Hochschule für Angewandte Wissenschaften Hamburg
Hamburg University of Applied Sciences

Hamburg University of Applied Sciences

Faculty Life Sciences

Environmental geochemistry of sediments from the estuary Unterwarnow

Bachelor thesis in the course of study Environmental Engineering

Written by

Silja Denise Kröger

Matriculation number [redacted]

28th June 2017, Hamburg

First reviewer: Prof. Dr.habil. Gesine Witt (Hamburg University of Applied Sciences)

Second reviewer: Dr. Thomas Leipe (Institute for Baltic Sea research, Rostock-Warnemünde)

The bachelor thesis was prepared in the laboratory of the Institute for Baltic Sea Research Warnemünde.

Self-declaration

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

The work was done under the guidance of Professor Gesine Witt, at the Hamburg University of applied sciences.

28th June 2017, Hamburg

Silja Denise Kröger

Summary

In this Bachelor thesis, the pollution of Unterwarnow is discussed. The Unterwarnow is the estuary of the Warnow which flows into the Baltic Sea in Warnemünde. The Unterwarnow is separated from the Oberwarnow by the weir at the Mühlendamm. It flows through the city Rostock, where areas on the banks are partly strongly urbanised. Also the outflow from the waste water treatment plant of Rostock flows into Unterwarnow. In the north of Unterwarnow is the Breitling, which is used as overseas port. The area of Breitling is strongly influenced by shipping.

Sediment samples were taken at 26 stations to determine the heavy metals concentration. The stations were distributed throughout the study area to demonstrate local differences. The sediment samples were sampled in the shipping channel to examine the fresh, young sediment. In this study, surface sediments were taken by a grap sampler.

The samples were prepared and digested by acids in the laboratory. A grain size analysis was made and the total carbon content and total inorganic carbon content were determined. The method of atomic adsorption spectrometry was used for the determination of mercury. In addition, total digestion extracts of the samples were measured by inductively coupled plasma with optical emission spectrometry and mass spectrometry. As result the heavy metal concentrations and the concentrations of manganese, iron and aluminum were measured.

Station 1, in particular, had high heavy metal contents. The reason for this is the inflow of the Oberwarnow. High heavy metal concentrations were also measured in the area of the city harbor. The reason for the high heavy metal concentrations there are the sealed areas. The station 24 had particularly high concentrations of heavy metals and enrichment factors. Here, the cruise center and the shipyard in Warnemünde can be assumed to be sources. Stations 18 and 22 had the lowest heavy metal concentrations. The reason therefore are the high sand contents at these two stations.

Zusammenfassung

In dieser Bachelorarbeit wird die Verschmutzung der Unterwarnow thematisiert. Die Unterwarnow ist das Ästuar der Warnow und mündet in Warnemünde in die Ostsee. Die Unterwarnow ist durch das Wehr am Mühlendamm von der Oberwarnow getrennt. Sie fließt durch die Hansestadt Rostock, wobei Bereiche an den Ufern zum Teil stark urbanisiert sind. Ebenfalls fließt der Kläranlagen Abfluss der Stadt Rostock in die Unterwarnow. Nördlich an die Unterwarnow schließt der Breitling an, welcher als Überseehafen stark vom Schiffverkehr geprägt ist.

Zur Bestimmung der Belastung mit Schwermetallen wurden Sedimentproben an 26 Stationen genommen. Die Stationen wurden über das gesamte Untersuchungsgebiet verteilt, um lokale Unterschiede aufzuzeigen. Die Sedimentproben wurden bewusst in der Fahrrinne genommen, um das frische, junge Sediment zu untersuchen. Dabei wurden mittels eines Backengreifers Oberflächensedimente genommen.

Die Proben wurden im Labor aufbereitet und aufgeschlossen. Es wurde eine Korngrößenanalyse durchgeführt und der gesamte Kohlenstoffgehalt und gesamt anorganischer Kohlenstoffgehalt wurden bestimmt. Für die Quecksilber Bestimmung wurde das Verfahren der Atom Adsorption Spektrometrie genutzt. Außerdem wurden Totalaufschlüsse der Proben mittels Induktiv gekoppeltem Plasma mit anschließender Optischer-Emissions-Spektrometrie und Massen Spektrometrie gemessen. Als Ergebnissen dieser Messung wurden sämtliche Schwermetalle bestimmt. Zusätzlich zu den Schwermetallen wurden auch die Elemente Mangan, Eisen und Aluminium gemessen.

Besonders die Station 1 wies hohe Schwermetall Gehalte auf. Der Grund dafür liegt am Zufluss der Oberwarnow. Ebenfalls wurde in dem Bereich des Statthafens hohe Schwermetall Konzentrationen gemessen. Diese stammen von versiegelten Flächen. Besonders hohe Schwermetall Konzentrationen und Anreicherungsfaktoren hatte die Station 24. Hier lassen sich das Cruise Center und die Werft in Warnemünde als Quellen vermuten. Station 18 und 22 hatten die geringsten Schwermetall Konzentrationen, das liegt an den hohen Sandgehalten.

Table of contents

List of abbreviations

AAS	Atomic adsorption spectrometry
Al	Aluminium
As	Arsenic
BFG	The German Federal Institute of Hydrology
$CaCO_3$	Calcium carbonate
Cd	Cadmium
CID	Collision-induced dissociation
CO_2	Carbon dioxide
Cr	Chrome
Cu	Copper
DM	Dry matter
EF	Enrichment Factor
EQS	Environmental quality standard
Fe	Iron
FRG	Federal Republic of Germany
GC	Gas chromatography
GDR	German Democratic Republic
H_3PO_4	phosphorus acid
HCl	Hydrochloric acid
$HClO_4$	Perchloric acid
HF	Hydrofluoric acid
Hg	Mercury
HNO_3	Nitric acid
ICP	Inductive coupled plasma
Mn	Manganese
MS	Mass spectrometry
NDIR	Not dispersive infrared spectroscopy
Ni	Nickel
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxide

O_2	Oxygen
OES	Optical emission spectrometry
OGewV	Oberflächengewässerverordnung
Pb	Lead
PE	Polyethylene
Sb	Antimony
SO_2	Sulphur dioxide
TC	Total carbon
TCD	Thermal conductivity detector
TIC	Total inorganic carbon
TN	Total nitrogen
TS	Total sulphur
Zn	Zinc

List of figures

List of tables

1. Introduction

“Estuaries receive significant anthropogenic inputs from both point and non-point upstream sources and from metropolitan areas, tourism and industries located along the estuarine edges” (Caeiro et al., 2005). The Unterwarnow estuary was strong influenced by human activity and anthropogenic pollution. In the last decades, there were a lot of dredging and bank reinforcements for shipping and tourism (Leipe, 2016). There was dumping of polluted sediments and an island was created by pumping dredged material in the Unterwarnow estuary (Leipe, 2016).

Actually, there is a discussion in Rostock about the pollution of the sediments from the Unterwarnow. Every year the Hanse Sail takes place in the city of Rostock (Leipe, 2016). Therefor a lot of ships enter to the city harbour. For some ships, the shipping channel is not deep enough so they cannot dock in city harbour. In 2018 the city of Rostock becomes 800 years old (Leipe, 2016). For this anniversary, political representatives want to deepen the channel in the city harbour up to 6.5 metres (Meyer, 2017). As result from the deepening tall ships should be able to dock in the city harbour. This might be an attraction for tourism (Meyer, 2017). For the anniversary of the city of Rostock an expertise about the sediment pollution was made. This expertise is private, just some data were published by the newspaper Osteezeitung at the 9th February 2017. In the article, the data for concentration of chloride and sulphate in the water column and hydrocarbons in sediment were published. The data are from an expertise of The German Federal Institute of Hydrology (BfG) (Meyer, 2017).

The last data of sediments from the estuary Unterwarnow, except the date from the expertise, are from the 1990 century (Leipe, 2016). The idea for this study developed because there are no actual data from the Unterwarnow sediments. Also my sampling campaign has got more stations than the campaigns made before (Bachor, 2005; Leipe, 2016). In the future, the data from this study can be used for modelling the inputs and outputs of the Baltic Sea.

In August 2016 samples of surface sediments at 26 stations were taken with a grap sampler. Goal of the campaign is to show local differences in the sediments from the Unterwarnow estuary. The project should give some new information about the sediment

quality. My bachelor thesis is included into the project „Phosphor von der Quelle bis ins Meer – Integriertes Phosphor- und Wasserressourcenmanagement für nachhaltigen Gewässerschutz "(PhosWaM). I supported the work of the work package 2.3 „Bedeutung des Übergangsbereichs zwischen Einzugsgebiet und Meer für P-Konzentration, P-Transformation und P-Retention". The samples play an important role for local phosphorus differences in the sediments. For the PhosWaM project were also sediment cores at four stations and water samples collected. For my I looked at the surface sediment samples. My focus is onto the heavy metals in the sediments from the Unterwarnow estuary, but in this thesis I will also present the results for selected other elements like Al, Mn and Fe.

Heavy metals are toxic depending from the doses (van der Voet et al., 2000). Also, small doses can cause effects on ecosystems and human healthy. "Metals tend to accumulate in soils and sediment with immobilisation due only to geological, and therefore extremely slow, processes"(van der Voet et al., 2000). In the last decades, there were a lot of poisoning of human affected by heavy metal pollution (Fent, 2013; van der Voet et al., 2000). In the Minamata Bay in Japan, with mercury polluted water was the cause for poising of hundreads people. The reason for this was that the people ate the fish which was polluted by methylmercury (Fent, 2013). In Japan was also a pollution with cadmium because cadmium rich waste water was put onto rice fields. "Lead in petrol has caused health problems in many cities, especially for children" (van der Voet, 20000).

Heavy metals has got a density of more than 6 g/cm³ (Fent, 2013). Some heavy metals are essential for organisms like Fe, Cu of Zn. But there are also non-essential heavy metals like Cd, Pb or Hg. Both groups of heavy metals can cause growth inhibition and metabolic disorders (Fent, 2013). Metals and heavy metals has got a few natural sources, like volcanic eruptions and decomposition of rocks (UBA, 2013). The concentration of metals which are set free into the environment by natural processes is called natural background (UBA, 2013). Due to human activity, more heavy metals than natural were set free to the environment (Sigg & Stumm, 2016). For the water bodies, there are a lot of different ways how heavy metals enter the aquatic systems. Following the biggest inputs of heavy metals into waters are announced (Böhm et al., 2001; UBA, 2013; Sigg & Stumm, 2016):

- Waste water from industry and cities
- Mining
- Erosion of agricultural grounds
- Atmospheric deposition
- Domestic waste water from old tubes made of Cu or Pb
- Drain water from sealed floors

In waters the metals are bonded to the suspended matter and the sediment or they are free in the water bodies (Sigg & Stumm, 2016). “More than 90 % of the heavy metal Ioad in aquatic systems is bound on particulates like suspended matter and sediments” (Calmano et al., 1993). There are a few chemical and physical factors which influence the distribution between the water bodies and the sediment (Sigg & Stumm, 2016; Calmano et al., 1993). “Type and stability of the heavy metal bonding on […] solid compounds are decisive factors for potential mobility and bioavailability” (Calmano et al., 1993).

The physicochemical conditions and geochemical properties of the sediment influence the bioavailability of the sediment compounds (Chippetta et al., 2016). For organisms, especially the free metals in the water bodies are dangerous because they are better bioavailable than the metals in the sediments. Because of a good bioavailability heavy metals bio accumulate in the food chain (Sigg & Stumm 2016; van der Voet et al., 2000). This means at least the heavy metals were eaten by human (van der Voet, 2000).

In this thesis the following hypotheses should be verified.

1. The inflow from the Oberwarnow plays an important role for the contamination of the Unterwarnow sediments next to the weir Mühlendamm.
2. The waste water treatment plant has got a high influence for the heavy metal pollution
3. Because of the high pollution of the sediments, a dredging is not possible.

2. Materials and methods

2.1. List of Materials

Table 1: Table of all materials used for the methods

Material	Comment	Producer
Ceramic vessels	For TIC analysis	
CNS Analyser	CHNSO Elemental Analyser	
Crucible	Made of ceramics	
Erlenmeyer flask	100 ml volume	
Exsiccator	With silica gel	
Grain size Analyser	CILAS 1180	Cilas
Grap sampler	Stainless steel	
Heating oven		
Heating plate		
Heating plate	Special plate for total digestion	
ICP-MS	ICap Q	Thermo Fisher Scientific
ICP-OES	Thermo Scientific iCAP 6300Duo and Perkin–Elmer Optima 3000XL	Thermo Fisher Scientific and Perkin Elmer
Mercury analyser	DMA-80	MLS GmbH
Metal rack	For the Teflon pressure vessels	
Metal vessels	For Mercury analysis	
Mortar	ceramics	
Muffle furnace		
Petri plate		
Polyethylene bottles	conditions with 2% HNO_3	
Sarstedt tube		Sarstedt

Scale	Different types for different analytical methods	
Spatula	Different sizes	
Syringe filters	45 µm	
Teflon pressure vessels	With caps	
TIC Analyser	Multi EA 4000	Analytik Jena
Tin cups	For CNS analysis	
Tweezer		

2.2. List of chemicals

Table 2: Tables of all necessary chemicals

Chemical	**Concentration**	**Comment**
ABSS		Home standard
External standard		
HCl	3.6 vol %	
HCl	18 vol %	
$HClO_4$		
Helium		For CNS analysis
HF	40 vol %	
HNO_3	65 vol %	
HNO_3	2 vol %	
Internal standard		
MBSS		Home standard
O_2		For TIC and Hg analysis
OBSS		Home standard
SGR-1		From USGS international standard
Standard 142-R		International standard
Standard TIC		

Ultrapure water		
Vanadium pentoxide		For CNS

2.3. Location of the sampling

The location of the sampling is the Unterwarnow which includes the location of Breitling (Figure 1). The Unterwarnow is the estuary of the river Warnow. It is in the north east of Germany and floats through the city of Rostock. Between the Unterwarnow and the Oberwarnow is a weir which is a barrier. The length of the Unterwarnow is about 9 kilometres except Breitling (Bachor, 2005). It starts at the Mühlendamm and floats through the city-harbour of Rostock to the RoRo and container terminal. In the north of the river the location of Breitling is affiliated. A part of Breitling is used for a military harbour. There is a dockyard which is producing ships for river cruise liners. In Breitling, also cruise liners dock for loading of tourism and goods but the most important shipping there are the ferries to Scandinavia. The Breitling is connected with the Baltic Sea by a maritime canal in Rostock-Warnemünde. The river Peezer Bach with a catchment area of 52 km² flows into the east of Breitling (Bachor, 2005).

The area of the whole sampling location is about 12.5 km² (Bachor, 2005; Schumann et al. 1992). The catchment area of Unterwarnow and Breitling is about 3222 km². In some areas, the area is urbanised (Bachor, 2005). The part of the city harbour is strong urbanised. At the north bank of the city harbour is an old landfill and there are old industry buildings (Meyer, 2017). In the district Bramow at the east bank of the Unterwarnow is the wastewater treatment plant of the city Rostock which final effluent flows in the Unterwarnow (Bachor, 2005; Leipe, 2016). About 83 % of the sewerage system of Rostock is separated (REMONDIS AG & Co. KG, 2017). That means the domestic and industrial wastewater is transported to the wastewater treatment plant (Einfeldt, 2015). The rain water is transported in a separate sewerage system and flows directly into the Unterwarnow (REMONDIS AG & Co. KG, 2017; Einfeldt, 2015).

