

# The tests on stabilization of the contaminated sediments for sustainable management in the Baltic Sea region

## Testy stabilizacji zanieczyszczonych osadów jako metoda zrównoważonego zarządzania w rejonie Morza Bałtyckiego

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**Abstract:** Sediments in ports usually contain very high concentrations of tributyltin (TBT), heavy metals, polycyclic aromatic hydrocarbons (PAHs) and other contaminants. The stabilization/solidification technology would reduce the environmental impact and it may also prove to be cost-effective and sustainable.

The Port of Gdynia in Poland serves as a case study to present some of the aspects of the dredged sediments stabilization. By using an echo sounder and digital side sonar the hydrographical measurements were made. On the basis of the analysis of seismic-acoustic records were set the sediment sampling points. 58 sediment samples were collected by using vibro corer and laboratorial analysis was performed on concentrations of trace metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chloro-organic pesticides, tributyltin (TBT) and mineral oil index in accordance with accredited methods. Determined concentrations of analysed parameters indicated heavy pollution in basin VI (close to Hungarian quay) in the Port of Gdynia. The determined content of TBT ranged from 0.89 to 4.40 mg Sn kg<sup>-1</sup> d.w.,  $\Sigma_7$ PAHs 0.677-9.0 mg kg<sup>-1</sup>,  $\Sigma_{16}$ PAHs 2.604-14.66 mg kg<sup>-1</sup> and  $\Sigma_7$ PCBs 0.479-3.693 mg kg<sup>-1</sup>. The stated concentration of Pb (299 mg kg<sup>-1</sup>) exceeded the limit value set by Polish law. The content of mineral oil index ranged from 251 to 2904 mg.kg<sup>-1</sup>. Leaching tests were performed for both the stabilized and unstabilized samples. The results of primary laboratory stabilization tests, the leaching tests and uniaxial compressive strength confirmed that the stabilization/solidification technology can be applied to managing of contaminated dredging sediment. The material obtained as a result of the stabilization process can be used for the construction of quays, roads or car parks.

**Keywords:** Contaminated sediments, dredging, stabilization, leaching, Baltic Sea

**Streszczenie:** Osady portowe zazwyczaj zawierają bardzo wysokie stężenia tributylocyny (TBT), metali ciężkich, wielopierścieniowych węglowodorów aromatycznych (WWA) i innych zanieczyszczeń. Technologia stabilizacji zanieczyszczonych osadów może pomóc zredukować negatywny wpływ jaki wywierają one na środowisko.

Badania nad zastosowaniem technologii stabilizacji urobku czerpalnego przeprowadzono w Porcie Gdynia. Punkty poboru próbek osadów dennych zostały wyznaczone na podstawie pomiarów hydrograficznych wykonanych echosondą i sonarem bocznym. Za pomocą vibro sondy zostało pobranych 58 próbek osadów. Przy zastosowaniu akredytowanych metod przeprowadzono badania zawartości metali śladowych, wielopierścieniowych węglowodorów aromatycznych (WWA), polichlorowanych bifenili

(PCB), pestycydów chloroorganicznych, trójbutylocyny (TBT) oraz indeksu oleju mineralnego Uzyskane wyniki wskazały zanieczyszczenie osadów w basenie portowym nr VI przy nabrzeżu Węgarskim. Oznaczona zawartość zanieczyszczeń wahała się od 0,89 do 4,40 mg kg<sup>-1</sup> Sn s.m. dla TBT,  $\Sigma_7$  WWA 0,677–9,0 mg kg<sup>-1</sup> s.m.,  $\Sigma_{16}$  WWA 2,604–14,66 kg<sup>-1</sup> s.m. i  $\Sigma_7$  PCB 0,479–3,693 kg<sup>-1</sup> s.m. Wartość indeksu oleju mineralnego wahała się w zakresie od 251 do 2904 mg. kg<sup>-1</sup> s.m. Natomiast stężenie Pb (299 mg kg<sup>-1</sup> s.m.) przekroczyło wartość graniczną określoną przez polskie prawodawstwo Testy wymywania prowadzono zarówno dla stabilizowanych, jak i dla nie ustabilizowanych próbek. Wstępne wyniki badań laboratoryjnych stabilizacji, testy wymywania i siły ściskania potwierdzają, że technologia stabilizacji może być stosowana do zagospodarowania zanieczyszczonego urobku. Materiał uzyskany w wyniku stabilizacji może być stosowany do budowy nabrzeży, dróg lub parkingów.

**Słowa kluczowe:** Zanieczyszczone osady, pogłębianie, stabilizacja, wymywanie, Morze Bałtyckie

## Introduction

Significant amounts of toxic hydrophobic organic contaminants (HOCs) accumulate on the sea-bed in benthic sediments because these compounds have poor solubility in water and tend to sorb to particles of suspended matter [1]. The Baltic Sea has many hot-spots with highly contaminated sediments in ports, estuaries etc. Human activities often take place in coastal areas and are affected by these hot-spots, e.g. land reclamation for new residential areas and dredging in ports and fairways due to more deep-draught ships [2, 3]. The removed material may be treated and used afterwards, or disposed of under strict environmental controls. Usually the sediments in ports contain very high concentrations of TBT, heavy metals, PAHs and other contaminants originating from anti-fouling paints and various harbour activities [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14]. Organotin compounds decompose rapidly in seawater but tend to adsorb on particles and aggregates in sediments, where degradation processes are considerably slower and may last for years [8, 15]. Sediments act as a sink for hazardous substances as long as they are not disturbed physically (e.g., dredging or hydrographic changes) or by biophysical disturbances (bioturbation by organisms). Disturbance of contaminated sediments may result in the resuspension of hazardous substances and increase their availability to chemical and biological processes [16]. Many historical and present point polluters have been located along rivers in the Baltic Sea catchment area. Depending on the river flow and the geomorphology of the estuary, discharges of hazardous substances may have been retained in the river estuary and estuarine sediments, in particular. Estuarine sediments are frequently disturbed by dredging, such as for harbour maintenance, maintenance of navigation channels and coastal construction works. Other construction activities, such as the construction of pipelines or windmills, may also reactivate the contaminants in the sediments. The major challenge is how to treat very soft and contaminated sediments remaining after dredging from the technical, environmental and economic viewpoint. The management alternatives for dredged material can be grouped into the following five main categories: sustainable relocation, beneficial use, open-water disposal, confined disposal and treatment. Treatment is defined as the processing of contaminated dredged material to reduce its quantity or to reduce the contamination. The treatment methods range from separa-

tion techniques, in which contaminated mud is separated from relatively clean sand, to incineration. Some techniques are well developed but others are still in the early stages of development. The emerging treatment technologies such as the stabilisation/solidification method allow beneficial use of the contaminated sediments as construction material in various applications, for instance new ports storage and transporting areas. The stabilization/solidification method helps to diminish the adverse environmental impact by a reduced need for natural resources. It may also prove to be a cost-effective and sustainable technique.

The aim of this paper is to provide knowledge that might benefit sustainable dredging actions all around the Baltic Sea and to present the results of laboratory tests of stabilization. The tests were performed in the framework of the EU flagship project Sustainable Management of Contaminated Sediments in the Baltic Sea - SMOCS No. 39 (Baltic Sea Region Programme 2007-2013). The concentrations of hazardous substances in sediments from the Port of Gdynia were determined. Also the leaching tests of unstabilized and stabilized sediment samples were performed.

## Materials and Methods

### Study area

The Port Gdynia (Fig. 1) is an international seaport located on the western coast of the Gulf of Gdansk. This port is a non-tidal port protected by a 2.5 km breakwater and has a total of 17.7 km of quays of which over 11 km are for commercial use. The port covers a total of 7.55 km<sup>2</sup> including 4.93 km<sup>2</sup> of land area. The Port of Gdynia can be entered from one of three main routes: from the sea to the east, from Gdansk city to the south and from Puck Bay to the north. The main entrance is 150 metres wide with a depth of 14.0 metres.

### Geophysical profiling

In the selected four basins (Fig. 1) of the Port of Gdynia the hydrographical measurements using multibeam echo sounder SeaBat 8101 (Reson) and Digital side sonar DF1000 (EdgeTech) were performed. In the measurement process



**Fig1.** Port of Gdynia with selected basins

the sonar worked at both frequencies, i.e. 100 and 400 kHz. The signal in both frequencies was store to the purpose to the better possibility of interpretation of obtained images of the bottom. For preparing sonar mosaic of the bottom the computer system of sonar data CODA was used. Registered data about depths of the sea along measuring profiles were reduced to the average level (NN Amsterdam net) including recommendations of tide gauges. Summary error of measurements of the depth with such a system should not exceed 0.2 m.

