ The analysis of water samples collected from piezometers as well as the coastal groundwaters discharged to the Bay of Puck were performed.
- ❑ The obtained results shown that pharmaceutical residues were present in selected piezometers and in identified discharge point's.
- ❑ Further studies are crucial in order to understand the nature and extent of pharmaceuticals fluxes via groundwater discharge and its effect on the marine environment.
- ❑ This investigation will be continued.

# THANK YOU!

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PharmSeepage 2016/21/B/ST10/01213 sponsored by National Science Center and WaterPUCK financed by the National Centre for Research and Development within BIOSTRATEG program.