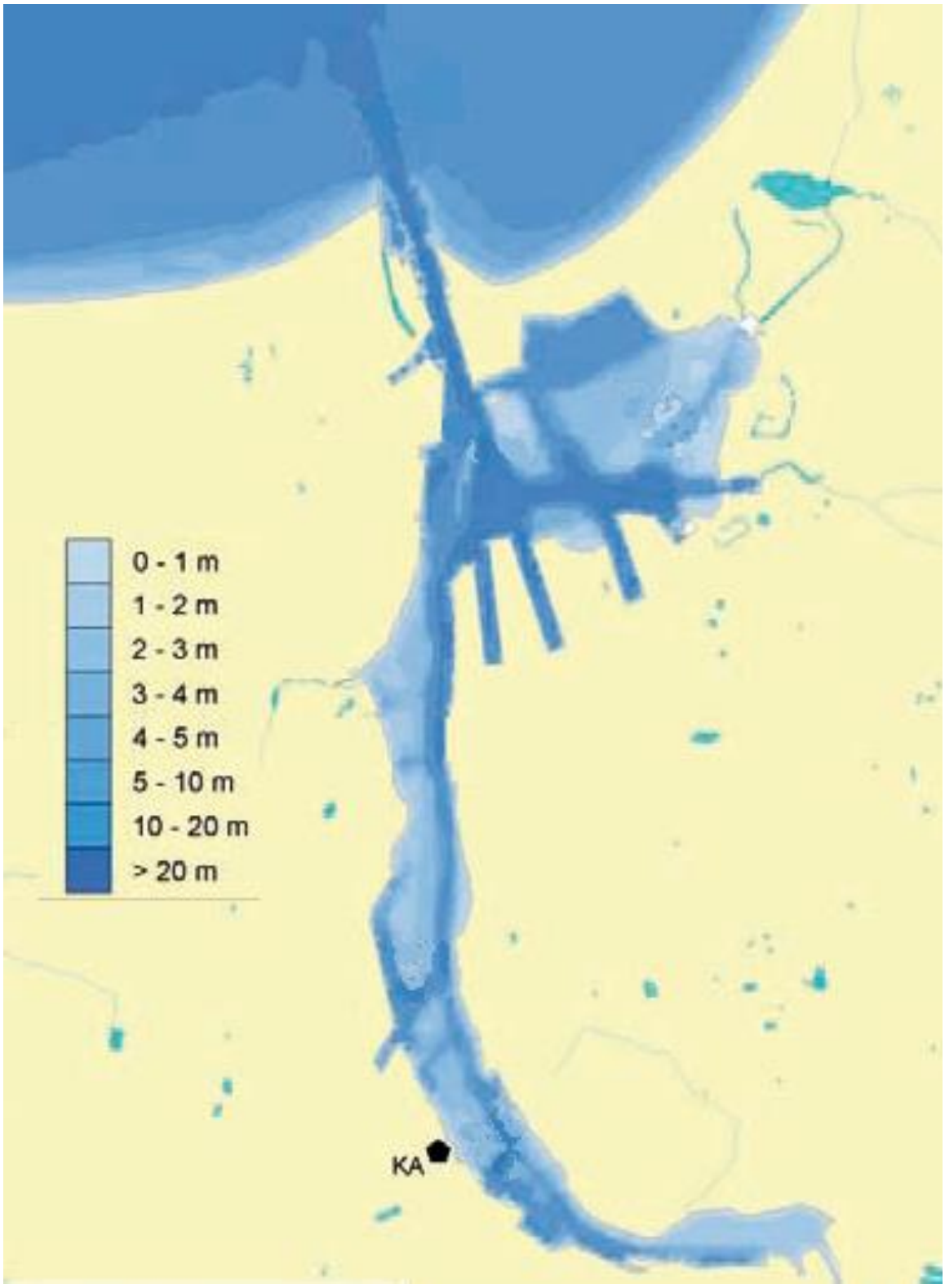

Figure 1: Map of the sampling area modified after Bachor (2005), KA stands for waste water treatment plant

The Unterwarnow is important for shipping so there is a channel which is frequently dredged. There are three different parts with different depth of the channel. The first part with a depth of 6.5 metres is from the city harbour to the fisheries harbour in Marienehe (Wasser- und Schifffahrtsamt Stralsund, 2016). In 1987 this part was dredged the last time. In 2005 there were dredging from the fisheries harbour to the RoRo and container terminal. The channel is 9.0 metres deep. The deepest part is from the RoRo and container terminal up to the Baltic Sea which includes also the channel of Breitling. The channel is 14.5 metres deep because of the cruise liners and ferries which need a deep channel like this. In 2014/15 was the last dredging (Wasser- und Schifffahrtsamt Stralsund, 2016). The figure 1 shows also the different water depth.

The variability of the salinity is high (Bachor, 2005). In the south of the Unterwarnow, in the location of the city harbour, sometimes the conditions are limnic. That depends from the influx of brackish water from the Baltic Sea and from the influx of fresh water from the Oberwarnow. Bachor (2005) said that, depending of the influxes from the Baltic Sea and the Oberwarnow, the Unterwarnow could have conditions like the Baltic Sea.

The classification of the Unterwarnow is made by the European Water Framework Directive (RL 2000/60/EG) from 2000. The estuary is a mesohaline coastal water (figure 2). This is the type code B2. This means that the salinity of the water bodies is between 5 and 18 PSU. The tidal range is lower than 1 metre. In the Unterwarnow the depth is lower than 30 metres, it is 14.5 metres at its deepest point. The current velocity of the water bodies is lower than 1 knot. For the interpretation and the environmental standards of the Oberflächengewässerverordnung (OGewV) 2016, the classification of the water bodies is essential.

Country		DE
Category		C
Eco Region		Baltic Sea
System used		B
Type Code		**B2**
Salinity		
	f.w. _ 0.5	
	0.5 _ 5	
	5 _ 18	XX
	18 _ 30	
	> 30	
Tidal Range		
[m]	< 1	X
	1 - 3	
	> 3	
Depth		
[m]	< 30	X
	> 30	
Current Velocity		
[kn]	< 1	X
	1 - 3	
	> 3	

Figure 2: Type specific parameters for a mesohaline coastal waters of the type B2 from the European Water Framework Directive (2000)

2.4. Sediment sampling

The sediment samples were collected by a grap sampler made of stainless steel. The upper 2 centimetres were put with a plastic spatula into Sarstedt tubes or Petri plates. In figure 3 is a map of the sampling stations. The samples were collected at 26 stations in the Unterwarnow estuary. At three stations, station 2, 22 and 25, two samples were collected to look if there is a big difference between the samples.

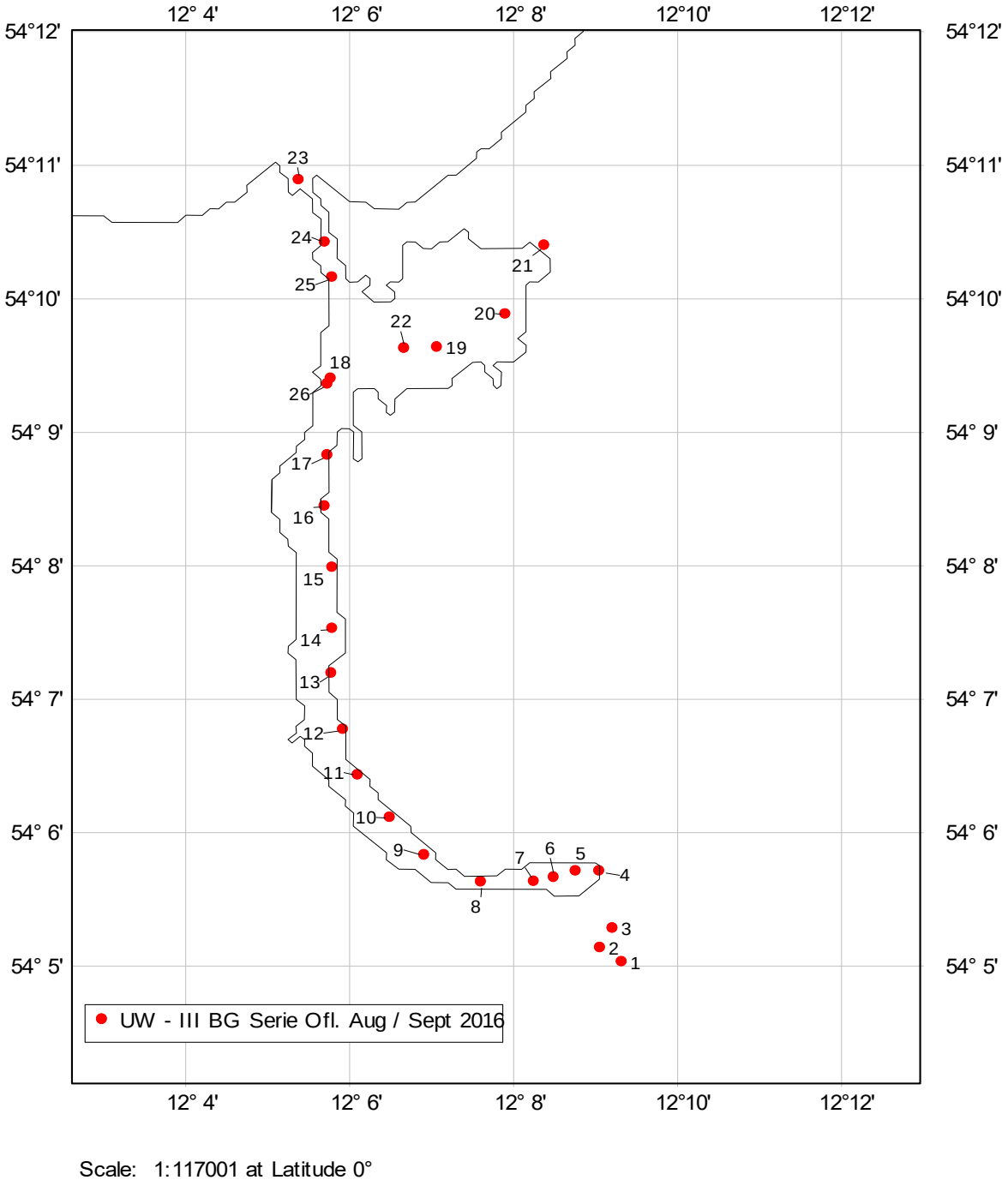

Figure 3: Catchment area with sampling stations

The station 1 is next to the weir at the Mühlendamm. There the water from the Oberwarnow floats into the Unterwarnow. The station 2 is next to the sluice which is not used since a few of years (Leipe, 2016). At station 3 the water flows from station 1 and 2 together. From station 1 to station 4 the water is in parts just 1.5 metres deep. The sampling stations 4 to 8 are located in the city harbour of Rostock. From station 4 to station 12 is a channel with 6.5 metres of deepness. Next to the station 10 is the waste water

treatment plant of the city of Rostock. Nearby station 12 the fishery harbour Marienehe is located. From this station, up to station 16 the channel is 9.0 metres deep. At the station 16 the RoRo and container terminal is located. Here the channel should be 14.5 metres deep because of tall ships which dock here.

The stations 20 and 21 are in Breitling. There is not everywhere a deep channel. At some points, the water is just 2.0 metres deep. The stations 24 and 25 are in the connection channel between the Unterwarnow and the Baltic Sea. Here the cruise liners like AIDAdiva dock. The station 23 is nearly in the Baltic Sea.

2.5. Preparation of the sediments

After the sampling the samples were transported by a temperature of 4 degree Celsius to the laboratory. In the laboratory the samples were freeze dried. This process takes about four days. After the process of freeze drying the samples were put into an exsiccator until the next preparation steps. Then they were homogenised by hand with a mortar. After the homogenisation the sediments were put into glass vials. They were stored dry and dark until the next steps.

2.6. Total digestion

For the measurement of trace metals, a total digestion of the sediment samples is necessary because just a total digestion with strong acids like HF can dissolve resistant silica minerals (Renberg et al., 2001). I made an acid digestion like Schnetger, 1997 described in his paper. At the beginning the samples were weight in into Teflon pressure vessels. About 50 mg per samples is needed for this step. Afterwards 1 mL of nitric acid (HNO_3) (65 vol %) is put into the vessels. The vessels are heated by 50 °C for 1 hour onto a special heating plate with 24 places for the Teflon pressure vessels (Schnetger, 1997; Dellwig, 2017). This step is necessary to eliminate the organic compounds from the samples. In the next step 2 mL hydrofluoric acid (HF) (40 vol %) and 2 mL perchloric acid ($HClO_4$) were give into the vessels. The pressure vessels were closed with the caps and fixed in a rack. They were put in the heating oven for 12 hours (Schnetger, 1997; Dellwig, 2017).

Afterwards the vessels were put onto the heating plate without caps. The samples were heat at 190°C until fumes are emitted. If there is still a small drop left in the vessel, 2 mL

of hydrochloric acid (HCl) (18 vol %) are added to the sample. This step is made three times. Then 5 mL HNO_3 (2 vol %) were put into the vessels (Schnetger, 1997; Dellwig 2017). The vessel is 5 minutes left onto the heating plate. Subsequent the total digestion extracts were transferred into Polyethylene (PE) bottles and they were filled up to 50 mL with ultrapure water (Dellwig, 2017). The extracts were stored by room temperature.

2.7. Measurement of mercury by atomic adsorption spectrometry

For mercury measurement, no extracts are necessary. The device DMA-80 from the producer MLS GmbH was used. The sediment could be measured directly if it is freeze dried and homogenised. About 50 mg per sample is weight in into little metal vessels. The vessels were put into the autosampler. From the autosampler the sample goes into the oven. There the temperature is 750°C (MLS GmbH). The sample is thermal decomposed. Oxygen (O_2) transfers the products of the combustion to the catalyse zone where thermal post-combustion takes place. The pyrolysis products were emitted in the catalyse zone. Now the gas passes the system to the amalgamator. There the mercury is bound and becomes amalgam. The amalgamator is heat up quick so the mercury is set free. With the O_2 gas the mercury is transmitted to the atomic adsorption spectrometry (AAS). For a higher sensitivity, this device uses two different spectral lines (MLS GmbH).

At the beginning of every measurement the calibration of the device is checked by one international standard BCR 142 R and one house standard MBSS-1. Two times a year the precision and accuracy of the device is checked by the ring trail Quasimeme. The precision and accuracy for the BCR 142 R is ≤ 6.4 % and ≤ 4.2 %, respectively.

2.8. Grain size analysis by laser measurement

For this grain size analysis, laser diffraction technique is used. The Laser is called CILAS 1180 and can analyse particles with a size range from 0.04 µm to 2500 µm. The classification of grain size is describe in the DIN 18123. For the samples from the Unterwarnow, the liquid mode is used (Leipe, 2016). “The fine particles are measured by the diffraction pattern, using Fraunhofer or Mie theory. The coarse particles are measured using a real-time Fast Fourier Transform of the image obtained with a CCD camera equipped with a digital processing unit […]” (Cilas).

For analyse less than 5 g of sediment is required. Ultra-pure water is added to the sediment samples. So, it becomes a suspension. Then the suspension is put into the device (Leipe, 2016). In the device the sample suspension passes a laser (figure 4). The particles diffract the laser (Klank, 2002; CILAS, unknown). So the angle of the laser light changes. A detector behind the column with the sample inside, measures the angle laser diffraction. Because of the high laser diffraction for small particles, there are two lasers in the device (see figure 4). For bigger particles the CILAS 1180 has got a CCD camera. “The third laser project images from the particles onto the camera” (Klank, 2002). The images were convert into light spectrum. By Fraunhofer or Mie theory, the different light spectrums were convert into particle sizes (Klank, 2002).

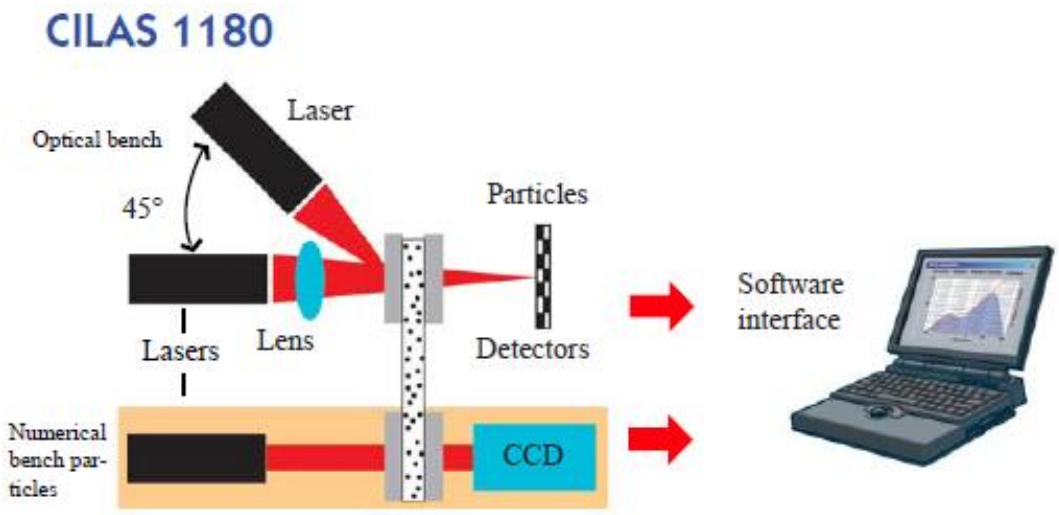

Figure 4: Grain size analyse by laser

2.9. Measurement of total carbon, total nitrogen an total sulphur

Analyse of total carbon (TC), total nitrogen (TN) and total sulphur (TS) (short CNS) is made with a Euro EA - CHNSO Elemental Analyser from HEKAtech GmbH. For the analyse 10 to 17 mg per freeze dried sample were weight in into a small cup made of tin. Afterwards a spade point of vanadium pentoxide is added to the cup. Then the cups is closed with the help of a tweezer. Helium is used as carrier gas (HEKAtech GmbH). The sample goes through the autosampler into the device.

In the device, the samples are ashes in the oven by temperature of 1010°C (HEKAtech GmbH). The oven is filled with oxygen (O_2). The gas is send trough the catalyser tube where

carbon compounds react with O_2 to carbon dioxide (CO_2), nitrogen compounds react to nitrogen oxides (NO_x) and sulphur becomes sulphur dioxide (SO_2). The gas flow passes the reduction tube where the excess Oxygen is bound and NO_x is reduced to nitrogen dioxide (NO_2). If there is water in the sample, it is bound to magnesia perchlorate. After this the gas flow passes a gas chromatography (GC) column. In the column, the different gases are separated by temperature of 70 °C. Afterwards the gases are detected by thermal conductivity in the thermal conductivity detector (TCD) (HEKAtech GmbH). The precision ≤6.2 % and accuracy ≤ 7.1 % is checked by the house standard MBSS-1.

2.10. Measurement of total inorganic carbon

The total inorganic carbon (TIC) is measured by a not dispersive infrared spectroscopy (NDIR) The device is called Multi EA 4000 from Analytik Jena. Nearly 50 mg of sediment is weight in into a vessel made of ceramics. The vessel is feed by the Autosampler into the combustion tube of the device. The sample is added with phosphorus acid (H_3PO_4) (40 vol %) during an O_2 steam (Analytik Jena). The inorganic carbon compounds reacts with phosphorus acid into the O_2 steam to CO_2, water and calcium phosphate.

The analyses gas and the carrier gas are transported to the NDIR. There a wire made of chrome and nickel is 850°C hot. The wire set free infrared energy. This energy is transferred into the measuring cell where the carrier – and analysis gas is transported through. If the CO_2 flows through the infrared radiation, it absorbed the infrared energy and set free a special spectrum a radiation. A filter selects the CO_2 typical radiation and let it passes to the NDIR. The amount of CO_2 is determined by the energetically difference between the carrier and the analyse gas (Analytik Jena).