### Sample collection

The points of collecting sediment samples were set on the basis of the analysis of seismic-acoustic records. The position of the sampling point was established after putting vibro corer on the bottom including the corer resetting with regard to the antenna of the positional system. A total of 58 sediment samples were collected from the four basins: No. III, V, VI, VIII (Fig. 1) in February 2012. The surface sediment samples (0-50 cm) were collected from each core. The sediment samples were stored at -20°C until analysis. The grain size distribution and organic matter content expressed as loss of ignition were performed for each sample.

The thirteen sediment samples collected in basin VI were analysed for the content of contaminants. To stabilization tests were selected six the most contaminated samples taken close to Hungarian quay (former Gdynia Shipyard area) (Fig. 2).

### Analytical techniques

#### Grain size distribution

The particle size distribution of sediment samples was carried out according to ISO/TS 17892-4:2004: *Geotechnical investigation and testing. Laboratory testing of soil. Part 4: Determination of particle size distribution*. The particle size distribution gives a description of sediments, based on a subdivision in discrete classes of particle sizes. The size of each class was determined by sieving and sedimentation.

### Physical parameters

#### Water content

The water content (w) measurement was carried out according to ISO/TS 17892-1:2004: *Geotechnical investigation and testing. Laboratory testing of soil. Part 1: Determination of water content*. The water

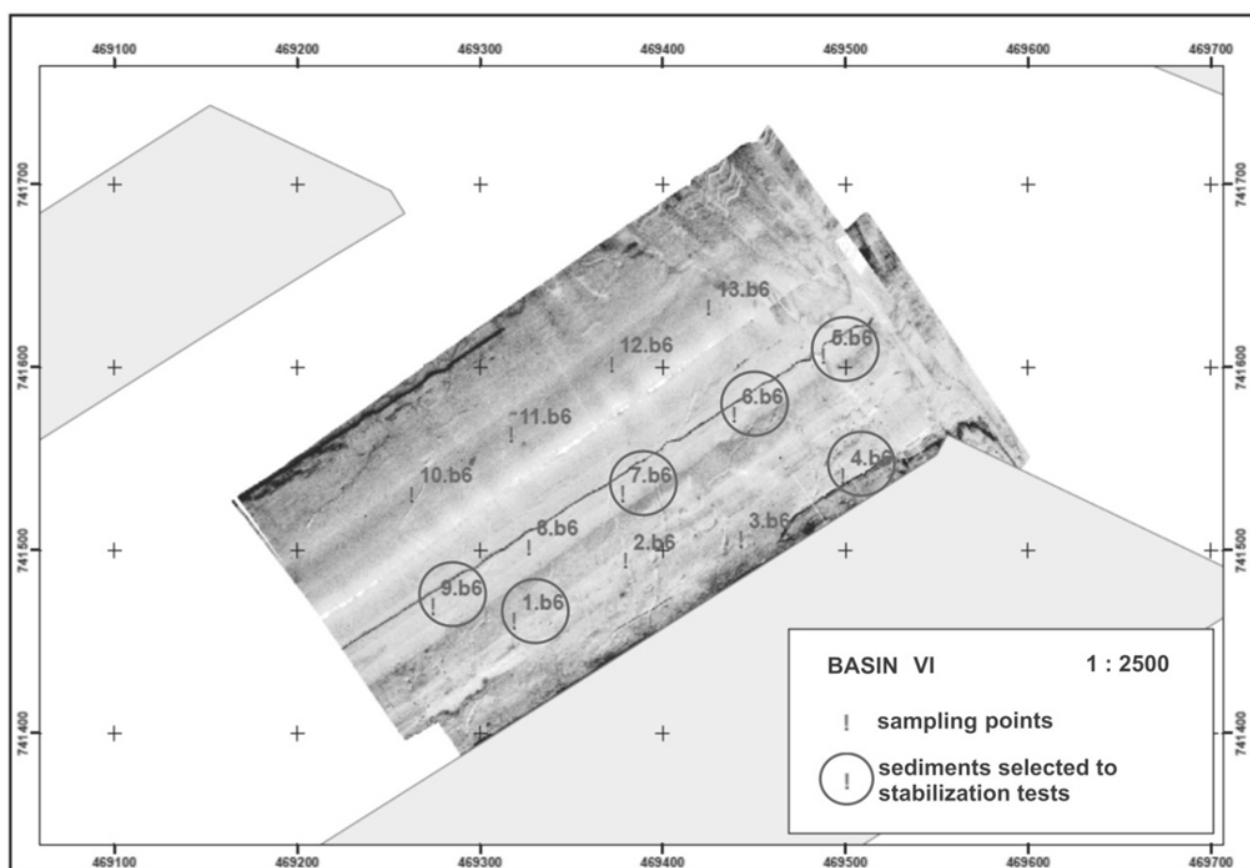


Fig 2. Location of sampling points in basin VI

content of sediment was determined by measuring the loss of mass in wet sediment during a 24-h drying procedure at constant temperature  $105^{\circ}\text{C} \pm 5^{\circ}\text{C}$  after reaching constant mass weight.

### Loss of ignition

The loss of ignition (LoI) was performed according to SFS-EN 1997-2. Eurocode 7: Geotechnical design. Part 2: Ground investigation and testing. Loss of ignition describes the content of the organic matter in the sample. LoI was determined by igniting the dry sediment sample in a muffle furnace at  $550^{\circ}\text{C}$  until reaching constant mass weight for 4 h [17].

### Density

Determination of density ( $\rho$ ) of the soil sample was carried out according to a modified method of CEN ISO/TS 17892-2. Geotechnical investigation and testing. Laboratory testing of soil. Part 2: Determination of density of fine grained soil. Density was calculated as the ratio of wet sediment sample mass to its volume.

### Chemical composition

#### Trace metals

The  $<2$  mm sediment fraction of 13 samples was dried, ground in an agate mill and analysed for trace (V, Cd, Cr, Ni, Cu, Co,

Zn, As, Pb, Hg) elements. Mercury was determined after the thermal decomposition. After that, the atomic absorption on the spectrometer MA-2, Nippon Corporation Instrument was used. Mineralization with the nitrohydrochloric acid (aqua regia) was used for analysis of other trace metals. Final analysis were performed by atomic emission spectrometry with excitation in inductively coupled plasma (ICP-OES) on the spectrometer Optima 2000 DV, PERKIN – Elmer.

#### Mineral oil index

The extraction of sediment samples was determined according to the norm PN-EN 14345:2008: Characterization of waste. Determination of hydrocarbon content by the gravimetric method. The final investigations of mineral oil index were performed using gas chromatograph Agilent Technologies 6890N with flame ionisation detector (GC/FID) according to the norm PN-EN 14039:2008: Characterization of waste - Determination of hydrocarbon content in the range from  $\text{C}_{10}$  to  $\text{C}_{40}$  by gas chromatography.

#### Polycyclic aromatic hydrocarbons (PAHs)

Sixteen PAHs (Naphthalene, Acenaphtylene, Acenaphtene, Fluorene, Phenantrene, Anthracene, Fluorantene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluorantene, Benzo(k)fluorantene, Benzo(a)pyrene, Dibenz(ah)anthracene, Benso(ghi)perylene, Indeno(123cd)pyrene) were analysed. The sediment



samples were extracted with dichloromethane in an ultrasonic bath (1 h extraction at 30-35°C). The obtained extracts were purified in columns packed with silica gel using SPE (Solid Phase Extraction) [18, 19]. Than extracts concentrated to the volume of 1 cm<sup>3</sup> under nitrogen gas stream were finally analysed on gas chromatograph **Hewlett Packard HP 6890 with mass spectrometry HP 5973**.

### Polychlorinated biphenyls (PCBs)

The isolation of PCB congeners (IUPAC No 28, 52, 101, 118, 138, 153, 180) was performed by extraction with n-hexane/acetone mixture (2:1 vol) in a shaker (24h extraction at 21°C). The obtained extracts were purified in columns packed with silica gel using SPE and eluted from columns with dichloromethane [20; 21]. The extracts concentrated to the volume of 1 cm<sup>3</sup> under nitrogen gas stream were finally analysed on gas chromatograph **Hewlett Packard HP 6890 with mass spectrometry HP 5973**.

### Chloroorganic pesticides

Chloroorganic pesticides ( $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, HCB, heptachlor, aldrin, dieldrin, endrin, p,p'-DDE, p,p'-DDD, p,p'-DDT, metoxychlor) were analysed in sediment samples according to Sapota [22, 23] and PN-ISO 10382:2007: *Soil quality - Determination of organochlorine pesticides and polychlorinated biphenyls - Gas chromatographic method with electron capture detection*. The final analysis was performed using gas chromatograph **Agilent Technologies 6890N** with electron capture detector (GC/ECD).

### Tributyltin (TBT)

TBT was analysed in sediment samples according to EN-ISO 23161:2009: *Soil quality - Determination of selected organotin compounds - Gas-chromatographic method*. The isolation of TBT was performed by extraction with n-hexane and derivatization. The obtained extracts were purified in silica columns. The final analysis was performed using the high-efficient liquid chromatography in the arrangement of phases turned away (RP-HPLC) in combination with tandem mass spectrometry (MS/MS).