The precision ≤ 3.8 and accuracy ≤ 3.6 % were checked by a $CaCO_3$ standard.

2.11. Measuring by inductive coupled plasma: sample feeding

For the analyse of a few main group elements, rare earths, heavy metals and trace elements, I used the method of inductive coupled plasma (ICP). There were two different ways of detection. There is the mass spectrometry (MS) and the optical emission spectrometry (OES). With these different ways of detection more than 50 elements can be measured (Dellwig, 2017). The sample must be in a liquid form. For my measurements, I used the total digestion extracts. An internal standard was used.

In the device of ICP an inductive coupled plasma is generated. For that a plasma torch is necessary. The injection tube is encased by two concentric silica tubes (Marquardt, 2012). The induction coil is wound around the outer quartz tube and connected to a high-frequency generator. In the magnetic field of this induction coil, the plasma is produced by the ignition of a Tesla spark. The carrier gas argon and the sample, which is presented as aerosol, are introduced into the torch via the injection tube (Marquardt, 2012; Knöll, 2012).

2.11.1. Inductive coupled plasma with optical emission spectrometry

For the ICP OES an ICP called “Thermo Scientific iCAP 6300Duo” with an OES called “Perkin–Elmer Optima 3000XL” is used. The plasma stimulate the elements from the sample (Knöll, 2012). As reaction of the stimulation, the elements contained in the sample emit light of characteristic wavelengths (Dellwig, 2017). The emitted light is spectrally decomposed in the optics of the device. Subsequently, detection takes place with collision-induced dissociation (CID) detectors. In the device, the optical emission is measured axially and radially, resulting in a higher sensitivity of the measurement (Marquardt, 2012; Dellwig 2017). The accuracy was checked by the international reference standard SGR-1 from USGS. The precision is < 5.0 % and the accuracy < 6.9 %.

2.11.2. Inductive coupled plasma with mass spectrometry

For the ICP MS the device called “iCAP Q” from Thermo Fisher Scientific was used. It is a single quadrupole MS (Dellwig, 2017). In the plasma the sample is ionized (Knöll, 2012). A quadrupole has got 4 electrodes with a DC voltage. Respectively the two electrodes on the opposite sides have a voltage with the same sign (Knöll, 2012). The quadrupole ensures that just ions of a specific mass-to-charge ratio can pass to the detector. In figure 5 a schematic representation shows how the ICP-MS work.

The precision (<5.9%) and the accuracy (<10.2%) were determined by the international standard reference material SGR-1 from USGS.

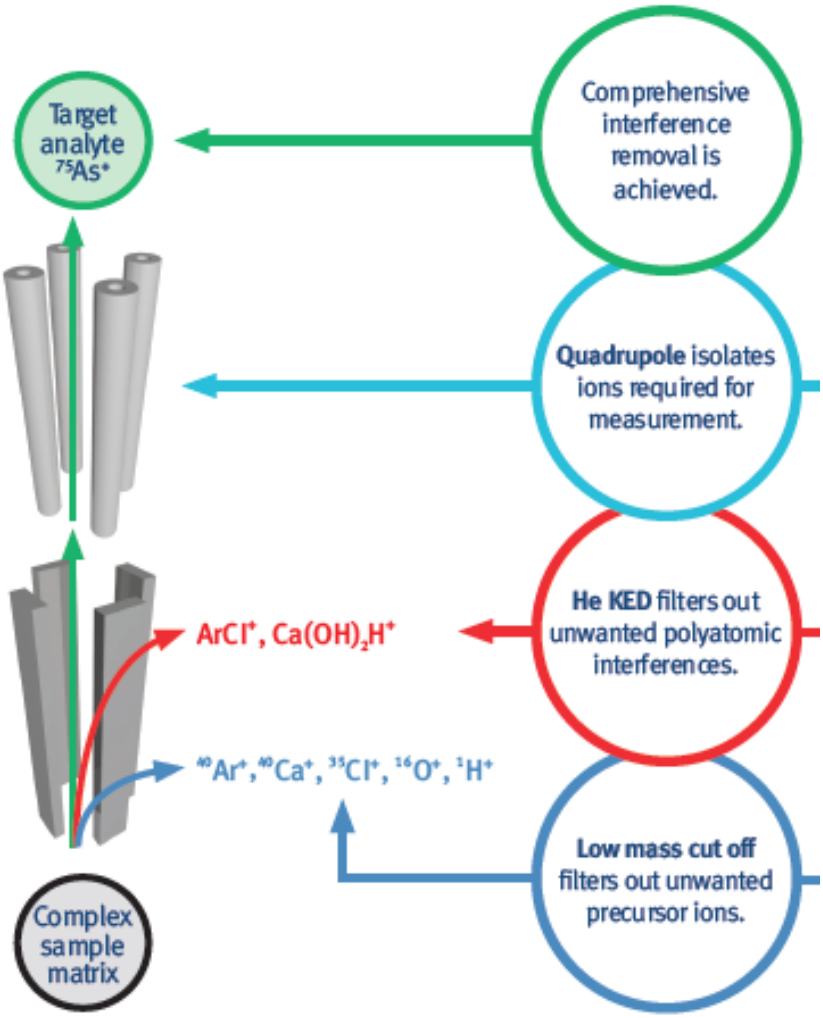

Figure 5: Schematic representation of the iCap Q from Thermo Fisher Scientific (Thermo Fisher Scientific Inc., 2016)

2.12. Schematically overview of the used methods

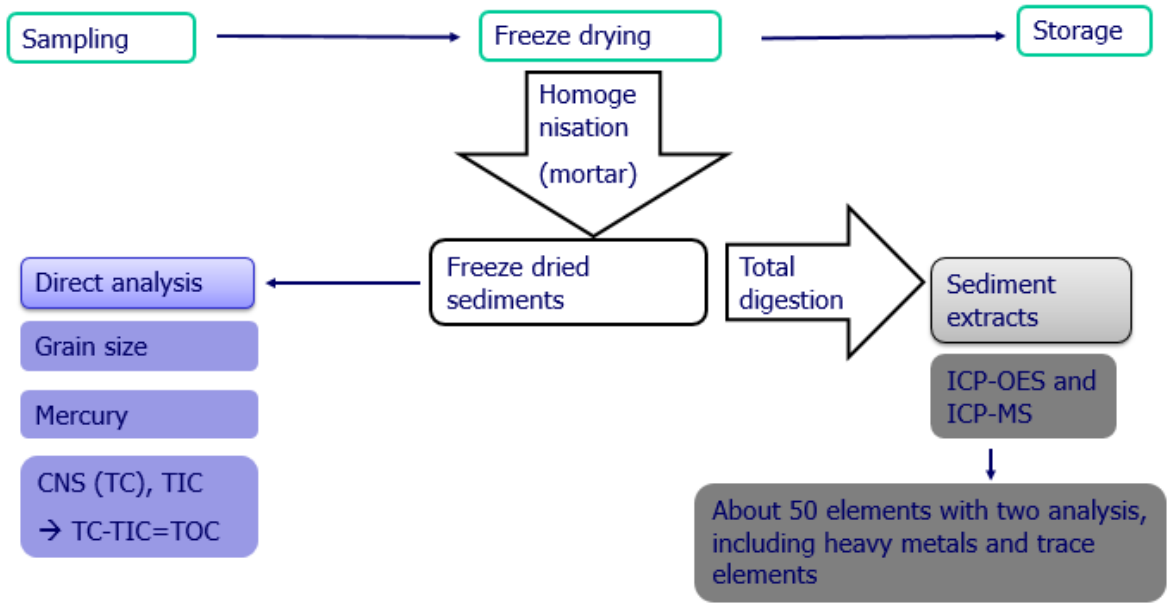

Figure 6: Schematically overview of the different methods

Figure 6 shows the chronological order of the different methods. After the sampling the sediments were freeze dried. One part of the freeze dried sample was stored. The other part was homogenised by hand with a mortar made of ceramics.

One part of the homogenised samples were directly analysed. Direct analyse methods are:

- Grain size
- Mercury
- CNS
- TIC

For analyse by ICP-OES and ICP-MS a total digestion of the homogenised sediment is necessary because the ICP needs the sample in a liquid form.

3. Results

3.1. Grain size analysis

The size of the particles was measured by laser diffraction grain size analyser CILAS 1180. The different particle size were classified by the DIN 18123. As result there are the three grain size class sand, silt and clay. The results for the whole grain size analyse are presented in the attachment in table 10.

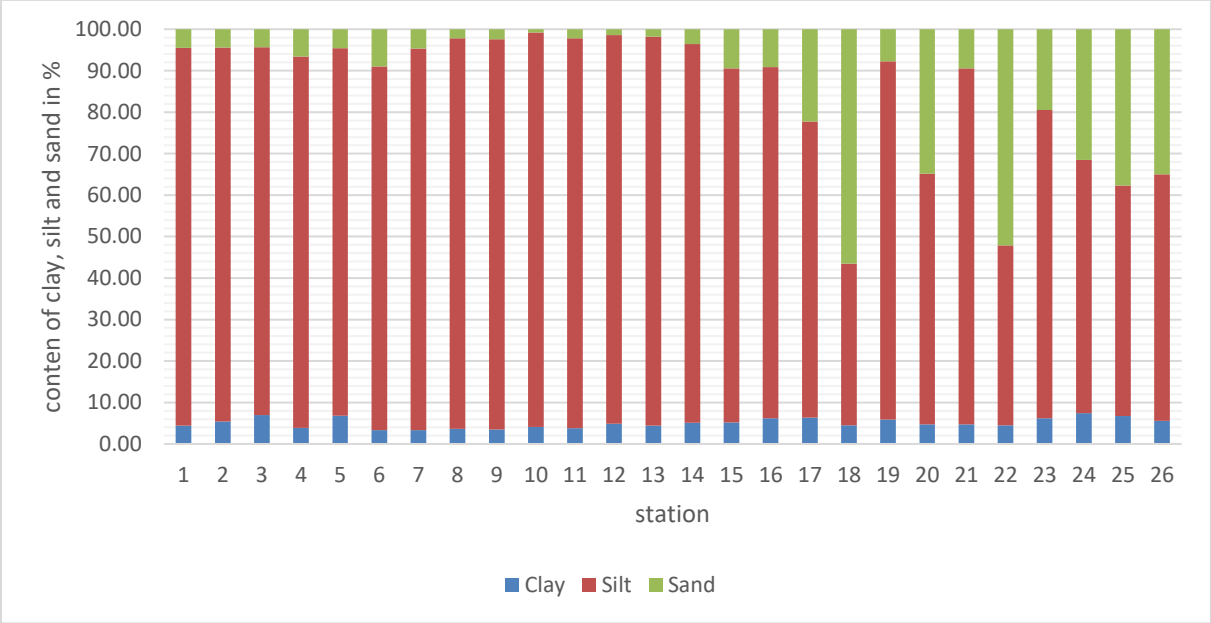

Figure 7: Particle size analyses: content of sand from station 1 to station 26

The figure 7 shows the sand content from the station 1 to station 26. The trend shows that the content of sand increase from the Mühlendamm up to the Baltic Sea. The highest sand contents are at the stations 18 and 22 with more than 50 percent. The lowest contents of sand are at the stations 10, 12 and 13 with less than 2 percent. The stations 1 to 16, except station 10, 12 and 13, has got all less than 10 percent of sand. The content of silt is higher than 90 percent. The stations 19 and 21 have also got less than 10 percent of sand. The stations 20, 24, 2 and 26 have all sand contents between 30 and 40 percent of sand. The station 17 and 23 have between 19 and 23 percent of sand.

3.2. Total carbon, total inorganic carbon and total organic carbon

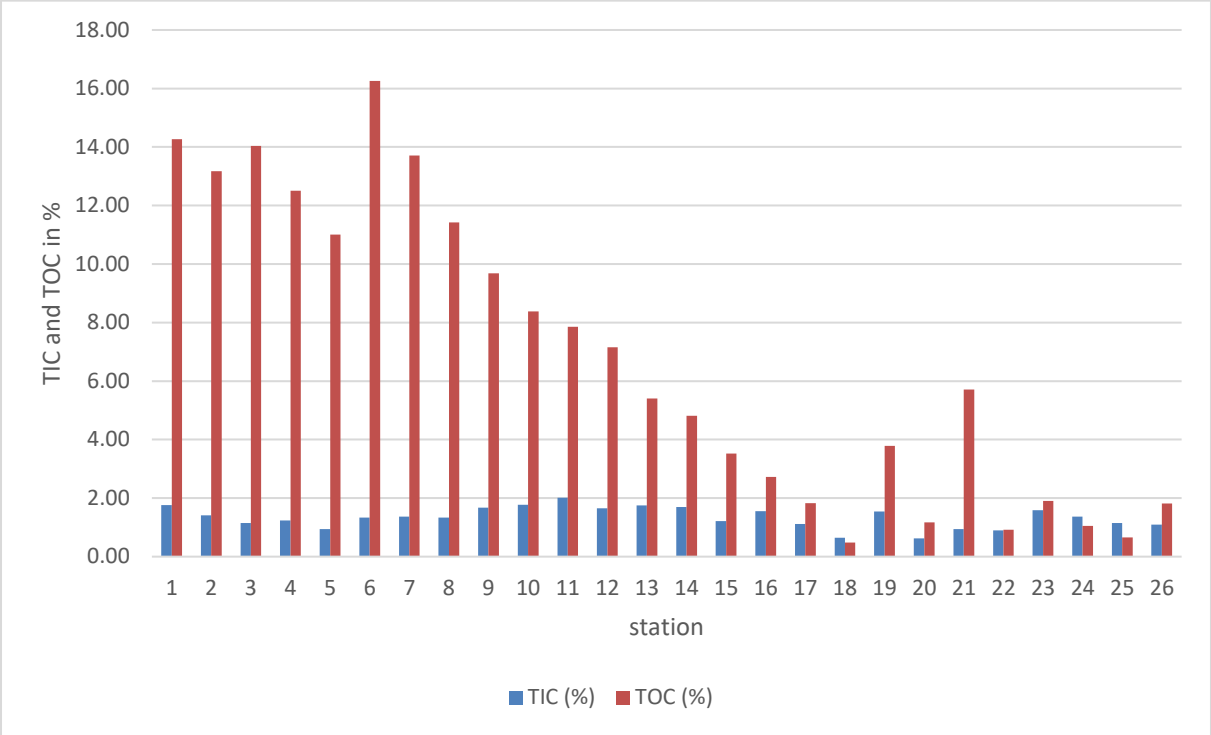

Figure 8: Contents for TIC and TOC from the sediment samples from the Unterwarnow estuary in %

The original data from CNS analyse are in the attachment in table 11. The figure 8 shows the TIC and the TOC content in the samples from the Unterwarnow estuary. The sum of both is the TC content of the sediment sample. The TIC is between 0.6 and 2.0 percent for all samples. The station 18 and 20 has the lowest TIC value with 0.6 percent. The sample from station 11 has the highest TIC content with 2.0 percent. There is no trend recognisable for the values of the TIC.

The TOC content of the stations is pictured in the red pillar. The trend shows that it decreases from station 1 to station 26. The stations 17, 18, 20, 22, 23, 24, 25 and 26 have less than 2.0 percent of TOC. The samples 1 to 8 have a TOC with more than 10 percent. The sample from station 6 has the highest TOC with 16.25 percent. The lowest TOC has station 18 with 0.4 percent. There is no relation between TIC and TOC in the sediments from the Unterwarnow estuary

3.3. Heavy metals in the sediments of the Unterwarnow estuary

The original data for the following figures 9 to 21 can be find in the attachment in table 12.

„Werden Sedimente und Schwebstoffe mittels Absetzbecken oder Sammelkästen entnommen, beziehen sich die Umweltqualitätsnormen […] bei Metallen auf die Fraktion kleiner als 63 µm“ (OGewV, 2016)

This mean in English that the results of the samples can just be compared with the environmental quality standards (EQS) from the OGewV 2016, if the content of sand is eliminated from the results. The results must be standardised by the sand content. For my results, I used the sand contents from chapter 3.1. To eliminate the sand content, I used the following equation:

Equation 1: Factors for the sand content elimination

$$F = {}^{100}/_{(100 - C_S)}$$

With:

F: Factor for the elimination of the sand content

C_S: content of the fraction which is not of interest (values see table 10)

The factors for the sand content elimination were used to multiply the values of the individual heavy metals with it. So, the content of heavy metals becomes higher because the factors are higher than 1. For the assessment of the sediments by the Dredged Material Ordinance, just the fraction < 20 µm is used. For this elimination I also used the equation 1 above.

For the following figures 9 to 21 I standardised the samples by the sand content. The values for this can be found in table 13 in the attachment.

3.3.1. The concentration of arsenic in the sediments from the estuary Unterwarnow

Figure 9 illustrate the concentration of arsenic (As) at the 26 stations of the sampling campaign. For the arsenic concentration is no trend identifiable. Peculiar is that the stations 18 and 20 has got less than 4.0 mg/kg DM of arsenic. The samples of station 6 and 7 has got the highest values with more than 14.0 mg/kg DM of arsenic. Also, the stations 1 and 8 have got high concentrations of arsenic with 13.76 and 13.79 mg/kg DM. Station has got a higher concentration than the following stations. The concentration from station 2 is 9.56 mg/kg DM.

The stations 3 to 5 have concentrations between 10.70 and 11.80 mg/kg DM. From the station 8 to station 11 the concentration of As in the sediments decreases down to 11.57 mg/kg DM. At the stations 12 and 15 the concentrations are approximately the same with 11.81 and 11.95 mg/kg DM. At the station 16 the concentration is 10.72 mg/kg DM. At the station 17 the arsenic concentration amounts 7.71 mg/kg DM. A concentration of 10.18 and 10.27 mg/kg DM have got the stations 19 and 21. From station 22 to station 24 the concentration of As increase from 4.20 mg/kg DM up to 8.27 mg/kg DM. At station 25 the concentration is 5.29 mg/kg DM. The As concentration at station 26 is 6.03 mg/kg DM.

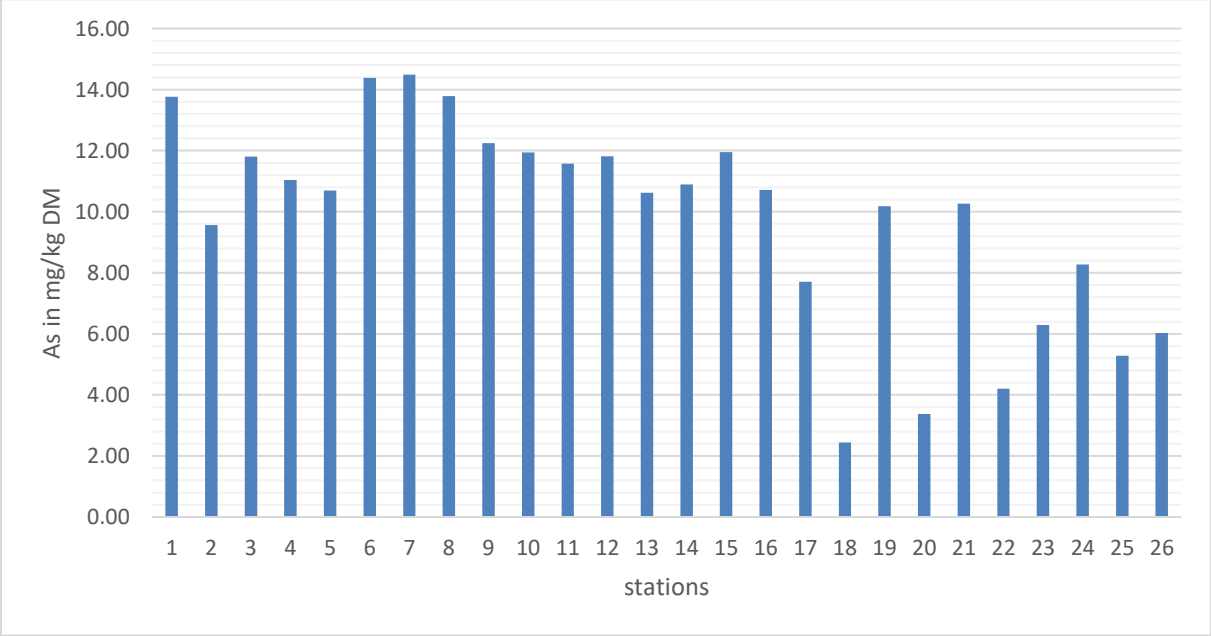

Figure 9: Arsenic concentrations at the sampling stations in mg/kg DM

3.3.2. The distribution of cadmium in the sediments from the Unterwarnow estuary

In figure 10 the concentration of cadmium (Cd) in mg/kg DM is shown. In the table 13 in the attachment the concentrations are listed. In contrast to the other heavy metals the concentration of Cd is not the highest at station 24. The highest concentration is at the station 9. Here the concentration is 1.35 mg/kg DM. The lowest concentration of Cd is at station 18 with about 0.29 mg/kg DM. The trend of figure 10 shows that the concentration of Cd increases from station 5 with 0.39 mg/kg DM to its highest concentration at station 9. In the part from station 2 to station 5 the station 4 looks like an outlier because there the concentration of Cd is about 0.2 mg/kg DM higher than at the other stations from this part.

From station 9 the concentration decreases down to 0.50 mg/kg DM at station 15. From that point, the concentration of Cd stays between 0.29 and 0.70 mg/kg DM with the outlier of station 24. At this station, the Cd concentration is 1.23 mg/kg DM. Like in all the other results for heavy metals the concentration at station 24 is higher than at the other stations around.

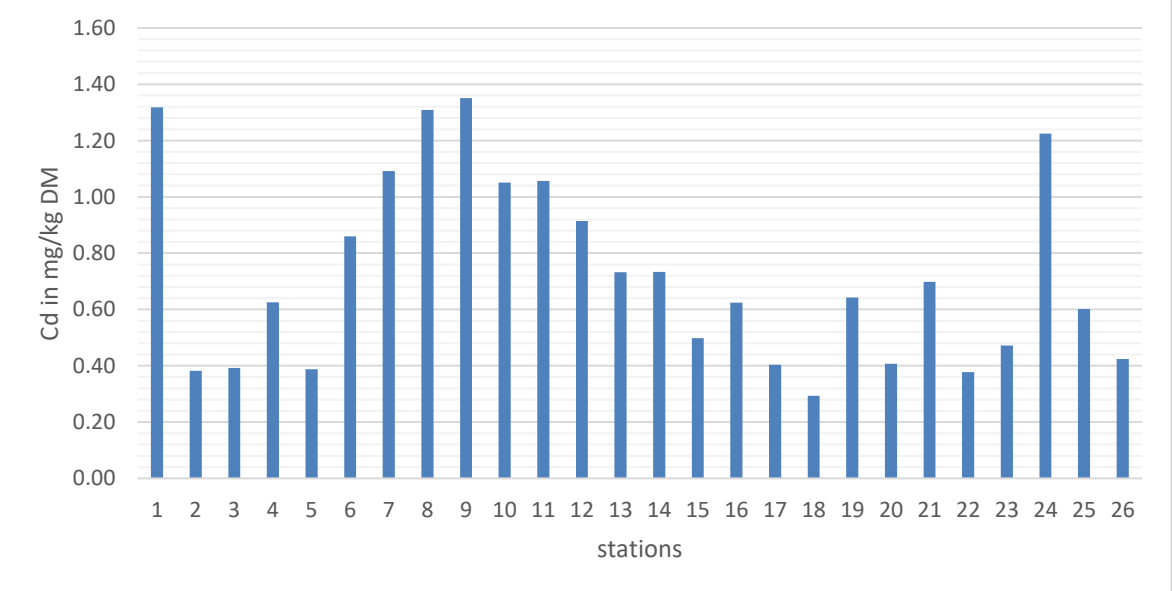

Figure 10: The concentration of cadmium in mg/kg DM in the Unterwarnow sediments from station 1 to station 26

3.3.3. Sediment samples: chrome concentrations

In figure 11 the distribution of chrome (Cr) in the sediments from the estuary Unterwarnow is shown in mg/kg DM. The values for the figure are in table 13 in the attachment. Noticeable is that the Cr concentrations do not have a peak from station 6 to 15 like the most of the other heavy metals have. The highest concentration of Cr is at station 24. Here the concentration amounts 125.52 mg/kg DM. The lowest concentration is at station 18 with 17.65 mg/kg DM. At station 1 the concentration is 56.14 mg/kg DM. There the concentration is higher than at the following stations 2 to 7.

From station 3 to station 8 the concentration of Cr increases slowly from 27.75 mg/kg DM up to 59.78 mg/kg DM. Then there is a minor decreasing peak till station 16. The concentration decreases down to 47.27 mg/kg DM. At station 16 the concentration is 62.85 mg/kg DM. At station 17 the concentration decreases down to 37.17 mg/kg DM before the lowest concentration at station 18 is reached. At the stations 19, 21, 22, 23, 25 and 26 the Cr concentration is between 43.63 mg/kg DM at station 26 and 59.28 mg/kg DM at station 22. Station 20 has got a Cr concentration of 28.27 mg/kg DM.

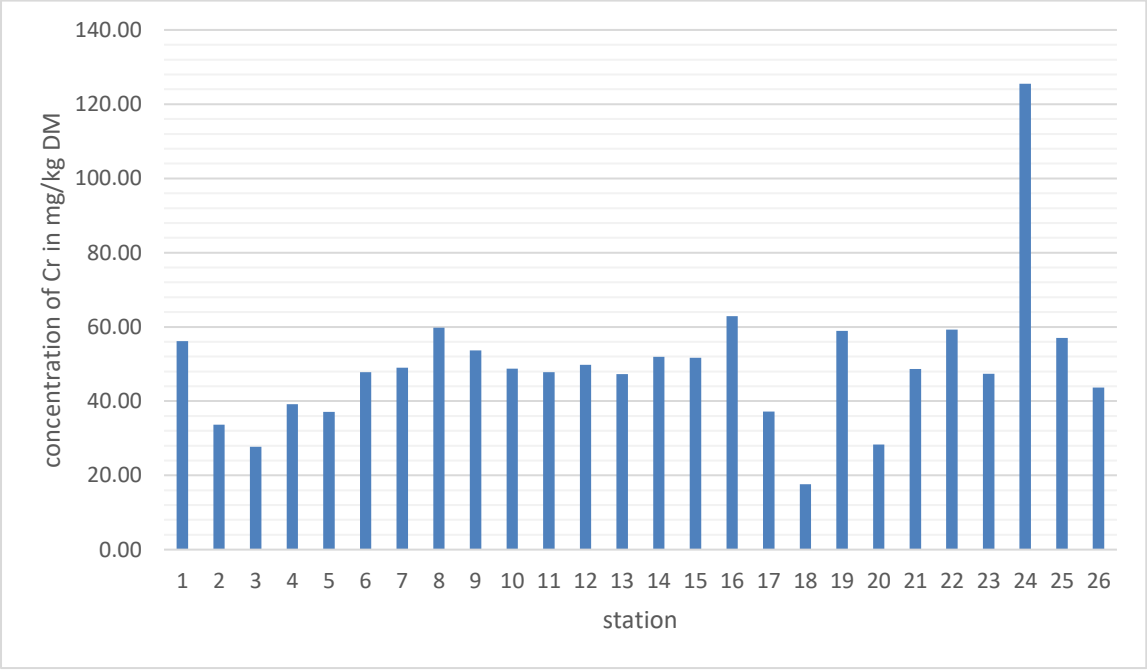

Figure 11: Chrome concentrations in the sediments from the estuary Unterwarnow in mg/kg DM

3.3.4. Copper in the sediments from the Unterwarnow estuary

Instead of all the other heavy metals the concentration of copper (Cu) is not recognisable higher at station 24 than at the other stations. In comparison with the results for the other heavy metals, the Cu concentration at station 24 is low. The lowest concentration is at station 18. Here the concentration is 18.01 mg/kg DM. The figure 12 shows that the concentration at station 1 is with 73.90 mg/kg DM of Cu higher than the concentrations from station 2 to station 5. At station 5 the concentration is 28.60 mg/kg DM. From station 6 to station 9 the concentration increases from 49.76 mg/kg DM Cu up to 106.93 mg/kg DM. Then at station 10 the concentration decreases down to 89.66 mg/kg DM.

An outlier of this trend is station 11. Here the concentration of Cu is higher than at station 10 and 12. Here the concentration amounts 130.43 mg/kg DM which is also the highest concentration for Cu of all samples from the Unterwarnow. At station 12 a decreasing trend of the Cu concentration starts. Here the concentration decreases from 79.17 mg/kg DM at station 12 to 37.70 mg/kg DM at station 15. The stations 16, 19, 21 and 24 has got Cu concentrations between 54.89 and 38.78 mg/kg DM. The stations 17, 18, 20, 22, 23, 25 and 26 has got concentrations between 18.01 and 25.65 mg/kg DM Cu.

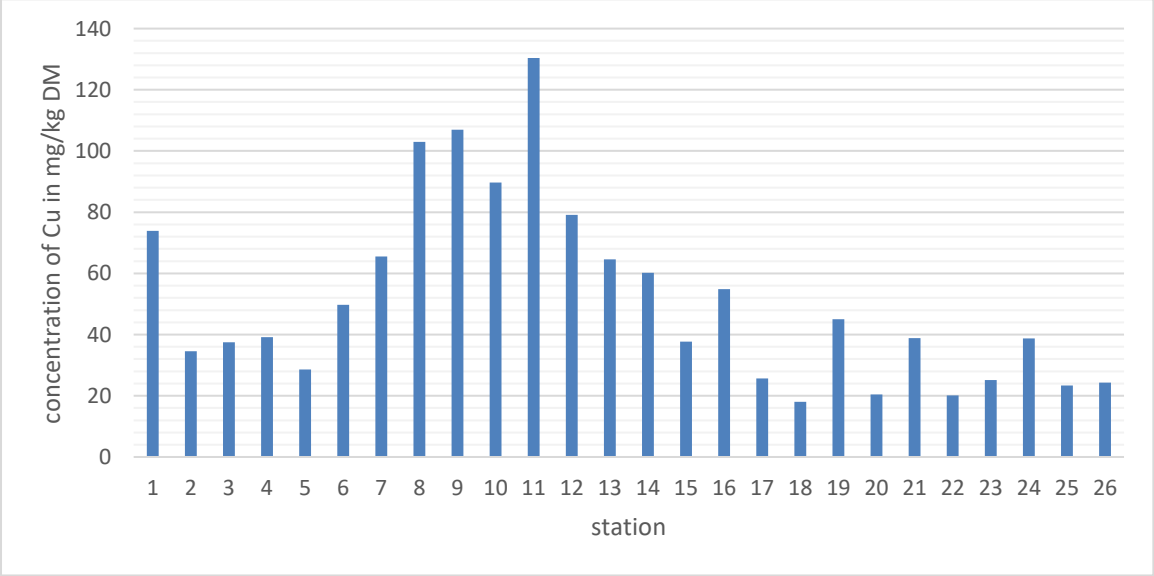

Figure 12: Copper distribution in the sediment samples in mg/kg DM

3.3.5. Mercury in surface sediments

Mercury (Hg) was measured by AAS. The results standardised by the sand content are in table 13 of the attachment. Figure 13 shows the concentration of Hg in the Unterwarnow surface sediments in µg/kg DM. At station 1 the Hg concentration is higher than 800 µg/kg DM. From station 2 to 5 there it is less than 300 µg/kg DM of Hg. At station 6 the concentration of Hg increases strong from 488.74 to 2177.34 µg/kg DM from station 6 to 9. At station 9 the Hg concentration of all samples has got the highest value. From that point, the values decrease. At station 13 is still 439.09 µg/kg DM of mercury inside the surface sediments.

At station 13 and 14 the Hg concentration is nearly the same with about 430 µg/kg DM. In comparison with the values at station 6 to 14 the Hg concentration decreases now to less than 220 µg/kg DM for the remaining stations. Just the stations 21 and 24 has got more than 220 µg/kg DM of Hg. At station 21 the concentration is 279.02 and at station 24 611.74 µg/kg DM. The stations 18 has got 53.18 µg/kg DM of mercury and the station 22 just 46.81 µg/kg DM. These are the lowest concentrations of Hg although the content of sand is eliminated. The trend of the samples shows that there is a peak of Hg at station 9. The stations next to station 9 have also got higher Hg values than the rest. Also interesting are the stations 1, 21 and 24 because they do not fit into the trend.

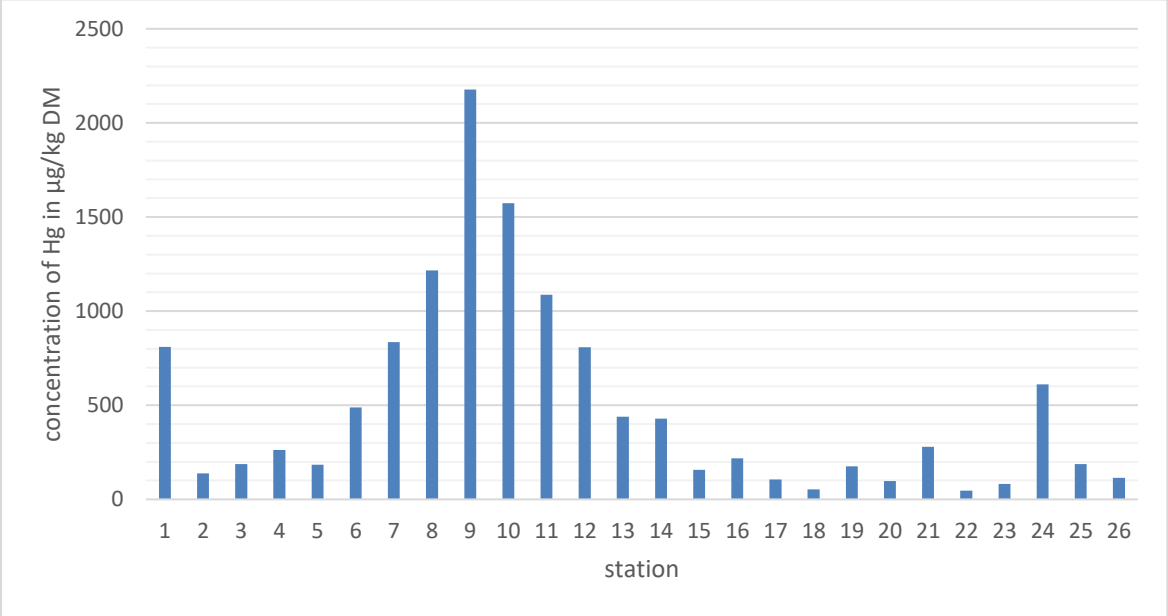

Figure 13: The distribution of mercury in the sediments from the Unterwarnow estuary, station1 is next to the weir called "Mühlendamm" and station 23 is in the Baltic Sea

For a better comprehension of the Hg in the Unterwarnow sediments, I normalised the results by TOC. That means, I divided all the results through the TOC value (values see table 3) for that sample. In figure 14 the results are represented. The figure shows that the highest Hg/TOC is at station 24. At station 24 the content of TOC is just 1.0 %, but the concentration of Hg is 612 µg/kg DM. For this low content of TOC, the Hg concentration is high so the ratio of Hg/TOC is with 400 the highest from all samples.