Methods and determination limits of the performed analysis are certified by the Polish Centre of Accreditation No. AB 646 and listed in table 1.

### Stabilization test

The laboratory tests of sediments stabilization were conducted in March 2012 by an accredited laboratory of the Department of Environmental Protection Maritime Institute in Gdansk. To stabilization tests were selected six the most contaminated samples taken close to Hungarian quay (former Gdynia Shipyard area). For stabilization the aggregated sediment sample combined and averaged in equal proportions from sediments col-

Tab. I. Low determination limits of analysed parameters

	UNIT	SEDIMENT	LEACHING TEST
V	mg kg <sup>-1</sup>	0.25	
Cd	mg kg <sup>-1</sup>	0.05	0.005
Cr	mg kg <sup>-1</sup>	0.25	0.05
Ni	mg kg <sup>-1</sup>	0.25	0.05
Cu	mg kg <sup>-1</sup>	0.25	0.06
Co	mg kg <sup>-1</sup>	0.25	-
Zn	mg kg <sup>-1</sup>	0.25	0.22
As	mg kg <sup>-1</sup>	1.25	0.005
Pb	mg kg <sup>-1</sup>	0.25	0.05
Hg	mg kg <sup>-1</sup>	0.01	0.005
Ba	mg kg <sup>-1</sup>	-	0.01
Mo	mg kg <sup>-1</sup>	-	0.08
Sb	mg kg <sup>-1</sup>	-	0.005
Se	mg kg <sup>-1</sup>	-	0.01
Mineral oil index	mg kg <sup>-1</sup>	27	0.01
PAHs	mg kg <sup>-1</sup>	0.001	0.001
PCBs	mg kg <sup>-1</sup>	0.0001	0.0001
Chloroorganic pesticides	mg kg <sup>-1</sup>	0.001	-
TBT	mg kg <sup>-1</sup>	0.01	-
Fluorides	mg kg <sup>-1</sup>	-	1.0
Chlorides	mg kg <sup>-1</sup>	-	50
Sulphates	mg kg <sup>-1</sup>	-	50
TDS	mg kg <sup>-1</sup>	-	100
W	%	0.1	-
Lol	%	0.1	-

PAHs – Polycyclic Aromatic Hydrocarbons

PCBs – Polychlorinated biphenyls

TBT – Tributyltin

TDS - Total dissolved solids

W – humidity

Lol – loss of ignition

lected from the following points: 1.b6, 4.b6, 5.b6, 6.b6, 7.b6, 9.b6 (Fig. 2) were used. Before stabilisation process a geochemical composition of each used binders was performed. Geochemical composition of exemplary used binders is shown in Table 2.

Preliminary stabilisation tests of sediments from the Port of Gdynia were performed according to a procedure used in the Swedish Geological Institute (SGI) in Linköping. Acrylic tubes (internal diameter 36 mm, high 125 mm) were used for tests. The stabilization was performed as following:

- ♦ Homogenisation of sediment sample and mixing with binders
- ♦ Filling the cylinders (4 parallel samples for each recipe)
- ♦ Packing the tubes into plastic bags (protection from drying out)
- ♦ Storage the samples at temperature +7°C in refrigerator (7 and 28 days).

**Tab. II.** Geochemical composition of exemplary used binders (calculation on dry weight)

PARAMETERS / BINDER CODE		LT_ga	M_s	C_PI	LIMIT VALUE*
w	%	0.036	4.07	0.14	nl
Q	kg m <sup>-3</sup>	960	1334	1083	nl
LoI	%	3.1	0.31	1.18	nl
Cd	mg kg <sup>-1</sup>	0.32	p.0.05	0.61	≥7.5
Cr	mg kg <sup>-1</sup>	22.4	1.1	30.8	≥200
Co	mg kg <sup>-1</sup>	8.23	0.45	3.79	nl
Pb	mg kg <sup>-1</sup>	24.5	1.26	19.4	≥200
Cu	mg kg <sup>-1</sup>	65.6	1.31	60.1	≥150
Hg	mg kg <sup>-1</sup>	0.02	0.07	0.03	≥1
Ni	mg kg <sup>-1</sup>	16.6	1.01	12.5	≥75
Zn	mg kg <sup>-1</sup>	43.4	4.52	111	≥1000
As	mg kg <sup>-1</sup>	9.4	p.1.25	3.97	≥30
V	mg kg <sup>-1</sup>	63.1	1.08	35.3	nl
Mineral oil index	mg kg <sup>-1</sup>	p.0.01	p.0.01	p.0.01	nl
Σ <sub>16</sub> PAHs	mg kg <sup>-1</sup>	0.004	0.011	0.001	
Σ <sub>7</sub> PAHs	mg kg <sup>-1</sup>	0.008	0.012	0.010	≥8.5
PCB 28	mg kg <sup>-1</sup>	0.0006	0.0002	p.0.0001	
PCB 52	mg kg <sup>-1</sup>	p.0.0001	0.0001	0.0002	
PCB 101	mg kg <sup>-1</sup>	0.0023	0.0027	0.0013	
PCB 118	mg kg <sup>-1</sup>	0.0001	0.0002	p.0.0001	
PCB 138	mg kg <sup>-1</sup>	p.0.0001	0.0004	p.0.0001	
PCB 153	mg kg <sup>-1</sup>	0.0001	p.0.0001	p.0.0001	
PCB 180	mg kg <sup>-1</sup>	0.0001	0.0004	0.0004	
Σ <sub>7</sub> PCBs	mg kg <sup>-1</sup>	0.0032	0.0040	0.0019	≥0.3

LT\_ga – fly ash from Gdynia (Poland)

M\_s – middle sand

C\_PI – Portland cement without fly ash, class 32,5 (Poland)

p. – below determination limit

nl – no limit value

\* Regulation of the Polish Minister of Environment (11 May 2015) on the the recovery of waste outside installations and equipment

The following Finnish and Polish binders were used for the tests:

- ♦ C\_F – gypsum (Finland)
- ♦ C\_PL – gypsum (Poland)
- ♦ Z – slag (Finland)
- ♦ LT\_gd – fly ash from Gdansk (Poland)
- ♦ LT\_ga – fly ash from Gdynia (Poland)
- ♦ C\_F – Portland cement with fly ash, class 32,5 (Finland)
- ♦ C\_PI – Portland cement without fly ash, class 32,5 (Poland)
- ♦ S – sediment
- ♦ M\_s – middle sand

The used recipes (proportions of binders and sediment sample) are shown in table 3.

Four parallel samples for each recipe have been prepared. Two samples of each recipe were analysed on leaching of contami-

nants after 7 days of stabilization. The remaining two samples were investigated after 28 days of stabilization. The results of leaching test after first and second step of stabilization were compared with the limit values of the primary test in accordance with Annex No. 4 to the Decree of the Polish Minister of Economy and Labour of 8 January 2013 *on criteria and procedures for the release of waste for disposal at the landfill of different waste type* (Journal 2013 No. 0, item 38).

### Characterisation of used recipes

Binders will usually be selected according to some mix design criteria which depend on the application. The application could be e.g. ordinary infrastructure construction on weak ground, development of contaminated site, reuse of waste as aggregate in the construction, or landfilling. Also using binders available on the local market can reduce costs of investment.

### Leaching test

Leaching tests in unstabilized and stabilized sediment samples were performed according to PN-EN 12457-2:2006: *Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sediments - Part 2: Single-stage study at a ratio of liquid to solid 10 dm<sup>3</sup> per kg for materials with particle size below 4 mm (without reduction or with reduction in size)* and PN-EN ISO 5667-3:2005: *Water quality - Sampling - Part 3: Guidance on preservation and handling of water samples*. In water extract trace metals, PAHs, PCBs, mineral oil index, chlorides, fluorides, sulphates and total dissolved solids (TDS) were analysed.

### Trace metals

Bar, cadmium, chromium, copper, molybdenum, nickel, zinc, lead were analysed according PN-EN ISO 11885:2009: *Water quality - Determination of selected elements by optical emission spectrometry with inductively coupled plasma (ICP-OES)* using the spectrometer Optima 2000 DV, PERKIN – Elmer.

Arsenic was indicated according to PN-EN ISO 11885:2009: *Water quality - Determination of arsenic - atomic absorption spectrometric method (hydride technique)*. Selenium was analyzed according PN-EN ISO 9965:2001: *Water quality - Determination of selenium - atomic absorption spectrometric method (hydride technique)*. Final analysis of Sb and Se were performed by atomic absorption on the spectrometer SpektrAA-250 Varian with VGA-77 (HGAAS).

Mercury was analysed by atomic absorption on the spectrometer MA-2, Nippon Corporation Instrument.