Like at figure 13 a peak is also shown at station 9. From station 6 to station 9 the relation of mercury and TOC increase. Then, from station 9 to station 15 it decreases. After the moderate peak, the TOC/Hg stays constant except between 73 and 44. At station 22 the Hg/TOC ratio is the lowest with just 22 from all ratios. The station 23 and 26 has got also low values with 35 and 41. Station 25 has got a Hg/TOC ratio of 177.

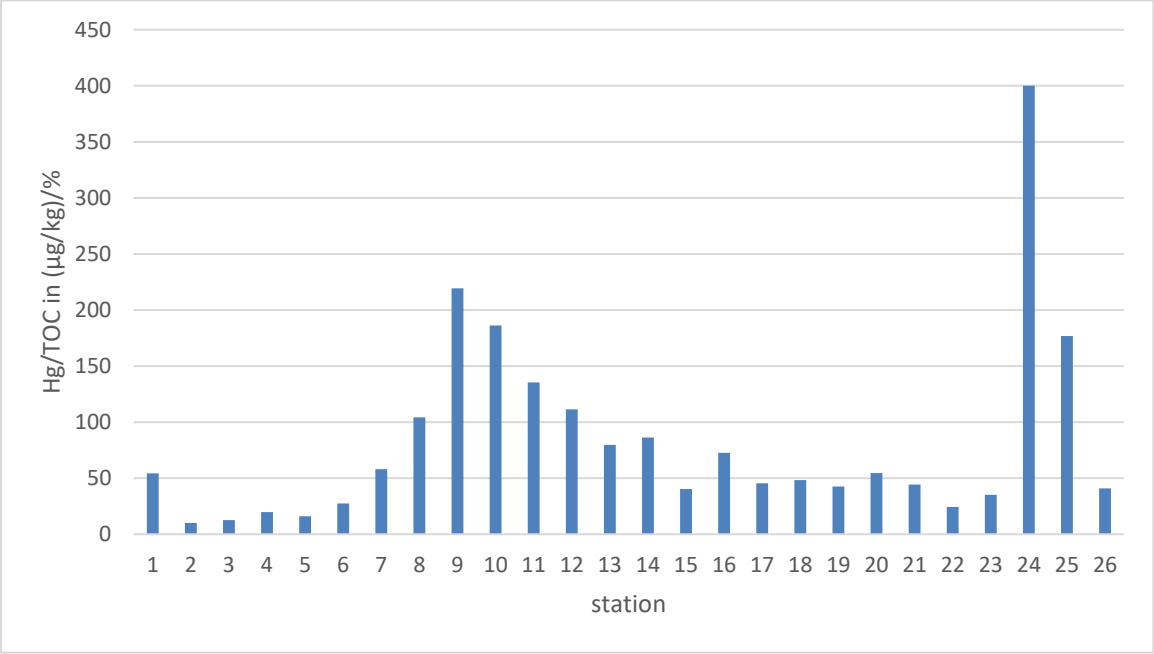

Figure 14: Hg/TOC ratio

Table 3: Hg/TOC ratios

Station	Hg/TOC in (µg/kg)/%
UWIII_1	54
UWIII_2	10
UWIII_3	13
UWIII_4	20
UWIII_5	16
UWIII_6	27
UWIII_7	58
UWIII_8	104
UWIII_9	219
UWIII_10	186
UWIII_11	135
UWIII_12	111
UWIII_13	80
UWIII_14	86
UWIII_15	40
UWIII_16	73
UWIII_17	45
UWIII_18	48
UWIII_19	43
UWIII_20	54
UWIII_21	44
UWIII_22	24
UWIII_23	35
UWIII_24	400
UWIII_25	177
UWIII_26	41

3.3.6. The concentrations of nickel at the stations from the Unterwarnow

The values for nickel (Ni) are listed in the table 13 of the attachment. The following figure 15 shows the concentration of Ni for the sampling stations in the Unterwarnow. At station 1 the concentration of Ni is 20.13 mg/kg DM. At the stations 2 and 3 the concentration is less than at station 1. Here the concentrations are 10.60 and 9.60 mg/kg DM. From station 4 to station 18 a wide peak with a moderate increase is noticeable. The highest concentration from this peak is at station 12 with about 21.87 mg/kg DM of nickel.

At station 20 the lowest Ni concentration is located. Here the Ni concentration is 11.56 mg/kg DM. At the stations 17 and 18 the concentrations are 14.18 and 14.80 mg/kg DM of Ni. At the station 19 is got the highest Ni concentration from all samples. Here the concentration amounts 24.42 mg/kg DM. From the station 21 to the station 26 the concentration of Ni is between 19.97 and 16.12 mg/kg DM.

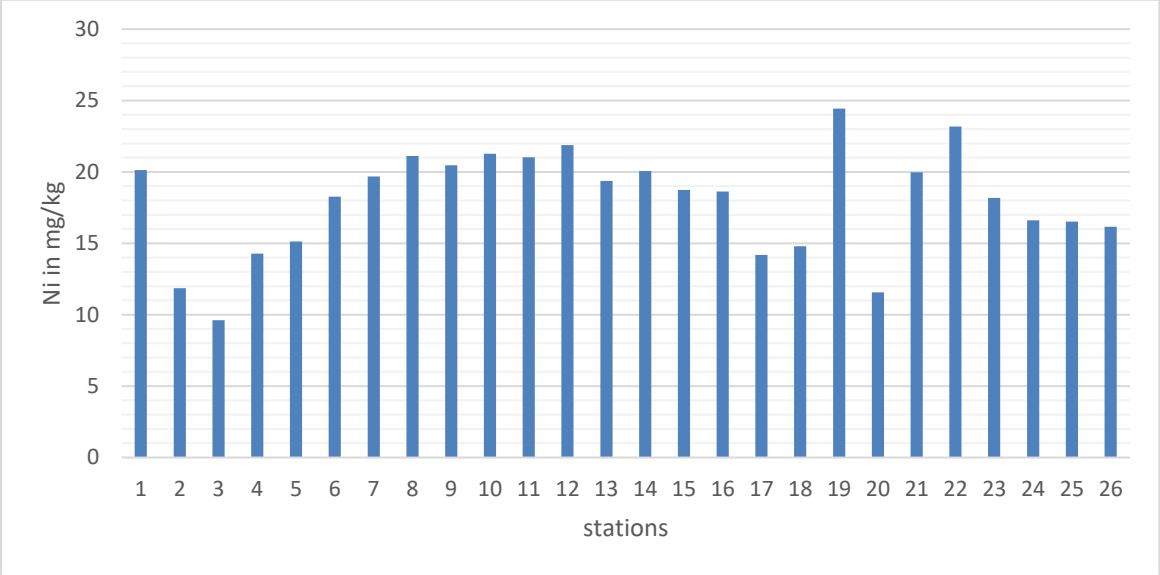

Figure 15: Concentrations of nickel in mg/kg DM in the investigation area of the Unterwarnow estuary

3.3.7. Lead concentrations in the sediments

The values for the lead (Pb) concentrations are in table 13 of the attachment. Figure 16 shows the concentration of Pb in mg/kg DM in the sediment samples. The figure shows that station 1 and 24 has the highest Pb concentrations. Sample 1 has got a high concentration of Pb with about 192.42 mg/kg DM. The trend shows that from station 5 to 9 the lead content increase from 30.66 mg/kg DM up to 75.38 mg/kg DM. Then, with the beginning at station 9, it decreases till station 15 down to 26.08 mg/kg DM. From station 15 to 23 the Pb concentration stays nearly constant between 21.54 mg/kg DM at station 18 and 32.46 mg/kg DM at station 19. At station 24 the concentration of Pb has got the highest value with 291.51 mg/kg DM. The station 20 has got the lowest Pb concentration with 21.27 mg/kg DM.

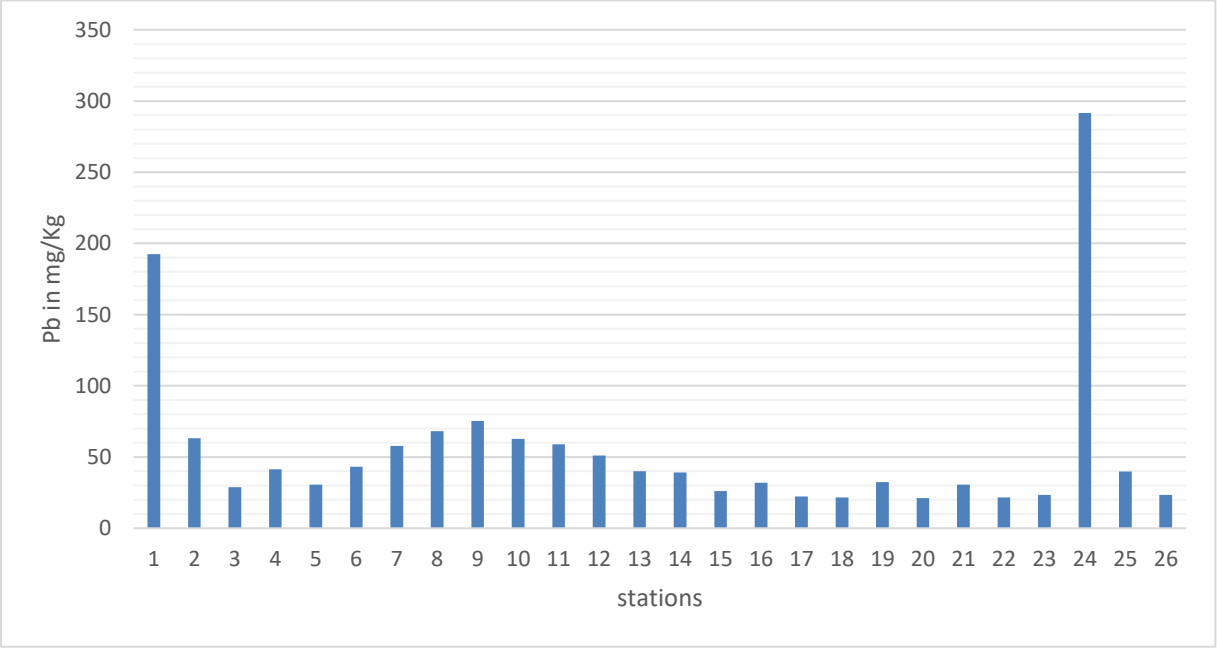

Figure 16: Lead in the sediments of the Unterwarnow estuary standardised by the sand content

3.3.8. Antimony in the Unterwarnow sediments

In table 13 of the attachment the concentrations for antimony (Sb) are listed. Figure 17 shows the concentrations of Sb in µg/g DM from the sample stations 1 to 26. The station 1 has got the highest concentration with 1.74 µg/g DM of Sb. At station 24 the concentration is just a little bit lower with 1.66 µg/g DM. The trend shows that the concentration of Sb decreases from station 1 to station 3 to 0.67 µg/g DM. Then the Sb concentration stays almost constant till station 6.

From station 6 with 0.71 µg/g DM of Sb the concentration increases up to 1.33 µg/g DM at station 8. From this point, the concentrations decrease to 0.97 µg/g DM at station 10. Station 11 does not fit in the trend because here the concentration is 1.19 µg/g DM. From station 12 to 16 the concentration of Sb stays almost constant with 0.8-0.9 µg/g DM. The following stations (17-26), excepting station 19 and 24, have got all a Sb concentration between 0.39 and 0.59 µg/g DM. Station 19 has got a concentration of 0.66 µg/g DM. The lowest concentration has got station 18 with 0.39 µg/g DM.

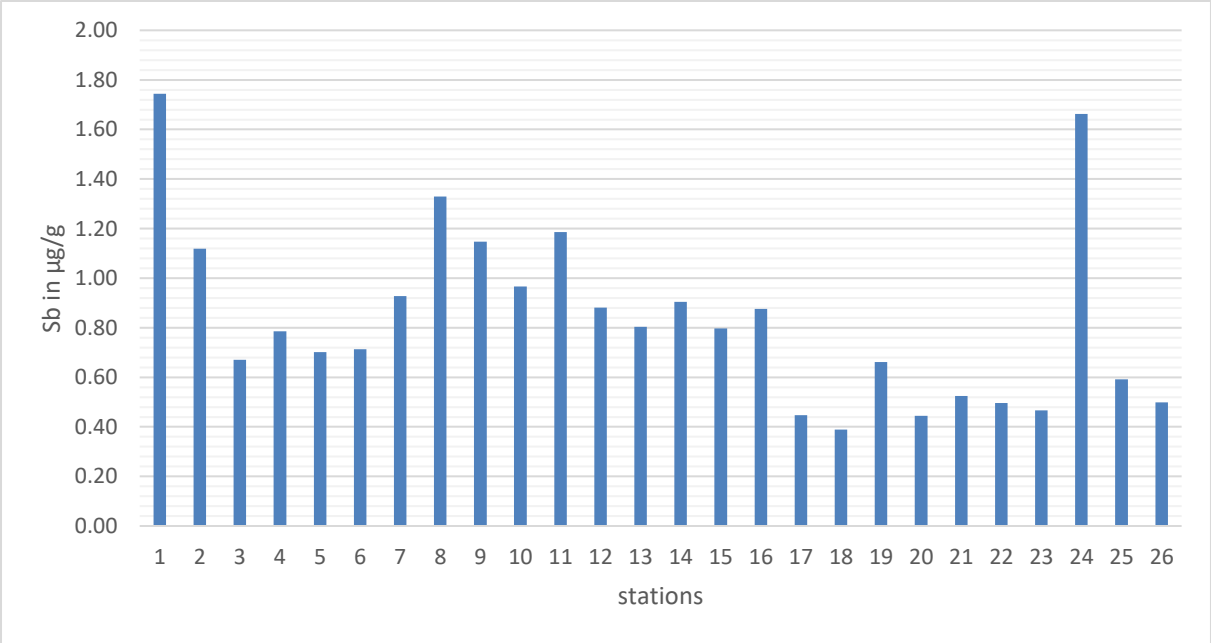

Figure 17: Antimony in the sediments from the Unterwarnow estuary in mg/kg DM

3.3.9. Zinc concentrations in the sediments from station 1 to station 26

The values of zinc (Zn) standardised by the sand content are in table 13 of the attachment. The Zn concentration of the samples is shown in figure 18. The sample 24 has got the highest concentration with more than 1750 mg/kg DM of Zn. Because of the unproportioned high concentration of Zn at station 24, I decided to make the diagram in figure 18 larger than the other diagrams from this chapter 3. At station 1 the concentration of Zn is higher than all the other stations expected station 24. At station 1 the concentration amounts 499.77 mg/kg DM. From station 5 to 12 there is the typical moderate peak, which is also by the most other heavy metals. The highest point from this peak is at station 8 with 450.53 mg/kg DM.

The lowest Zn concentration is at station 18. Here the concentration amounts 66.01 mg/kg DM. The station 22 has also got a small concentration of Zn with 67.12 mg/kg DM. The stations 17, 20, 23 and 26 have concentrations between 83.06 and 89.81 mg/kg DM.