### Mineral oil index

Mineral oil index was analysed according to PN-EN ISO 9377-2:2003: *Water quality - Determination of mineral oil index - Part 2: Method using solvent extraction and gas chromatography* and finally on gas chromatograph **Agilent Technologies 6890N** with flame ionisation detector (GC/FID).

### PAHs and PCBs

PAHs and PCBs analysis were performed by SPE extraction with hexane/acetone mixture and finally investigated on gas chromatograph **Hewlett Packard HP 6890 with mass spectrometry HP 5973**.

### Chemical parameters

**Chlorides were analysed according to** PN-ISO 9297:1994: *Water quality. Determination of chlorides. Titration method with silver nitrate in the presence of chromate as indicator (Mohr method)*. **Fluorides were analysed according to** PN-78/C-04588.03: *Water and sewage - Research the content of fluorine compounds - Determination of fluoride by potentiometric method using ion-selective electrode*. Sulphates were analysed by turbidimetric method and TDS by weighting method.

Tab. III. Characterisation of used recipes

SAMPLE CODE	RECIPE (BINDERS)	PROPORTION [%]
2	S + C_F + Z	80 + 10 + 10
3	S + C_F + Z + LT_gd + G_F	80 + 5 + 5 + 5 + 5
4	S + C_F + Z + LT_ga	80 + 5 + 5 + 10
5	S + C_F + Z + LT_ga + G_PL	80 + 5 + 5 + 5 + 5
6	S + LT_ga + C_PL	77 + 20 + 3
7	S + M_s + LT_ga + C_PL	30 + 47 + 20 + 3
8	S + M_s + LT_ga + C_PL	30 + 48.5 + 20 + 1.5
9	S + M_s + LT_ga + C_PL	40 + 45 + 10 + 5

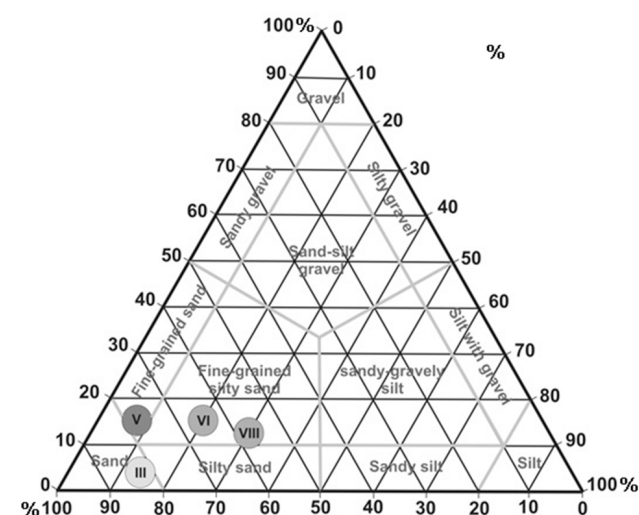


Fig.3. Type of sediments in the Port of Gdynia (basins: III, V, VI and VIII)

dimetric method and TDS by weighting method. Dissolved organic carbon (DOC) was analyzed by catalytic burning of organic matter to the carbon dioxide in temperature 900°C and determination of the carbon dioxide content was performed with IR method.

### Uniaxial compressive strength

Compression strength was measured as the maximum load that can be applied to stabilized material under specified conditions before it is crushed.

### Results and discussion

#### Grain-size distribution

The grain-size distribution of the surface sediments (0-50 cm) by percentage in the investigated basins of the Port of Gdynia is shown in Fig. 3. The sediments ranging from sand to fine grained silty sand. In general, the sediments display a good correlation with the organic matter content expressed as Lol (Fig. 4).

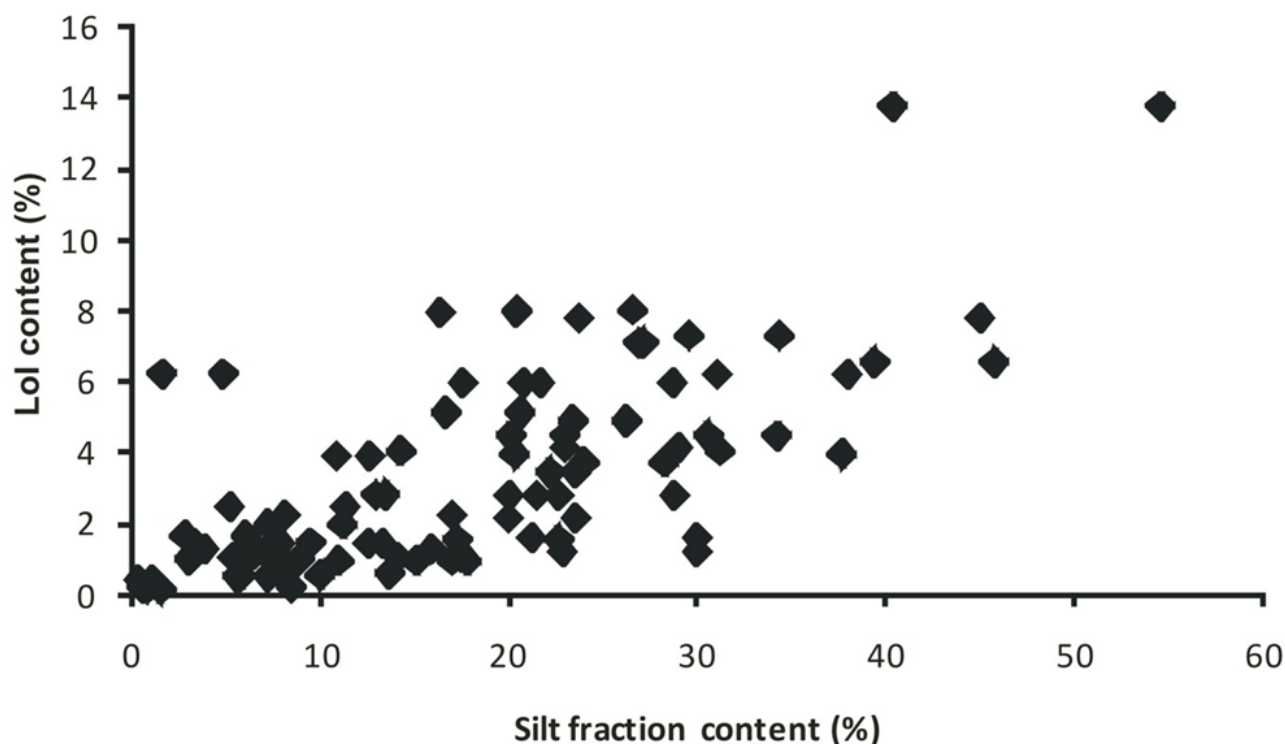


Fig. 4. Relationship between the sediment organic matter content (Lol) and silt fraction (<0.63 mm) content

### Content of contaminants

Following a screening test for contaminants in bottom sediments in selected basins in the Port of Gdynia was found that by far the highest concentrations of pollutants are in sediments from basin VI. This is a result of proximity to the Gdynia shipyard repair. Therefore, for further detailed studies and stabilization tests thirteen sediment samples from basin VI were collected. Concentrations of those compounds in basins III, V and VIII were much lower. The content of trace metals, mineral oil index and organic pollutants is shown in table 4.

In the analyzed samples high concentrations of TBT were found. The determined content of TBT in sediments from the Port of Gdynia ranged from 0.89 to 4.40 mg Sn kg<sup>-1</sup> d.w. and it is similar to or higher than those presented by Filipkowska et al. [24] for the Port of Gdynia (basin III – 0.037 mg Sn kg<sup>-1</sup> d.w., basin IX (Naval Shipyard) – 1.61 mg Sn kg<sup>-1</sup> d.w., Gdynia Shipyard – 1.91 mg Sn kg<sup>-1</sup> d.w.), by Falandysz et al [7] (Ship RepairYard ‘Nauta’—total BTs: 0.64 mg Sn kg<sup>-1</sup> d.w., Gdynia Shipyard—total BTs: 0.34 mg Sn kg<sup>-1</sup> d.w.) and by Szpunar et al. (1997) for the Port of Gdynia (total BTs 1.30–5.52 mg Sn kg<sup>-1</sup> d.w.). The results are also similar or lower than those reported by Filipkowska et al. [24] for the Port of Gdansk (Gdansk Shipyard – 4.34 mg Sn kg<sup>-1</sup> d.w., Ship Repair Yard ‘Remontowa’ – 15.78 mg Sn kg<sup>-1</sup> d.w., ‘Górnicy’ basin – 0.38 mg Sn kg<sup>-1</sup> d.w. and North Port – 0.013 mg Sn kg<sup>-1</sup> d.w.), by Senthilkumar et al. [11] (total BTs 2.90–69.10 mg Sn kg<sup>-1</sup> d.w.), by Falandysz et al. [7] (total BTs 0.17–30.0 mg Sn kg<sup>-1</sup> d.w.) and Radke et al. [9] (total BTs 0.16–9.34 mg Sn kg<sup>-1</sup> d.w.). Other authors reported concentration of TBT in Baltic and North Sea

sediments 0.033–6.97 mg Sn kg<sup>-1</sup> d.w. [4] and in sediments from Stockholm harbour 0.027–0.53 mg Sn kg<sup>-1</sup> d.w. [5]. In the 1980s and the 1990s, many countries included in their legislation a number of restrictions on the use of tributyltin-based antifouling paints. However, the evolution of TBT bans is rather complex, and multiple levels and areas of legislation (international and national) still present problems [25, 26, 27, and 28].

The concentrations of PAHs and PCBs determined in sediment samples from the basin VI of the Port of Gdynia ranged respectively:  $\Sigma_7$ PAHs 0.677–9.0 mg kg<sup>-1</sup>,  $\Sigma_{16}$ PAHs 2.604–14.66 mg kg<sup>-1</sup> and  $\Sigma_7$ PCBs 0.479–3.693 mg kg<sup>-1</sup> (Table 4). The similar to or lower contents of PAHs and PCBs in sediments were reported by Staniszevska et al. [13] from the Port of Gdansk ( $\Sigma_7$ PAHs 2.2 mg kg<sup>-1</sup> and  $\Sigma_7$ PCBs 0.011 mg kg<sup>-1</sup>), by Baumard et al [29] from Port of Kiel ( $\Sigma_{18}$ PAHs 0.47–30.1 mg kg<sup>-1</sup>) and Port of Warnemünde ( $\Sigma_{18}$ PAHs 0.005–0.25 mgkg<sup>-1</sup> and by Leipe et al. [30] for dumping site on Mecklenburg Bay ( $\Sigma_{18}$ PAHs 2 mg kg<sup>-1</sup>). In comparison maximum concentration determined in sediments from fjords (North Spitsbergen) of  $\Sigma_{16}$ PAHs and  $\Sigma_7$ PCBs were respectively 0.036 mg kg<sup>-1</sup> and 0.004 mg kg<sup>-1</sup> [31].

Heavy metals are elements that occur naturally in the environment. However, the high concentration of heavy metals in sediments clearly indicated an anthropogenic impact. The contents of trace metals determined in analysed sediments (Table 4) were: Cr 7.84–41.8 mg kg<sup>-1</sup>, Ni 5.33–9.78 mg kg<sup>-1</sup>, Cu 38.5–135 mg kg<sup>-1</sup>, Pb 61.6–299 mg kg<sup>-1</sup>, Zn 183–451 mg kg<sup>-1</sup>, Cd 0.76–1.8 mg kg<sup>-1</sup>, As 2.60–4.01 mg kg<sup>-1</sup>, Hg 0.11–0.48 mg kg<sup>-1</sup>. The concentration of Pb exceeded the limit value set by the Polish law. Leipe et al. [30] reported for



Tab. IV. Geochemical composition of surface sediments from the basin VI of the Port of Gdynia (calculation on dry weight of sediment)

PARAMETERS/ SAMPLE CODE		1.B6	2.B6	3.B6	4.B6	5.B6	6.B6	7.B6	8.B6	9.B6	10.B6	11.B6	12.B6	13.B6	AGGREGATE SAMPLE <sup>a</sup>	LIMIT VALUE <sup>a,b</sup>
w	%	44.10	53.00	40.20	45.30	37.30	32.80	50.20	39.00	45.50	51.10	40.20	43.50	45.60	41.70	nl
Q	kg m <sup>-3</sup>	1600	1460	1630	1430	1400	1580	1410	1480	1670	1450	1590	1520	1490	1520	nl
Lol	%	6.18	13.71	7.24	7.74	4.51	4.16	7.91	7.97	5.93	5.92	4.12	4.46	7.07	6.18	nl
Cd	mg kg <sup>-1</sup>	1.30	1.65	1.63	1.51	0.76	0.83	1.80	1.04	1.73	1.54	1.51	1.43	1.75	1.43	≥7.5
Cr	mg kg <sup>-1</sup>	41.8	15.3	23.0	22.2	10.3	7.84	18.2	9.52	18.6	20.3	13.9	14.0	15.9	20.2	≥200
Co	mg kg <sup>-1</sup>	6.59	4.45	1.72	3.64	2.81	2.32	3.84	3.07	3.81	5.06	4.02	3.58	3.74	3.97	nl
Pb	mg kg <sup>-1</sup>	173.0	171.0	<b>299.0</b>	<b>219.6</b>	61.6	82.4	133.1	109	119.1	109.0	106.8	94.5	81.3	133	≥200
Cu	mg kg <sup>-1</sup>	135.0	114.0	115.0	84.3	58.2	38.5	83.2	57.6	99.6	130.0	88.0	72.7	79.5	87.2	≥150
Hg	mg kg <sup>-1</sup>	0.36	0.19	0.25	0.14	0.38	0.40	0.31	0.48	0.13	0.11	0.43	0.43	0.17	0.24	≥1
Ni	mg kg <sup>-1</sup>	8.88	9.52	9.78	8.85	6.43	5.33	8.80	6.67	7.76	9.72	7.26	7.96	8.40	7.18	≥75
Zn	mg kg <sup>-1</sup>	451	443	562	419	206	183	361	235	346	346	313	284	309	325	≥1000
As	mg kg <sup>-1</sup>	2.60	3.41	4.01	3.57	2.84	2.61	3.49	2.85	2.83	3.16	3.68	3.70	3.71	2.69	≥30
V	mg kg <sup>-1</sup>	21.1	15.6	14.9	12.6	11.4	7.86	14.0	11.4	14.1	17.6	14.1	13.2	12.9	13.1	nl
Mineral oil index	mg kg <sup>-1</sup>	603	2 904	626	636	368	857	419	707	529	304	354	251	410	532	nl
Σ <sub>16</sub> PAHs	mg kg <sup>-1</sup>	6.318	13.772	14.391	12.609	2.604	8.175	5.594	14.666	5.238	4.740	7.667	5.456	3.223	5.128	
Σ <sub>7</sub> PAHs	mg kg <sup>-1</sup>	2.054	9.000	7.549	6.591	1.349	3.854	1.951	7.399	1.730	1.685	1.675	0.677	1.241	2.126	≥8.5
Σ <sub>7</sub> PCBs	mg kg <sup>-1</sup>	<b>1.950</b>	<b>2.740</b>	<b>3.693</b>	<b>2.418</b>	<b>1.048</b>	<b>1.839</b>	<b>1.741</b>	<b>2.012</b>	<b>1.192</b>	<b>0.479</b>	<b>1.286</b>	<b>1.692</b>	<b>0.991</b>	<b>1.611</b>	≥0.3
α-HCH	mg kg <sup>-1</sup>	0.001	0.002	0.002	0.012	0.001	p.0.001	p.0.001	0.001	0.006	p.0.001	0.001	0.003	0.001	0.001	nl
β-HCH	mg kg <sup>-1</sup>	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	nl
γ-HCH	mg kg <sup>-1</sup>	0.114	0.110	0.133	0.191	0.011	0.019	0.004	0.011	0.125	0.100	0.010	0.113	0.053	0.096	nl
δ-HCH	mg kg <sup>-1</sup>	0.004	0.002	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	nl
HCB	mg kg <sup>-1</sup>	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	0.001	p.0.001	nl
heptachlor	mg kgv	0.001	0.002	0.001	p.0.001	0.001	0.002	0.002	0.014	0.042	p.0.001	0.002	0.070	0.015	0.002	nl
Aldrin	mg kg <sup>-1</sup>	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	nl
Dieldrin	mg kg <sup>-1</sup>	p.0.001	0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	nl
Endrin	mg kg <sup>-1</sup>	p.0.001	0.001	p.0.001	0.001	p.0.001	p.0.001	p.0.001	0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	nl
p,p'-DDE	mg kg <sup>-1</sup>	0.001	p.0.001	0.001	0.001	p.0.001	0.001	0.001	0.001	0.001	p.0.001	0.001	0.001	0.001	0.001	nl
p,p'-DDD	mg kg <sup>-1</sup>	0.004	0.004	0.008	0.005	0.006	0.005	0.007	0.007	0.007	0.003	0.005	0.005	0.007	0.005	nl
p,p'-DDT	mg kg <sup>-1</sup>	0.001	0.001	0.001	0.002	0.001	0.002	0.001	0.003	0.001	0.001	0.001	0.002	0.001	0.001	nl
metoxychlor	mg kg <sup>-1</sup>	p.0.001	0.001	p.0.001	0.001	p.0.001	0.002	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	p.0.001	nl
TBT	mg kg <sup>-1</sup>	2.10	4.40	2.24	3.27	2.43	0.89	4.12	1.07	3.40	3.80	2.48	1.35	2.50	2.63	nl

p. – below determination limit

nl – no limit value

<sup>a</sup> aggregate sample - sediment combined and averaged in equal proportions from samples: 1.b6, 4.b6, 5.b6, 6.b6, 7.b6, 9.b6