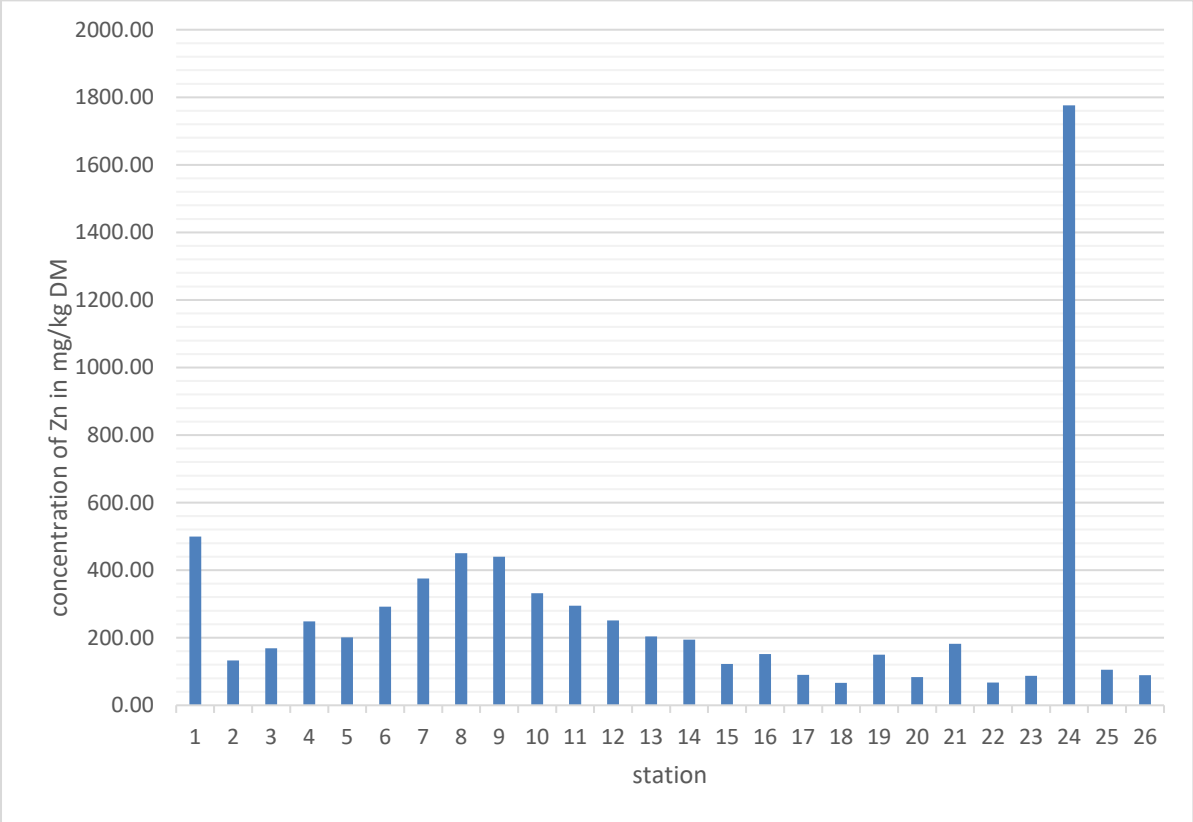

Figure 18: Zinc distribution in the Unterwarnow sediments in mg/kg DM

3.4. Manganese concentrations in the Unterwarnow estuary from station 1 to station 26

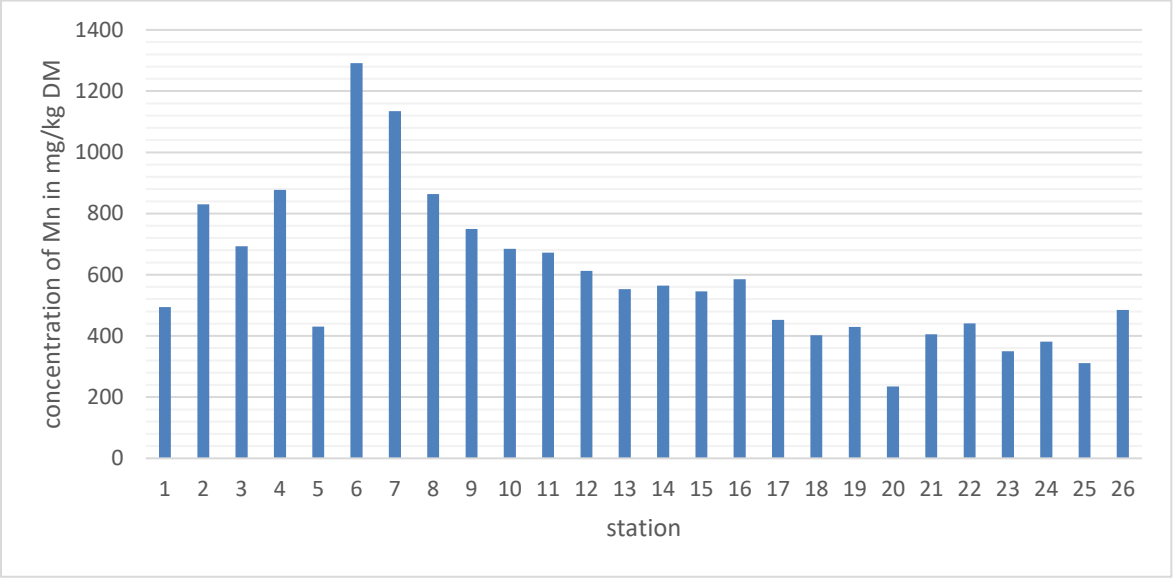

Figure 19: The concentration of manganese in the Unterwarnow in mg/kg DM

The values for the manganese (Mn) concentration is listed in table 13 in the attachment. The figure 19 shows the Mn concentration of the sampling stations in mg/kg DM. The concentration of Mn in the Unterwarnow estuary does not fit into the trend of the heavy metals which results were presented in the chapters before.

The concentration of Mn at station 1 is lower than the concentration at the following stations. The Mn concentration at station 1 amounts 494.15 mg/kg DM. At the stations 2 to 4 the concentrations are between 692.94 and 877.23 mg/kg DM. The typical moderate peak from station 5 to 12 is missing. The highest Mn concentration is at station 6 with about 1291.88 mg/kg DM. Also, the station 7 has got a high Mn concentration with 1134.62 mg/kg DM. From station 7 to station 15 the Mn concentration decreases down to 545.66 mg/kg DM.

At station 16 the concentration of Mn is 585.70 mg/kg DM. The Mn concentrations of the stations 17, 18, 19, 21 and 22 is nearly the same with values between 402.41 and 452.82 mg/kg DM. The lowest Mn concentration has the station 20 with 235.36 mg/kg DM. At the stations 23, 24 and 25 the concentration is between 311.12 and 380.89 mg/kg DM. At station 26 the concentration is 484.57 mg/kg DM.

3.5. Aluminium contents in the sediments from the Unterwarnow estuary

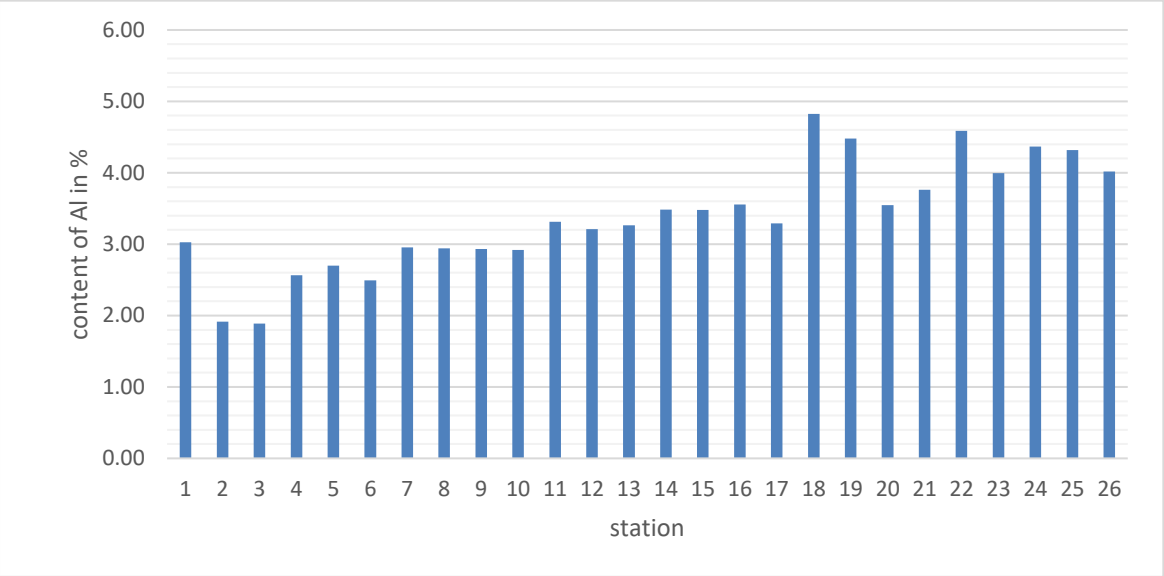

Figure 20: Aluminium contents in the sediments from the Unterwarnow estuary in %

The values for the aluminium (Al) content in the Unterwarnow sediments are listed in table 13 of the attachment. In figure 20 the Al content for the stations 1 to 26 is shown. The content of aluminium increase from the weir Mühlendamm to the Baltic Sea. Station 1 at the weir has got a content of 3.03 %. The stations 2 and 3 has got a content of Al from about 1.90 %. From station 4 to station 16 a moderate increasing trend is apparent. The content of Al increases from 2.56 % up to 3.55 %.

At station 17 the Al content is 3.29 %. At station 18 the Al content is the highest from all samples. Here the Al proportion is 4.83 %. The contents of Al are also at stations 19 and 22 high with 4.48 and 4.59 %. From station 20 to station 24 is also an increasing trend apparent excepting the station 22. The aluminium content increases from 3.54 % to 4.37 %. At station 25 and 26 the content of Al decreases down to 4.02 %.

3.6. Iron in the sediments

The values for the iron (Fe) content for the Unterwarnow sediments are listed in table 13 in the attachment. The contents of Fe in the sediments from the estuary Unterwarnow are showed in figure 21. The highest content of Fe is at station 1 with about 4.50 %. At the station 20 the lowest content of Fe with 1.45 % is located. At the stations 2 and 3 the content of Fe is nearly the same with about 2.65 and 2.66 %. At the stations 4 and 5 the content is 3.42 and 3.13 %. At the stations 6 to 12 the content of Fe is similar. For these stations, it is between 4.39 and 3.80 %.

Also, the samples from the stations 13 to 16 have similar contents of approximately 3.10 % to 2.90 %. At the stations 17 and 18 the content of Fe is 2.15 and 1.79 %. At the stations 19 and 21 the content of Fe is approximately the same with 3.26 and 3.16 %. At the stations 22 to 25 the content auf Fe is about 2.10 %. At the station 26 the content is 2.27 %.

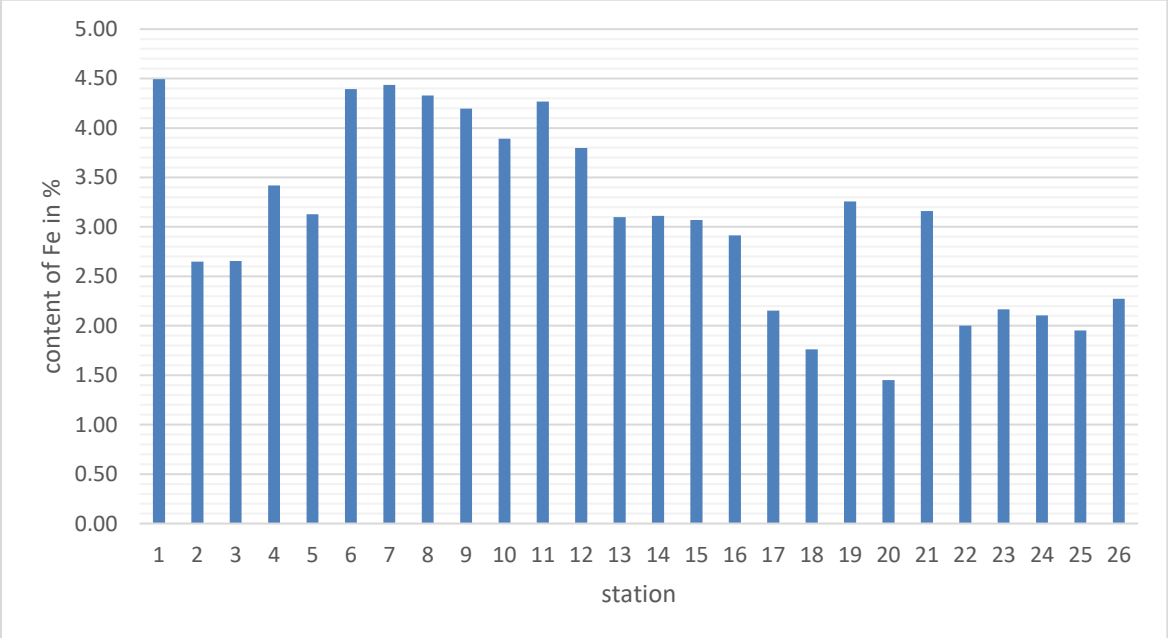

Figure 21: Content of iron in the Unterwarnow sediments indicated in %

3.7. Enrichment Factors

For a better determination of natural and anthropogenic sources the Enrichment Factor (EF) is used (Xu et al., 2015). For the EF calculation, it is important to choose the right values for the background reference. I decided to use the values from Wedepohl et al. (1972) because the background references were measured by sediments from the North and the Baltic Sea. The background references are listed in the following table 4.

Table 4: Background reference values for Heavy metals/Al ratios from Wedepohl et al. (1972)

Natural Background	As/Al	Cd/Al	Cu/Al	Cr/Al	Ni/Al	Pb/Al	Zn/Al
EF	1.12	0.015	5.1	10	7.6	2.5	10.7

Because of the effects resulting from the grain size of the samples, conservative elements like Al, Fe, Co, Sc, etc. are chosen for reference elements (Xu et al., 2015; Parra et al., 2015). For my study, I used Al as reference element. Heavy metals are adsorbed by clay minerals which is a product of minerals from aluminosilicates (Schropp & Windom, 1988; Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2001). For the calculation of the EF the following equation 2 was used:

Equation 2: Enrichment factors Xu et al., 2015

$$EF = \frac{x_s / Al_s}{x_B / Al_B}$$

With:

X_S : metal concentration of the sample

Al_s : aluminium concentration of the sample

X_B : concentration of the baseline element

Al_B : aluminium concentration of the baseline

The enrichment classes were defined by the paper Xu et al., 2015. An EF < 1.5 means that there is no enrichment. If the EF is between 1.5 and 3.0 it is a minor enrichment. Moderate enrichment means that the EF is higher 3.0 but lower 5.0. If there is a strong enrichment, the EF is higher than 5. I defined it a little bit different as you can see in the table 5 below. The reason for my modification is that with the classification of Xu et al., 2015 it is not possible to classificatory all samples.

Table 5: Classification of the EF modified after Xu et al., 2015

EF	**≤ 1.5**	**1.5<EF≤3.0**	**3.0<EF≤5.0**	**5.0<EF**
class	No enrichment	Minor enrichment	Moderate enrichment	Strong enrichment

The table 6 shows the EF for As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, Zn and Mn. Also the classification of all samples is shown. For Hg there is no EF because Hg could not be measured by ICP. Therefor I standardised Hg by TOC in chapter 3.3.5.

For Fe it is noticeable that the highest EF is at station 6 with 3.3. There the Fe is moderate enriched in the sediments. The lowest EF is at station 18 with 0.7. The trend shows that the EF are higher at the first stations than at the last stations. From station 1 to station 15 is a minor or moderate enrichment. At the following stations there is no enrichment for Fe excepted station 21 with a minor enrichment.

Mn has his highest EF at station 6. There the EF is 5.4. So Mn is strong enriched in the sediment of station 6. At the stations 2, 3, 4, 7 and 8 there is a minor enrichment of Mn. Mn has his lowest EF at station 20 with 0.7. From station 17 to 26 there is no enrichment determined in the sediment of the Unterwarnow estuary. The stations 1, 5 and 9 to 16 has got a minor enrichment of Mn.

As have the highest EF at the stations 3 and 6 with 5.6 and 5.2. There As is strong enriched in the sediment. For the stations 1, 2, 4, 5, 7 to 12 and 15 the EF are higher than3 and less or equal 5. At that stations there is a moderate enrichment of As. At the stations 18, 20, 22, 23, 25 and 26 the EF for As is lower than 1.5. So there is no enrichment for As in the sediments. At the stations 13, 14, 16, 17, 19, 21 and 24 is a minor enrichment of As.

Table 6: Enrichment Factors with classification

Station	Fe	Mn	As	Cd	Cr	Cu	Ni	Pb	Sb	Zn
UWIII_1	2,8	1,7	4,0	28,6	1,8	4,7	0,9	25,0	5,2	15,2
UWIII_2	2,5	4,4	4,5	13,1	1,7	2,8	0,7	9,0	5,3	6,4
UWIII_3	2,6	3,8	5,6	13,8	1,5	3,9	0,7	6,1	3,2	8,4
UWIII_4	2,5	3,6	3,8	16,3	1,5	3,0	0,7	6,5	2,8	9,0
UWIII_5	2,5	2,3	4,9	13,2	1,9	2,9	1,0	6,2	3,2	9,6
UWIII_6	3,3	5,4	5,2	23,0	1,9	3,9	1,0	7,0	2,6	10,9
UWIII_7	2,8	4,0	4,4	24,6	1,7	4,3	0,9	7,8	2,9	11,9
UWIII_8	2,7	3,1	4,2	29,7	2,0	6,9	0,9	9,3	4,1	14,3
UWIII_9	2,6	2,7	3,7	30,7	1,8	7,1	0,9	10,3	3,6	14,0
UWIII_10	2,5	2,4	3,7	24,0	1,7	6,0	1,0	8,6	3,0	10,6
UWIII_11	2,4	2,1	3,1	21,3	1,4	7,7	0,8	7,1	3,3	8,3
UWIII_12	2,2	2,0	3,3	19,0	1,6	4,8	0,9	6,4	2,5	7,3
UWIII_13	1,8	1,8	2,9	15,0	1,4	3,9	0,8	4,9	2,2	5,8
UWIII_14	1,7	1,7	2,8	14,0	1,5	3,4	0,8	4,5	2,4	5,2
UWIII_15	1,6	1,6	3,1	9,5	1,5	2,1	0,7	3,0	2,1	3,3
UWIII_16	1,5	1,7	2,7	11,7	1,8	3,0	0,7	3,6	2,2	4,0
UWIII_17	1,2	1,4	2,1	8,2	1,1	1,5	0,6	2,7	1,2	2,6
UWIII_18	0,7	0,9	0,5	4,1	0,4	0,7	0,4	1,8	0,7	1,3
UWIII_19	1,3	1,0	2,0	9,6	1,3	2,0	0,7	2,9	1,3	3,1
UWIII_20	0,8	0,7	0,9	7,7	0,8	1,1	0,4	2,4	1,1	2,2
UWIII_21	1,6	1,1	2,4	12,4	1,3	2,0	0,7	3,2	1,3	4,5
UWIII_22	0,8	1,0	0,9	5,4	1,3	0,8	0,5	2,0	1,0	1,4
UWIII_23	1,0	0,9	1,4	7,9	1,2	1,2	0,6	2,3	1,1	2,0
UWIII_24	0,9	0,9	1,7	18,7	2,9	1,7	0,5	26,7	3,5	38,0
UWIII_25	0,8	0,8	1,1	8,3	1,3	1,0	0,5	3,0	1,3	2,3
UWIII_26	1,0	1,3	1,3	7,0	1,1	1,2	0,5	2,3	1,1	2,1

For Ni all EF are coloured green. That means that there is no enrichment for Ni in the sediment from the Unterwarnow estuary. For Cr the highest EF is 2.9 at station 24. The lowest is 0.8 at station 18. Cr is minor or not enriched in the sediments.