<sup>b</sup> Regulation of the Polish Minister of Environment (11 May 2015) *on the recovery of waste outside installations and equipment*

Σ<sub>7</sub> PAHs: Benzo(a)anthracene, Benzo(b)fluorantene, Benzo(k)fluorantene, Benzo(a)pyrene, Dibenz(ah)anthracene, Benzo(ghi)perylene, Indeno(123cd)pyrene

Σ<sub>16</sub> PAHs: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluorantene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluorantene, Benzo(k)fluorantene, Benzo(a)pyrene, Dibenz(ah)anthracene, Benzo(ghi)perylene, Indeno(123cd)pyrene

dumping site on Mecklenburg Bay concentrations of heavy metals as follows: Cr 75 mg kg<sup>-1</sup>, Ni 38 mg kg<sup>-1</sup>, Cu 88 mg kg<sup>-1</sup>, Pb 450 mg kg<sup>-1</sup>, Zn 900 mg kg<sup>-1</sup>, Cd 1.87 mg kg<sup>-1</sup>, As 48 mg kg<sup>-1</sup>, Hg 0.95 mg kg<sup>-1</sup>. The comparable contents of trace metals were obtained in sediments from Klaipeda Port: Cr 27-160 mg kg<sup>-1</sup>, Ni 0.2-64 mg kg<sup>-1</sup>, Cu 9.1-128.4 mg kg<sup>-1</sup>, Pb 0.06-512 mg kg<sup>-1</sup>, Zn 2-1001 mg kg<sup>-1</sup>, Cd 0.04-1.5 mg kg<sup>-1</sup>, Hg 0.04-0.26 mg kg<sup>-1</sup> [32]. Ussenkov [33] reported concentrations of trace metals in sediments from Russian ports: St. Petersburg, Lomonosov and Kronshtadt. The highest concentrations of metals were observed in sediments from Kronshtadt Port: mean concentration of Cu 212 mg kg<sup>-1</sup> and Hg 2.1 mg kg<sup>-1</sup>. In sediments from Lomonosov Port stated content of Pb was 148 mg kg<sup>-1</sup> and Cu 92 mg kg<sup>-1</sup> and in St. Petersburg Port determined concentration of Cu was 76 mg kg<sup>-1</sup>.

Oil pollution is very dangerous for the environment and can destroy habitats of many plants and animals, including the spawning areas of fish [34, 35]. The main sources of oil pollutions into the environment are riverine outflow and shipping accidents, illegal oil discharges, atmospheric deposition, damages of oil's pipelines and also ports activity. The content of mineral oil index stated in analysed sediments from the Port of Gdynia ranged from 251 to 2904 mg kg<sup>-1</sup>. The lower content of oil hydrocarbons were determined in Klaipeda Port where concentrations varied from 8.33 to 216.6 mg kg<sup>-1</sup>, absolute maximum of oil hydrocarbons concentration was 545.2 mg kg<sup>-1</sup> [32].

Generally, the integrated chemical status (according to HELCOM classification) of coastal Baltic areas varied from high to bad without particular consistency. The coastal areas that received the highest status classifications were located in the Åland Islands area, in the Kaliningrad coastal area, on the Lithuanian coast, in the Kattegat and on the Finnish side of the Gulf of Bothnia. There was some tendency for the areas with the poorest status to be located either near big cities or ports (Tallinn, Klaipeda) or to be estuarine areas (Ruotsinpyhtää in the Gulf of Finland, Kvädöfjärden in the Western Gotland Basin) or coastal sites (the Kiel Bay area). The areas near large coastal cities were generally classified as having a 'moderate' hazardous substances status (e.g., St. Petersburg, Helsinki, Stockholm, Riga, Gdansk and Copenhagen) [2, 3].

### Leaching tests

The results of leaching test after first and second step of stabilization are shown in table 5. The contaminated sediments (and other types of waste materials) establish another heterogeneous group of materials which could be used for the infrastructure construction in case the contaminants can be immobilised or solidified within the material. This is possible in many cases by using cement or composites of cement and other stabilisers. Stabilisation and solidification treatments include a wide range of processes that usually involve mixing inorganic binders (like different types of cement) into the soil or waste to transform it into a new, solid and non-leachable material. In case of waste or contaminated soil, the treated product encapsulates potentially hazardous contaminants, reducing contact between the waste/

contaminated soil and any potential leachant (like rain water). In addition to this, various interaction and chemical effects may occur that lock contaminants into the product, further reducing the potential for pollutant transfer into the environment [36]. In impact assessments in relation to utilisation of contaminated soils and waste materials, human health effects, groundwater and surface water impacts are of primary concern. Conventionally, decisions have been based upon measurements of the total content of contaminants in soils which may be combined with analysis of groundwater or surface water. However, it is well known that for both inorganic and organic compounds only part of the total content of contaminants is available for leaching and subsequent transport to groundwater or surface water [37].

Several leaching methods for organic compounds have been published for testing the leaching of organic compounds from soil [38, 39, 40, and 41]. The studies have especially focussed on parameters and testing conditions influencing the leaching of polycyclic aromatic hydrocarbons from soils. However, also PCBs, petroleum hydrocarbons and chlorophenols have been target parameters for evaluating leaching tests.

In principle, the management strategies for excavated soil and waste material are almost identical. However, for these materials the characterization of leaching properties does not necessarily include identical leaching tests or intensity of testing. Waste materials often occurs as a specific waste stream where only minor changes in leaching properties takes place over time. These streams can be characterized once and for all (basic characterization). Once it has been subjected to basic characterization, a waste stream only needs to demonstrate consistency with the expected properties at regular intervals, using relatively simple test methods [37].

The major differences between leaching tests for organic compounds and leaching tests for inorganic components are related to their very different properties. Leaching tests for organic compounds must be designed to meet the specific requirements associated with these compounds. In contaminated soils the organic compounds may with time become embedded in the soil structure which significantly changes the leaching properties. For waste materials, leaching tests for inorganic compounds have traditionally been divided into the categories 'compliance test' and 'basic characterisation test' (according to the test hierarchy defined by CEN/TC 292 *Characterisation of Waste*). However, for contaminated soil the usefulness of this distinction may not be as obvious as for waste. The choice of leaching tests applicable for a specific application. The appropriate tests to assess release under the specified conditions should be selected and performed. However, one leaching test alone does not cover all aspect of leaching, and a combination of two or more leaching methods will provide a more complete picture of the leaching properties of both waste materials and contaminated soils.

Generally, the extent of the leaching programme will depend not only on the specific scenario but also parameters like the quantity of contaminated material, the available budget and

**Tab. V.** Results of leaching tests in stabilized sediment samples

SAMPLE CODE/ PARAMETERS	mg kg <sup>-1</sup> d.w.																			Density kgm <sup>3</sup>
	Cr	Zn	Cd	Cu	Ni	Pb	Ba	Mo	Hg	As	Sb	Se	ΣPCBs	ΣPAHS	Mineral oil index	Cl <sup>-</sup>	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	TDS	
0	0.08	0.40	0.005	0.07	0.05	0.08	0.49	0.30	0.010	0.019	0.160	p.0.01	0.0004	0.009	0.043	1746	2.82	1740	7218	1510
Leaching after 7 days of stabilization																				
1	0.08	0.40	0.005	0.07	0.05	0.08	0.51	0.27	0.010	0.030	0.110	0.06	0.0004	0.010	0.044	2961	3.16	2554	10578	1520
2	0.05	p.0.22	0.010	2.38	0.46	0.08	3.54	0.87	0.009	p.0.005	0.013	0.03	p.0.0001	0.008	0.036	389	5.24	1690	13016	1540
3	0.11	p.0.22	0.012	1.60	0.42	0.13	2.62	0.48	0.008	0.007	p.0.005	0.02	0.0460	0.004	0.035	431	6.35	14060	25708	1570
4	p.0.05	p.0.22	0.005	1.58	0.42	0.08	2.11	0.46	0.009	p.0.005	0.008	0.02	0.0310	0.006	0.028	403	7.42	2760	11584	1580
5	0.12	p.0.22	0.009	1.52	0.48	0.11	2.66	0.69	0.010	p.0.005	p.0.005	0.03	0.0350	0.008	0.029	431	4.66	11900	23044	1500
6	0.10	p.0.22	p.0.005	2.14	0.40	p.0.05	0.38	0.85	0.007	0.025	0.090	0.05	p.0.0001	p.0.001	0.020	643	8.46	1097	9968	1529
7	0.13	p.0.22	p.0.005	2.15	0.16	p.0.05	1.09	0.52	0.007	0.010	0.030	0.05	p.0.0001	p.0.001	0.031	163	8.62	574	7803	1724
8	0.15	p.0.22	p.0.005	1.30	0.11	p.0.05	0.59	0.52	0.006	0.024	0.100	0.10	p.0.0001	p.0.001	0.023	199	8.62	557	5746	1918
9	0.10	p.0.22	p.0.005	2.67	0.23	p.0.05	0.58	0.40	0.005	0.008	0.060	0.04	p.0.0001	p.0.001	0.022	252	7.67	522	7850	1822
Leaching after 28 days of stabilization																				
1	0.08	0.40	0.005	0.07	0.05	0.08	0.53	0.29	0.010	0.032	0.121	0.04	0.0004	0.009	0.041	3158	3.92	2987	11634	1527
2	0.04	p.0.22	p.0.005	1.98	0.48	0.06	2.08	0.68	0.007	p.0.005	0.009	0.01	p.0.0001	0.009	0.024	357	5.19	994	11002	1596
3	0.06	p.0.22	p.0.005	1.15	0.53	0.11	1.63	0.23	0.008	p.0.005	p.0.005	0.01	p.0.0001	0.007	0.100	430	6.35	7688	17480	1620
4	0.06	p.0.22	p.0.005	2.32	0.65	0.10	2.96	0.57	0.008	p.0.005	0.020	0.02	p.0.0001	0.010	0.020	459	7.71	1580	10460	1610
5	0.06	p.0.22	p.0.005	1.46	0.62	0.09	1.92	0.33	0.010	p.0.005	p.0.005	0.02	p.0.0001	0.011	0.040	459	5.44	4498	13520	1580
6	0.12	p.0.22	p.0.005	2.33	0.52	p.0.05	0.57	0.72	0.011	0.017	0.080	0.07	0.0003	p.0.001	0.023	666	8.79	1386	99970	1603
7	0.18	p.0.22	p.0.005	3.54	0.23	p.0.05	1.49	0.49	0.007	0.010	0.040	0.06	0.0002	p.0.001	0.022	152	8.46	486	7475	1780
8	0.13	p.0.22	p.0.005	1.96	0.16	p.0.05	0.81	0.49	0.010	0.018	0.060	0.07	0.0003	p.0.001	0.020	184	7.23	483	5855	1876
9	0.12	p.0.22	p.0.005	4.10	0.28	p.0.05	0.75	0.39	0.006	0.008	0.040	0.05	0.0003	p.0.001	0.019	245	7.82	678	7875	1905

p.- below determination limit

sample code 0 - unstabilized sediment

sample code 1—sediment stabilised without binders (blank sample)

the feasibility of alternative solutions. In current work was conducted 'compliance test' of leaching. The type of material must be also identified as the options for management may depend on the category of soil or waste (e.g. hazardous waste). The European Waste Catalogue may be used [42].

The results obtained in leaching test indicated small leaching from not stabilized sediment. However, results of sulphates and TDS exceeded the limits of leaching set by the Polish law for disposal at the inert waste landfill (Table 6). Similar results of leaching after 7 and 28 days of stabilization were stated for Zn, Cu, Pb, Hg, Ba, As, Sb, Se, PAHs and fluorides. The small decrease of the leaching after 28 days in relation to the results after 7 days were observed for Cr, Cd, Mo, PCBs, sulphates and TDS. However, for Ni and chlorides a slight increase in the content was observed. Nickel can cause some problems in the sta-

bilization process [43, 44]. Ni leaching usually increases during the stabilization, because it is a component of many binders and by-products, which are added to the stabilized sludge.

The price of binder plays a significant role in the final cost estimate of the stabilization process. Before making a final decision regarding the composition of the binder local market prices should be taken into account. The choice of mixtures of binders containing by-products generated in the production of energy can significantly reduce the final cost [45].

### Compressive strength

The tests of compressive strength in sediments have been performed by the Swedish Geotechnical Institute (SGI). The results of the investigations are shown in table 7.

**Tab. VI.** Permissible limits of leaching for certain types of waste landfills

	mg kg <sup>-1</sup> d.w.																			Mineral oil index	Cl <sup>-</sup>	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	TDS	Density kg m <sup>3</sup>
	Cr	Zn	Cd	Cu	Ni	Pb	Ba	Mo	Hg	As	Sb	Se	ΣPCBs	ΣPAHs											
	PERMISSIBLE LIMITS OF LEACHING*																								
Inert waste landfill	0.5	4.0	0.04	2.0	0.4	0.5	2.0	0.5	0.01	0.5	0.06	0.1	1.0	1.0	500	800	10.0	1 000	4 000	nl					
Other than inert and hazardous waste landfill	10	50	1.0	50	10	10	100	10	0.2	2.0	0.7	0.5	nl	nl	nl	15 000	150	20 000	60 000	nl					
Hazardous waste landfill	70	200	5.0	100	40	50	300	30	2.0	25	5.0	7.0	nl	nl	nl	25 000	500	50 000	100 000	nl					

nl – no limit value

\* Regulation of the Polish Minister of Economy and Labour (8 January 2013) on criteria and procedures for the release of waste for disposal at the landfill of different waste type (Journal of Laws 2013, No. 0, item 38)

**Tab. VII.** Results of compressive strength analysis determined in stabilized sediments from the Port of Gdynia

Sample code	Stabilization time (days)	Storage temperature (°C)	ρ (kg m <sup>-3</sup> )	W (%)	Compressive strength (rfu) (kPa)
	7	ca +30			58.9
2	40	ca +7	1860	30	287.0
	90	ca +8			219.8
3	7	ca +30	1843	23	457.3
	90	ca +8			706.2
4	7	ca +30	1860	29	159.3
	40	ca +7			342.0
5	7	ca +30	1850	30	389.4
	40	ca +7			346.0
6	28	ca +7	1603	47	17.5
7	28	ca +7	1780	31	148.7
8	28	ca +7	1876	34	61.8
9	28	ca +7	1905	34	69.8

ρ - density

W - humidity

## Conclusions

As a result of the analysis of pollutants in sediments from the Port of Gdynia a high content of lead, PCBs, TBT and oil products was found.

The leaching tests in stabilized sediments conducted by the MIG laboratory showed some excess for leaching of Ni, sulphates and chloride after 28 days in relation to the results after 7 days of stabilization. Some increase of leaching in relation to the unstabilized sediment was observed for some more analysed parameters. However, the preliminary testing of the sediment and binder mixtures shows that it is possible to achieve good results of stabilization of the sediments of

the Port of Gdynia. Further tests of stabilization, particularly in terms of TBT leaching tests are planned.

The results of studies also show that the by-products can be a component of many good recipes to stabilization. Research shows that the best recipes are No. 2 (cement + slag) and recipe No. 5 (cement + slag + fly ash from power station in Gdynia + Polish gypsum). Also, recipe No. 8 (cement + middle sand + fly ash from power station in Gdynia + Polish gypsum) gives fairly good results. For recipes, No. 3 and 5 the results are also good for uniaxial compression strength. The stabilization/solidification technology can be recommended for sustainable management of contaminated sediments.