The completely opposite of As and Cr is Cd. There almost all samples have got a strong enrichment. Just the sample 18 has got a minor enrichment with an EF of 4.1. The highest EF for Cd is at station 9 with 30.7.

For Pb the station 24 has the highest EF with 26.7. Also the stations 1 to 12 and the station 24 has got a strong enrichment of Pb. There the EF are higher than 5. At the stations 13, 14, 16 and 21 the Pb in the sediment is moderate enriched. At the remaining stations Pb is minor enriched. For Pb there is no station without an enrichment.

At the stations 1 and 2 the EF for Sb are the highest with 5.2 and 5.3. There Sb is strong enriched. From the stations 17 to 26 excepted station24 there is no enrichment of Sb in the sediments. For the stations 3, 5, 8, 9, 11 and 24 there is a moderate enrichment. For the remaining stations the EF is higher than 1.5 and less or equal 3.0. That means that the enrichment there is minor.

For Cu there are four stations with a strong enrichment. These are the stations 8 to 11. The highest value for the EF is at station 11 with 7.7. The lowest EF for Cu is at station 18 with 0.8. For the stations 1, 3, 6, 7, 12, 13 and 14 the EF is higher than 3.0 and less or equal 5.0. For the stations 17, 18, 20, 22, 23, 25 and 26 there is no enrichment of Cu in the sediments determined. For the remaining stations there is a minor enrichment.

Zn has got a strong enrichment from station 1 to 14 and at station 24. At that stations the highest value for the EF of Zn is 38.0. At the station 18 Zn has the lowest EF with 1.3. Just the stations 18 and 22 have no enrichment of Zn. For the station 15, 16, 19 and 21 there is a moderate enrichment of Zn. At the station 17, 20, 23, 25 and 26 Zn is minor enriched.

If you investigate the EF from the individual stations, it is noticeable that from station 1 to 16 the EF are higher than from station 17 to 26. Also station 24 has got noticeable high concentrations for the EF and station 18 has got low concentrations for the EF.

4. Discussion

4.1. Iron, manganese and aluminium in the Unterwarnow sediments

Under anoxic conditions heavy metals were bonded to Fe and Mn (Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2000). Therefore the concentration and distribution of Fe and Mn in the water body and the sediment plays an important role. “Iron, aluminium, and manganese oxide [can built] sediment coatings” (Kay et al., 2001). Especially heavy metals are adsorbed by these coatings (Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2000). Because of the changing of the oxic and anoxic conditions heavy metals can set free from the sediment to the water body. Heavy metals are more dangerous in the dissolved form (Sigg & Stumm 2016; van der Voet et al., 2000).

In figure 22 the concentrations and contents for Al, Fe and Mn is shown. The Al and Fe contents are given in %. The red and blue pillars are the Al and Fe contents. The green line shows the concentration of Mn in the samples in mg/kg DM. The left scale is for Al and Fe and the right scale is for Mn. In chapter 3.7 also the EF for Fe and Mn are listed.

For a better interpretation of the chemical bonding of heavy metals in sediment, a sequential extraction like Förstner & Calmano (1982) describe is necessary. My results just describe the whole chemical forms of the elements. Al has got higher concentrations at the stations next to the Baltic Sea. There in general the heavy metal concentrations were lower. There are also high sand contents and low TOC levels. This means that the content of Al increases with the sand content. At the stations 22 and 18 there were the highest sand contents from all samples ad there are also the highest Al contents.

The figure 21 shows also that, Mn and Fe have the same trend. At the stations next to the weir Mühlendamm the concentrations are higher than at the stations next to the Baltic Sea. Mn and Fe have the lowest concentration/content at station 20 and high concentrations/contents next to station 6. Station 1 has a different behaviour for FE and Mn. The reason for this is not found.

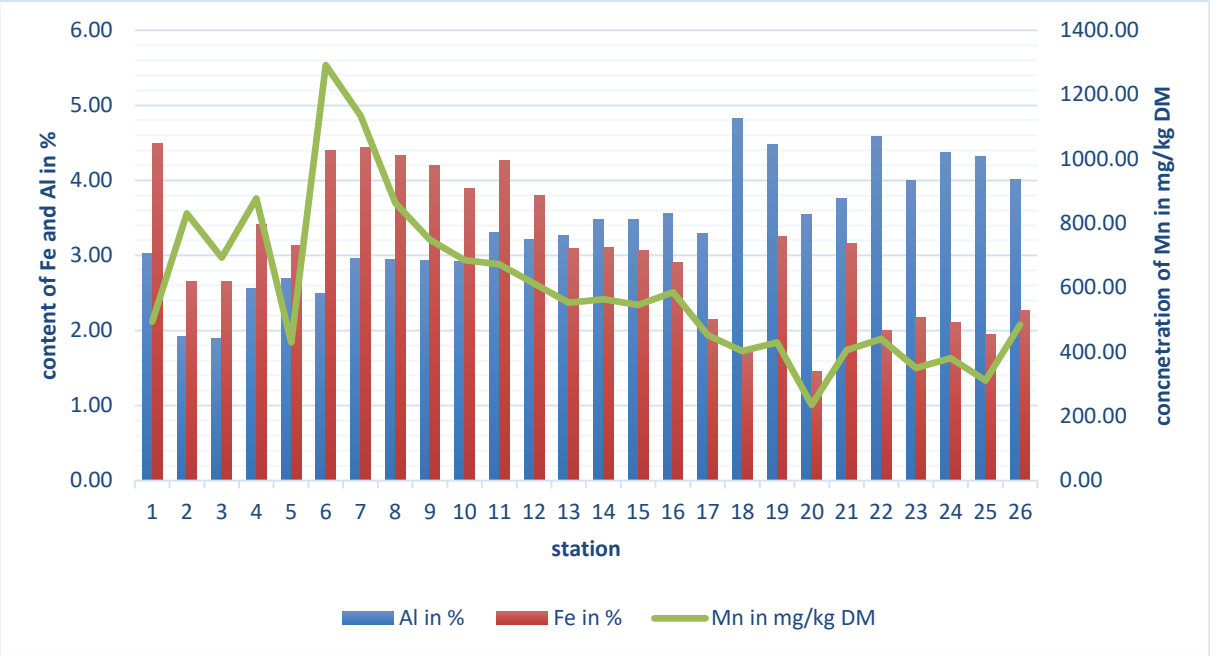

Figure 22: The content of Al and Fe in % and the concentration of Mn in mg/kg DM

Mn and Fe has got higher EF from station 1 to 15 than from station 16 to 26. The distribution of the EF shows that Mn and Fe have the same behaviour in the Unterwarnow sediments. A high enrichment of Mn has also a high enrichment of Fe as result. It is thinkable that the enrichment of Mn and Fe depends from the TOC level at the sampling stations. If the TOC is high, there are also high contents of Mn and FE in the sediment.

4.2. The distribution of heavy metals in the Unterwarnow: a location consideration

For the interpretation of the results it is important to make a location consideration of the sediment sampling stations. Therefore, I modified the figure 23. I know that my modification is a little bit untypically because of the different axis labelling. But I made this modification to show the distribution of all heavy metals in the Unterwarnow estuary. The figure shows the concentrations of all heavy metals in one diagram. At the left scale, there is the concentration of Cr, Cu, Ni and Pb in mg/kg DM. On the right scale, there is the concentration of Zn in mg/kg DM and the concentration for Hg and Cd in µg/kg DM.

The results for the EF were presented in chapter 3.7. Like you can see by the different colours in table 6 there are some elements with a strong enrichment and there are also some elements with no enrichment in the surface sediments from the Unterwarnow estuary. In figure 24 I put all EF for the heavy metals together in one diagram. There are also the different classifications mentioned. All results under the green line means that

there is no enrichment of the element in the sediment. The results under the yellow line has got a moderate enrichment. The orange line symbolised the classification of moderate enrichment. All results higher than the orange line has got a strong enrichment. The classifications moderate and strong enrichment shows an anthropogenic source of pollution. A minor enrichment could be caused by natural effects.

The figure 23 shows that at station 24 the most elements have got a peak expected Ni and As. Also, the EF for these elements are often high at station 24 (figure 24). As you can see in figure 25, the station 24 is in the maritime channel between Breitling and the Baltic Sea. At that point is a cruise center for the cruise liners of the AIDA group. The ships dock there for passenger exchange. Also the food stocks are filled up and the waste is disposed there. Sometimes there dock three AIDA ships at the same time next to station 24. At that station is also a small channel which comes from the dockyard in Warnemünde. In the dockyard of Warnemünde especially Offshore projects and ships were realised (Nordic Yards).

Especially the concentration values for Zn is striking high at station 24 in comparison with the other stations of the sampling campaign. It is also noticeable that the EF for Zn at station 24 is the highest from all samples. This concludes an anthropogenic source for the Zn pollution at station 24. Zn is often used for sacrificial anodes of ships (Zamani, 1988). This means that the Zn of the sacrificial anode corrodes. Positive Zn ions were lose into the water body to protect the ship (Zamani, 1988). The free Zn^{2+} ions were adsorbed by the suspended matter or bind with other ions or complexes to not easily dissoluble chemical combinations (UBA, 2005). After sedimentation the Zn stays in the sediment.

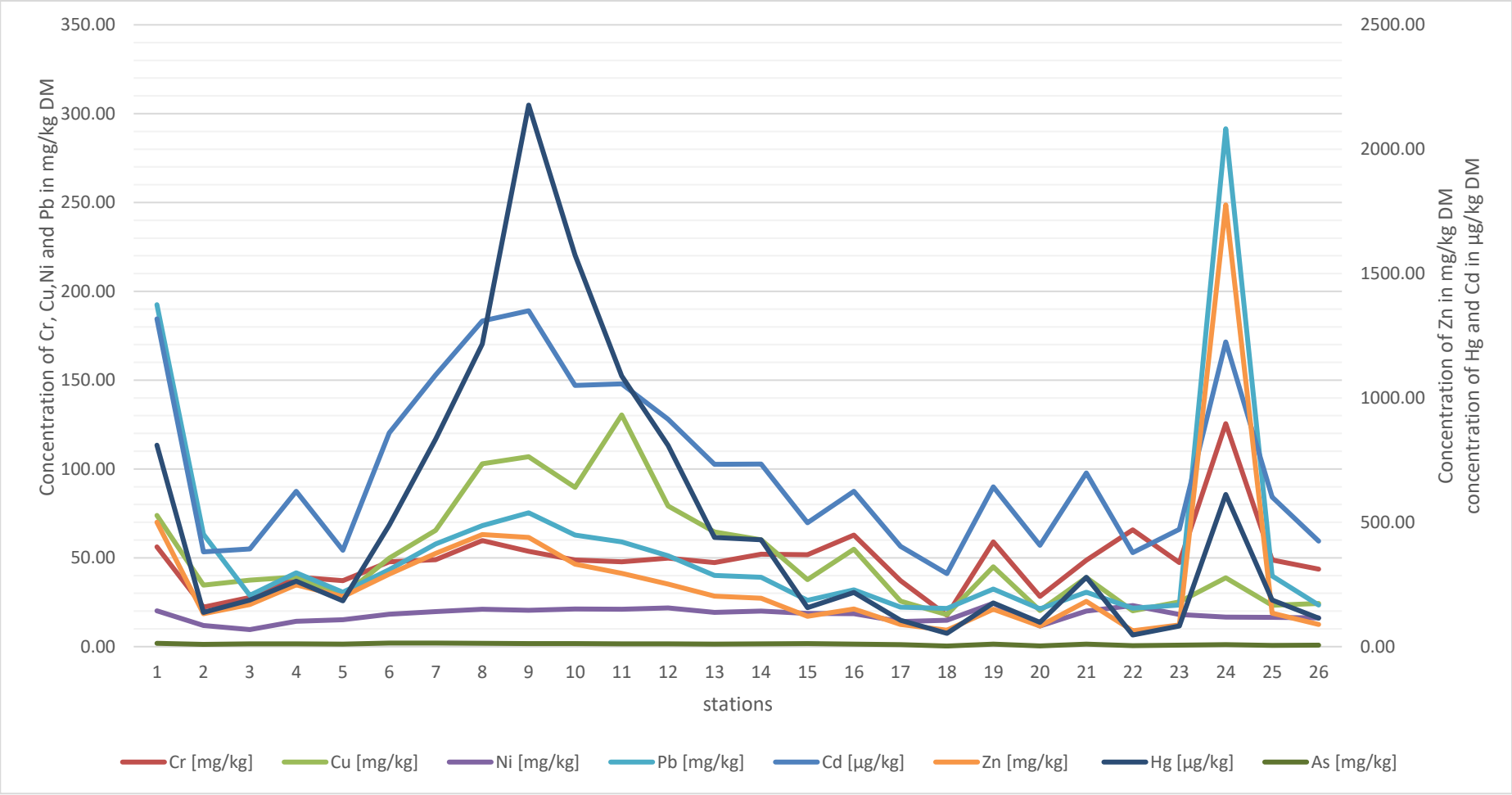

Figure 23: All heavy metals together in one diagram. At the left scale, there is the concentration of Cr, Cu, Ni and Pb in mg/kg DM. On the right scale, there is the concentration of Zn in mg/kg DM and the concentration for Hg and Cd in µg/kg DM.

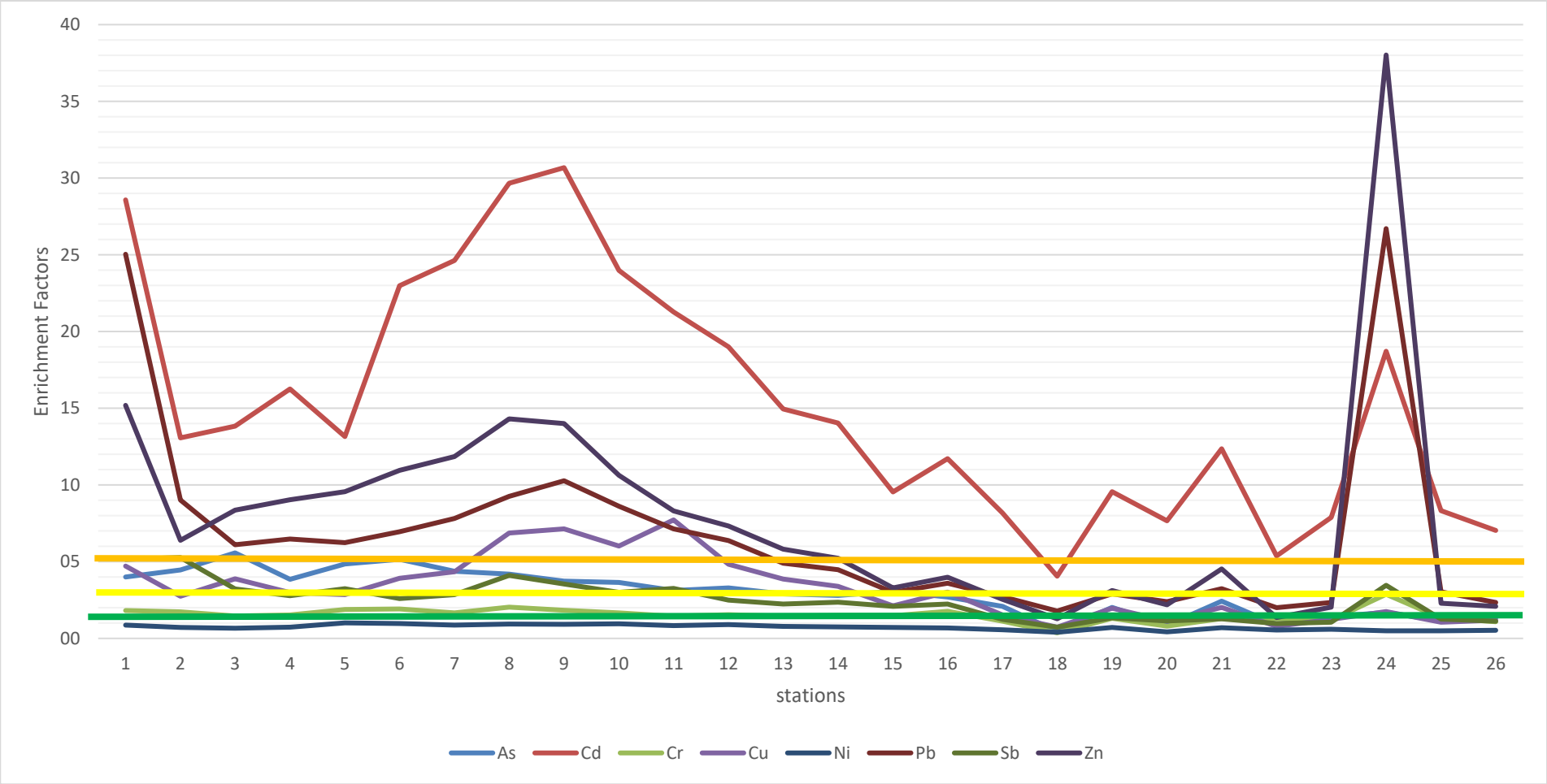

Figure 24: All EF for the investigation area together in one diagram

Also a big source for Zn in waters are the urban areas (UBA, 2005). Zn is used for galvanising against corrosion of metals. A few different types of Zn galvanising exists. So Zn is used in care tiers. The tire abrasion is also a big source for Zn I waters (UBA, 2005). In Rostock is a separate sewage system (REMONDIS AG & Co. KG, 2017). I fit is raining the Zn from the urban areas floats with the rain water directly into the Unterwarnow. It might be possible that at station 24 is also a rainwater discharge. The AIDA ships, the dockyard and a possible rainwater discharge could be the reasons for the high pollution with Zn at station 24.