## References:

- [1] Oren, A., Aizenshtat, Z. & Chefetz, B. (2006). Persistent organic pollutants and sedimentary organic matter properties: a case study in the Kishon River, Israel. *Environ. Pollut.* 141: 265–274.
- [2] HELCOM (2010a). Hazardous substances in the Baltic Sea - An integrated thematic assessment of hazardous substances in the Baltic Sea, Baltic Sea Environment Proceedings No. 120B, Helsinki Commission, Baltic Marine Environment Protection Commission.
- [3] HELCOM (2010b). Ecosystem Health of the Baltic Sea 2003-2007, HELCOM Initial Holistic Assessment Baltic Sea Environment Proceedings No. 122, Helsinki Commission, Baltic Marine Environment Protection Commission.
- [4] Biselli, S., Bester, K., Hühnerfuss, H. & Fent, K. (2000). Concentrations of the antifouling compound Irgarol 1051 and of organotins in water and sediments of German North and Baltic Sea marinas. *Mar. Pollut. Bull.* 40(3): 233–243.
- [5] Eklund, B., Elfström, M., Gallego, I., Bengtsson, B.-E. & Breitholtz, M. (2010). Biological and chemical characterization of harbour sediments from the Stockholm area. *J. Soils Sed.* 10(1): 127–141.
- [6] Falandysz, J., Brzostowski, A., Szpunar, J. & Rodriguez-Pereiro, I. (2002). Butyltins in sediments and threespined stickleback (*Gasterosteus aculeatus*) from the marinas of the Gulf of Gdansk, Baltic Sea. *J. Environ. Sci. Health Part A* 37(3): 353–363.
- [7] Falandysz, J., Albanis, T., Bachmann, J., Bettinetti, R., Bochenin, I., et al. (2006). Some chemical contaminant of surface sediments at the Baltic Sea coastal region with special emphasis on androgenic and anti-androgenic compounds. *J. Environ. Sci. Health Part A* 41(10): 2127–2162.
- [8] Hoch, M. (2001). Organotin compounds in the environment—an overview. *Appl. Geochem.* 16(7–8): 719–743.
- [9] Radke, B., Łęczyński, L., Wasik, A., Namieśnik, J. & Bolalek, J. (2008a). The content of butyl- and phenyltin derivatives in the sediment from the Port of Gdansk. *Chemosphere* 73(3): 407–414.
- [10] Radke, B., Staniszevska, M., Wasik, A., Namieśnik, J. & Bolalek, J. (2008b). Organotin compounds in marine sediments. *Polish J. Environ. Stud.* 17(5): 643–654.
- [11] Senthilkumar, K., Duda, C. A., Villeneuve, D. L., Kannan, K., Falandysz, J., et al. (1999). Butyltin compounds in sediment and fish from the Polish coast of the Baltic Sea. *Environ. Sci. Pollut. Res.* 6(4): 200–206.
- [12] Strand, J., Jacobsen, J. A., Pedersen, B., & Granmo Å. (2003). Butyltin compounds in sediment and molluscs from the shipping strait between Denmark and Sweden. *Environ. Pollut.* 124(1): 7–15.
- [13] Staniszevska, M., Burska, B., Sapota, G., Bogdaniuk, M., Borowiec, K., et al. (2011). The relationship between the concentrations and distribution of organic pollutants and black carbon content in benthic sediments in the Gulf of Gdansk, Baltic Sea. *Mar. Pollut. Bull.* 62: 1464–1475.
- [14] Szpunar, J., Falandysz, J., Schmitt, O. & Obrebska, E. (1997). Butyltins in marine and freshwater sediments of Poland. *Bull. Environ. Contam. Toxicol.* 58(6): 859–864.
- [15] Evans, S. M. (1999). Tributyltin pollution: The catastrophe that never happened. *Mar. Pollut. Bull.* 38(8): 629–636.
- [16] Díez, S., Jover, E., Albaigés, J. & Bayona, J. M. (2006). Occurrence and degradation of butyltins and wastewater marker compounds in sediments from Barcelona harbour, Spain. *Environment International* 32(7): 858–865.
- [17] Heiri, O., Lotter, A.F. & Lemcke, G. (2001). Loss-on-ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *J. Paleolimnol.* 25: 101–110.
- [18] Song, Y.F., Jing, X., Fleischmann, S. & Wilke B.M. (2002). Comparative study of extraction methods for the determination of PAHs from contaminated soils and sediments. *Chemosphere* 48(9): 993–1001.
- [19] Wolska, L. (2002). Miniaturised analytical procedure of determining polycyclic aromatic hydrocarbons and polychlorinated biphenyls in bottom sediments. *J. Chromatogr. A* 959: 173–180.
- [20] Wolska, L. & Namieśnik, J. (2002). Distribution of pollutants in the Odra river system. Part III. Organic pollutants in bottom sediments. *Pol. J. Environ. Stud.* 11: 663–668.
- [21] Smith, J.N., Lee, K., Gobeil, C. & Macdonald, R. (2009). Natural rates of sediment containment of PAH, PCB, and metal inventories in Sydney Harbour, Nova Scotia. *Sci. Total Environ.* 407: 4858–4869.
- [22] Sapota G. (1997). Chlorinated hydrocarbons in sediments from the Vistula Lagoon. *Oceanol. Stud.* 26(2–3): 61–69.
- [23] Sapota G. (2006). Persistent organic pollutants (POPs) in bottom sediments from the Baltic Sea. *Oceanol. and Hydrobiol. Stud.* 35(4): 295–306.
- [24] Filipkowska, A., Kowalewska, G., Pavoni, B. & Łęczyński, L. (2011). Organotin compounds in surface sediments from seaports on the Gulf of Gdansk (southern Baltic coast). *Environ Monit Assess* 182: 455–466. DOI 10.1007/s10661-011-1889-x.
- [25] Champ, M. A. (2000). A review of organotin regulatory strategies, pending actions, related costs and benefits. *Sci. Tot. Environ.* 258(1–2): 21–71.
- [26] Champ, M. A. (2001). New IMO convention to control harmful antifouling systems on ships. *Sea Technology* 42(11): 48–51.
- [27] Champ, M. A. (2003). Economic and environmental impacts on ports and harbours from the convention to ban harmful marine anti-fouling systems. *Mar. Pollut. Bull.* 46: 935–940.
- [28] Gipperth, L. (2009). The legal design of the international and European Union ban on tributyltin antifouling paint: Direct and indirect effects. *J. Environ. Manage.* 90(S1): S86–S95.
- [29] Baumard, P., Budzinski, H., Garrigues, P., Dizer, H. & Hansen, P.D. (1999). Polycyclic aromatic hydrocarbons in recent sediments and mussels (*Mytilus edulis*) from the Western Baltic Sea: occurrence, bioavailability and seasonal variations. *Mar. Environ. Res.* 47: 17–47.
- [30] Leipe, T., Kersten, M., Heise, S., Pohl, Ch., Witt, G., et al. (2005). Ecotoxicity assessment of natural attenuation effects at a historical dumping site in the western Baltic Sea. *Mar. Pollut. Bull.* 50: 446–459.
- [31] Sapota, G., Wojtasiak, B., Burska, D. & Nowiński, K. (2009). Persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) in surface sediments from selected fjords, tidal plains and lakes of the North Spitsbergen. *Polish Polar Res.* 30: 59–76.
- [32] Susdave, S. & Gulbinskas, S. (2010). Assessment of sediment contamination in Klaipeda Port area using long-term monitoring data. 2010 IEEE/OES US/EU Baltic International Symposium (BALTIC). IEEE Catalogue No. CFP10AME-ART, ISBN: 978-1-4244-9227-5/10/\$26.00/IEEE.
- [33] Ussenkov, S.M. (1997). Contamination of harbour sediments in the eastern Gulf of Finland (Neva Bay). *Baltic Sea. Environmental Geology* 32 (4): 274–280.
- [34] Baca, B.J. (1996). Effects of crude oil and dispersed crude oil in tropical ecosystems. Proc. of the 96 MTS/IEEE Oceans Conference, 23–26 September 1996 (pp. 469–486). Fort Lauderdale, USA. ISBN: 0780335201 ISBN13: 9780780335202 DDC: 551.46.
- [35] Brakstad, O.G. & Bonaunet, K. (2006). Biodegradation of petroleum hydrocarbons in seawater at low temperatures (0–5°C) and bacterial communities associated with degradation. *Biodegradation* 17: 71–82.
- [36] Majjala, A. (2006). Review of the state-of-the-art of cement stabilisation. Ramboll Finland Oy Report, pp.50.
- [37] Hansen, J.B., Gamst, J., Laine-Ylijoki, J., Wahlström, M., Larsson, L., et al. (2005). A framework for using leaching test for non-volatile organic compounds. NORDTEST Nordic Innovation Centre, ISSN 0283-7234 (pp.76), <http://www.nordicinnovation.net>
- [38] Comans, R.N.J., Roskam, G., Oosterhoff, A., Shor, L., Wahlström, M., et al. (2001). Development of standard leaching tests for organic pollutants in soils, sediments and granular waste materials. EU-project. Naturvårdsverket, Stockholm, ISBN 91-620-5557-7.pdf, ISSN 0282-7298.
- [39] Enell, A., Reichenberg, F., Warfvinge, P. & Ewald, G. (2004). A column method for determination of leaching of polycyclic aromatic hydrocarbons from aged contaminated soil. *Chemosphere* 54: 707–715.
- [40] Gamst, J., Kjeldsen, P., Hansen, J.B., Broholm, K. & Christensen, T.H. (2003). Leaching of PAH's from soil: Comparison of two conceptually different column tests and a batch tests. In Halm, D. & Grathwohl, P. (Eds.): Proceedings of the 2nd International Workshop on Groundwater Risk Assessment at Contaminated Sites (GRACOS) and Integrated Soil and Water Protection (SOWA), 20–21 March 2003 (pp. 173–177). Tübingen, Germany.
- [41] Hansen, J.B., Grøn, C., Hjelmar, O., Asmussen, O., Klem, S., et al. (2004). Leaching Tests for Non-Volatile Organic Compounds—Development and Testing. Report for NORDTEST, DHI Water & Environment, No. 1643-0
- [42] The European Waste Catalogue (EWC), Commission Decision 2000/532/EC
- [43] Sanchez, F. (2006). Leaching from granular waste materials used in highway infrastructures during infiltration coupled with freezing and thawing. Final Report of The Recycled Material Resource Center (RMRC) project # 29, University of New Hampshire.
- [44] Townsend, T.G. (1998). Leaching characteristics of Asphalt road waste. State University System of Florida, Report #98-2.
- [45] Sustainable Management of Contaminated Sediments. Guideline (2013). EU project Sustainable Management of Contaminated Sediments in the Baltic Sea (SMOCS), within The Baltic Sea Region programme 2007–2013 (#039), <http://www.smocs.eu>.

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