Also the Pb concentration and the Pb EF is the highest at station 24. The Pb pollution is a result from anthropogenic pollution. The biggest anthropogenic source for Pb are the urban areas (UBA, 2005). There the Pb comes from the burning of fuel or roof membranes (Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2001 comes from the waste water treatment plants play an important role. For drinking water tubes Pb was used (Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2001). The influx from waste water treatment plants do not play a role at station 24.

The curves for Cd has got in both figures nearly the same course. Cd has got really high EF. Excluded station 18 and 22, with a moderate enrichment, Cd is strong enriched in every sample. So the Cd in the Unterwarnow sediments has got an anthropogenic source. Cd has got his highest concentration at station 9. This could be an influence from the waste water treatment plant but I think more that the Cd comes from the sealed areas in the city of Rostock. Cadmium results from the burning of fossil fuels (Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2001). Cadmium adsorbed be fine particles or pollen lay down onto the sealed areas. If it is raining, the rain water floats directly into the Unterwarnow because of the separate sewage system of Rostock (REMONDIS AG & Co. KG, 2017).

As you can see in figure 23 the sediments in the city harbour of Rostock, station 4 to 12, are stronger polluted than the sediments from the other stations. The EF in this area are high, too. In that area the last dredging was 1987. These are the oldest sediments from the campaign. The strong pollution could be reasoned by the age of the sediments. An age determination by gamma spectrometry might be interesting. It is also thinkable that the pollution in the city harbour is a result from the sealed areas in the city. A few heavy metals

were set free into the environment by human activity. Böhm et al., 2001 showed that the highest input of heavy metals into the aquatic environment comes from sealed areas.

The figure 24 shows that the EF for the stations 16 to 26 in general are lower than the EF for the stations 1 to 16. A reason for this could be that the sediments from the stations next to the Baltic Sea are younger than the sediments from upstream. In Breitling next to the Baltic Sea the water channel is 14.5 metres deep. Here the last dredging was in 2014/15. Maybe the different times of dredging has got an influence onto the distribution of heavy metals. With dredging the heavy metals from the higher polluted areas in the surface sediments were removed.

At station 1 is the weir of the Mühlendamm. There the Oberwarnow flows into the Unterwarnow. My results show that the pollution with heavy metals is higher at station 1 than at the following to stations 2 and 3. The reason for this is that, the suspended matter from upstream flows through the weir into the Unterwarnow. The most heavy metals in the water column are bonded to suspended matter so they get into the Unterwarnow with the water flow from the Oberwarnow (Calmano et al. 1993). At station 2 is an old lock for small sips which is not used since a lot of years. That means that at station 2 no or just a little bit of water from the Oberwarnow get into the Unterwarnow. That is the reason why the heavy metal concentrations and the EF are much higher at station 1 than at station 2. My hypothesis that the inflow from the Oberwarnow plays an important role for the pollution of the Unterwarnow is confirmed.

For all heavy metals, station 18 has the lowest concentrations. Also, the EF are the lowest at this station. Station 18 has got the highest sand content from all stations. The station 22 has got a high sand content, too. There are also low heavy metal concentrations and EF at station 22. The results for these both stations shows that a sand content of more than 50 % has got a great influence for the pollution with heavy metals. The result from a high sand content is a low pollution with heavy metals.

The figure 23 also shows that the different heavy metals has got the same behaviour. Between the stations 16 and 20 it is good to see that all heavy metals in the sediment samples has got the same peaks and downs. A reason for this could be that at the stations next to the Baltic Sea the TOC content is low so there is no influence of the TOC for the

heavy metal behaviour. The samples there has got different contents of sand. If the sand content is high, the heavy metal pollution is low. At the stations with a low sand content the heavy metal concentrations and EF are higher.

The hotspot of Hg pollution is at station 9. Also the station 10 as got a concentration with more than 1500 µg/kg DM of Hg. Figure 23 just show the concentrations of Hg in the surface sediments form the Unterwarnow estuary, not the Hg/TOC ratios. The nomination of Hg by the TOC is more significant because the influences of the grain size are eliminated. The station 24 has got the highest Hg/TOC ratio. Also the stations 7 to 12 and the station 25 have higher Hg/TOC ratios than the other stations.

One of my hypothesis was that the concentrations of heavy metals are higher at the stations next to the waste water treatment plant of the city of Rostock. The waste water treatment plant is between the stations 10 and 11 (see figure 25). The results of my measurements show that the concentrations are not the highest at station 10 and 11. There is a moderate peak at these stations but not the highest heavy metal concentrations and EF from that peak are at station 10 and 11.

Maybe the current of the Unterwarnow estuary plays an important role for the distribution of the pollutants near to the waste water treatment plant. Because the highest heavy metal concentrations and EF are at station, except Cu. It is thinkable that the current in the Unterwarnow is upstream. Then the Pollution from the waste water treatment plant may sediment at station 9. It is also possible that the pollution at station 9 does not come from the waste water treatment plant. One of my hypothesis was that there are higher heavy metal concentrations at the water treatment plant. This hypothesis could not be confirmed or refuted with my research.

For nickel, there was no enrichment found in the samples. Ni is used as sheathing for ships. In combination with about 90% of Cu the alloy of Cu-Ni is really resistant against salt water. The alloys of Cu-Ni were used as “protection to corrosion and for biofouling in sea water since the 18 th century” (Powell, 1994). This means that the nickel in the samples is from natural sources. No anthropogenic influence was found for Ni. This agrees with the results of Ni in chapter 3.3.6. The concentrations of Ni is related to the other heavy metals is much lower. Ni is often used for alloys of ships. The results show that the Cu-Ni alloy which are

used for ships are resistant against environmental conditions. So there is nearly no Ni set free into the environment.

The stations 18 and 26 are next to each other like it is shown in figure 25. It is surprising that e results for station 28 and 2 are different from each other. A reason for this is the natural patchiness (Leipe, 2016). That means because of the natural influences the samples which are next to each other, must not be the same. There could be really high differences between these samples. Station 18 has got a high content of sand. This could be another reason for the low heavy metal concentrations.

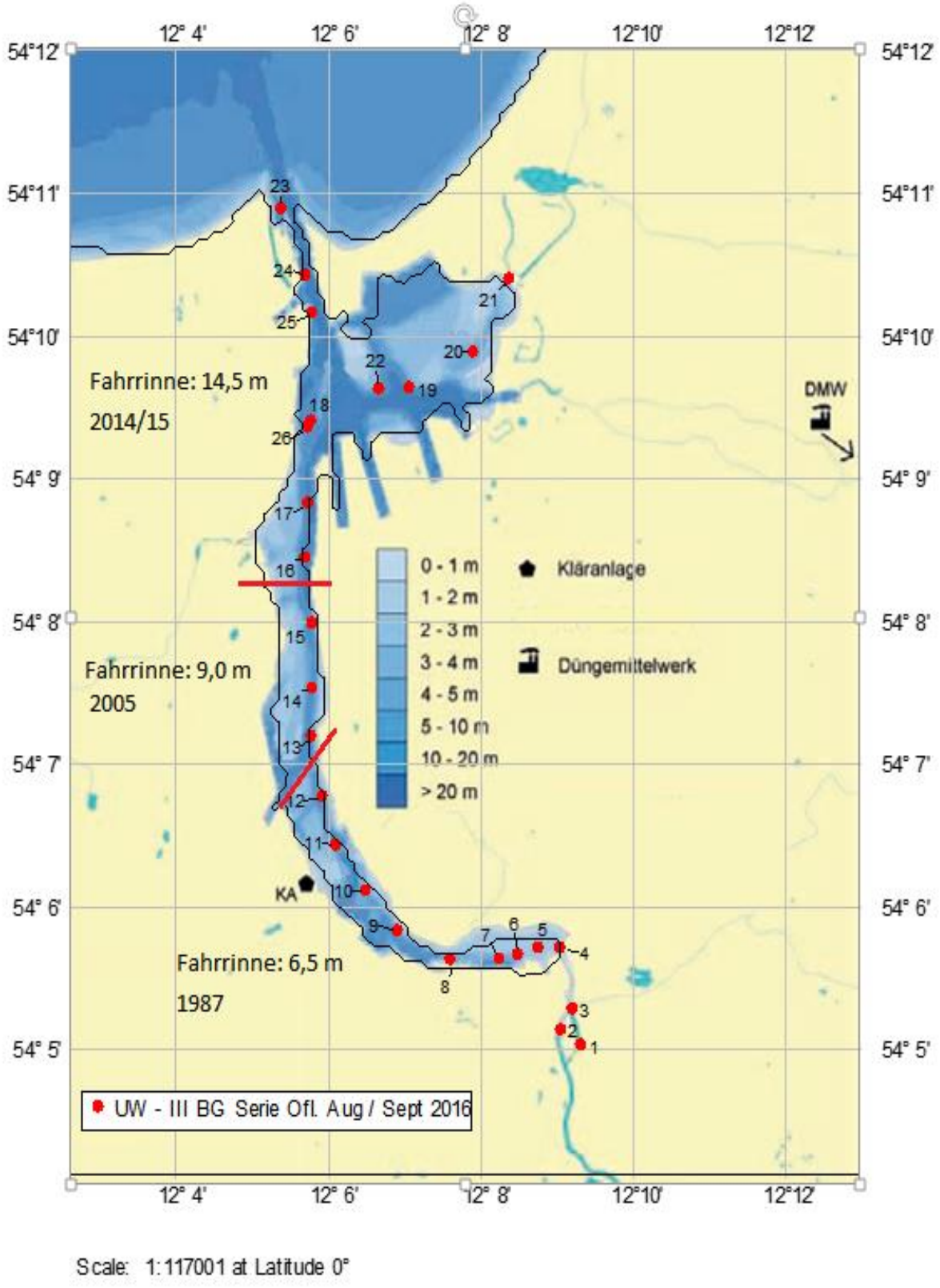

Figure 25: The Unterwarnow with the 26 sampling stations. There are also the different shipping channel depth listed, modified after Bachor (2005)

4.3. Quality assessment of the sediments with consideration of the regulations Oberflächengewässerverordnung, Dredged Material Ordinance and Sewage Ordinance

For four heavy metals I investigated are EQS in the OGewV 2016. In the following table 7 the EQS are listed.

Table 7: EQS for a good chemical quality for coastal waters from the OGewV 2016

Heavy metal	**EQS for coastal waters in suspended matter or sediment in mg/kg DM (grain size < 63 µm)***
Cu	160
Zn	800
As	40
Cr	640

**see chapter 3.3. for the explanation*

For Cu, As and Cr the EQS are observed at all sampling stations. That means that for these elements the chemical quality, like it is explained in the OGewV 2016, is good. For Zn the EQS of 800 mg/kg is exceed at station 24. There the concentration is 1776.2 mg/kg of Zn in the dry matter. The concentration there is more than two times higher than the EQS allows. For the chemical quality means that, that the quality of the Unterwarnow is bad. The sediments of the Unterwarnow estuary does not meet the expectations of the EU Water Framework Directive 2000 for the chemical quality of the river. This means that to city of Rostock of the Federal state Mecklenburg-Vorpommern must involve a concept for a good state of chemical quality.

In August 2009, the Federal state of Mecklenburg-Vorpommern and some other federal states in Germany decided the Dredged Material Ordinance from coastal waters (German “Baggergutverordnung”). In that guideline, the concentration of heavy metals is measured by a grain size smaller 20 µm. In the following table 8 I named all the guidelines for heavy metals in the coastal waters of the Baltic Sea.

Table 8: Limit values for the concentrations of heavy metals in the sediment by the Dredged Material Ordinance 2009

Heavy metal	**Limit values in sediment in mg/kg DM (grain size < 20 µm)***
As	60
Pb	300
Cd	66
Cr	270
Cu	210
Ni	210
Hg	1,2
Zn	750

**in the Dredged Material Ordinance the heavy metal concentration from the particles with a size < 20µm is determined*

In table 14 of the attachment I present the concentrations for the heavy metals standardised by the grain size < 20µm. For Pb, Cu, Ni, Hg and Zn the limit values are exceeded. The result of the limit value exceedance is that the dredging of the sediments has certain conditions. Before a dredging a lot of investigations and assessments of the sediments has to be made. A solution for the final storage of the polluted sediment has to be find. In the Dredged Material Ordinance 2012 in chapter 4.4.2.2 all steps for the deposition of high polluted dredged material are listed.

Table 9: Limit values from the Sewage Ordinance 2012

Heavy metal	**Limit values in sediment in mg/kg DM**
Pb	100
Cd	1,5
Cr	100
Cu	60
Ni	50
Hg	1
Zn	200

In table 9 the data from the Sewage Ordinance 2012 are listed. I decided to use the values from the Sewage Ordinance to show that it is not allowed to put the dredged sediment from the Unterwarnow onto agricultural areas. In the attachment in table 12 I present the original values of the sediment without the elimination of the sand content. The values for Pb are at the stations 1 and 24 higher than the Sewage Ordinance allows.

For Cd, Cr and Ni the limit values were complied. For Cu the stations 1 and from station 7 to 13 the heavy metal concentrations are higher than the limit values from the Sewage Ordinance. From the stations 8 to 11 the limit values for Hg were exceeded. Zn exceed the limit values at the stations 1, 4, 6 to 12 and at station 24. This shows that the dredged material could not bring onto agricultural areas.

For the 800 anniversary the city of Rostock want to dredge material from the city harbour. With the results from my Bachelor thesis I show in this chapter that the dredging of the Unterwarnow sediments is not so easy. The reason for this is that the limit values in three different Ordinances were exceeded. That means that the politicians has to make a lot of assessments ad investigations before a dredging is possible. One idea could be to dredge the material and to bring it onto a landfill. The problem is that this way has got high costs. Another idea could be to bring sediments onto agricultural grounds.

“Seafloor infrastructure projects always affect the seabed by resuspension of old sedimentary matter into the water column. “(Vallius, 2015). In my opinion the polluted sediment should stay in the Unterwarnow. A dredging has got the resuspension of heavy metals into the water body as result.

4.4. Conclusion and Outlook

Station 24 has got high values for the heavy metal concentrations and the EF. This result was surprising. The source for the high concentrations there could be the AIDA cruise centre or the shipyard. It is also thinkable that the pollution comes from sealed areas. Also station 1 has got high heavy metal concentrations. The source for these high concentrations is the Oberwarnow. The suspended matter comes from the Oberwarnow and sediment behind the weir at station 1.

The station 18 is the station with often the lowest concentrations and the lowest EF. Also the station22 has got low heavy metal concentrations. The reason for this is the low TOC and the high sand content at both stations.

The limit values from the Sewage Ordinance and the Dredged Material Ordinance are not observe. Also the EQS from the OGewV are not observe. A dredging of the polluted sediment in the area of the city harbour without additional conditions is not possible. The city of Rostock has to find a way for the deposition of the dredged sediment. Because the sediment is high polluted with heavy metals. In my opinion, the high polluted sediment should stay in the Unterwarnow. A dredging of these sediments will resuspend heavy metals in the water body and that is more dangerous for the ecosystem.

For more information about the sources for the pollution in the Unterwarnow estuary, more research is necessary. It is interesting how old the sediments samples are. So, an age determination by gamma spectrometry is useful. At the high polluted stations 1, 9 and 24 the investigation of sediment cores should be made. Also the measurement of organic pollutants is interesting.

5. Literature

Analytik Jena, unknown. Operating instructions for Multi EA 4000

Bachor, A., 2005. Nährstoff- und Schwermetallbilanzen der Küstengewässer Mecklenburg-Vorpommerns unter besonderer Berücksichtigung ihrer Sedimente. Landesamt für Umwelt Naturschutz und Geologie Mecklenburg-Vorpommern

Böhm, E.; Hillenbrand, T.; Marscheider-Weidemann, F.; Schempp, C.; Fuchs, S. & Scherer, U., 2001. Bilanzierung des Eintrags prioritärer Schwermetalle in Gewässer im Auftrag des UBA, http://www.umweltbundesamt.de/publikationen/bilanzierung-des-eintrags-prioritaerer , last date of opening 24.06.2017 12:13

Caeiro, S.; Costa, M.H.; Ramos, T.B.; Fernandes, F.; Silveira, N.; Coimbra, A.; Medeiros, G. & Painho, M., 2005. Assessing heavy metal contamination in Sado Estuary sediment: An index analysis approach. *Ecological Indicators 5*, 151–16

Calmano, W.; Hong, J. & Förstner, U., 1993. Binding and mobilization of heavy metals in contaminated sediments affected by pH and redoxpotential. *Wat. Sci. Tech. Vol. 28*, No. 8--9, pp. 223-235

Chiappetta, J.; Machado, W.; Santos, J. & Lessa, J.; 2016. Trace metal bioavailabilty in sediments from a reference site, Riberia Bay, Brazil. *Marine Pollution Bulletin 106*, 395-399

Cilas, unknown. Brochure Particle size analyse CILAS 1180

Dellwig, O., 2017. Personal communication

Dredged Material Ordinance, 2009. Gemeinsame Übergangsbestimmungen zum Umgang mit Baggergut in den Küstengewässern

Einfeldt, 2015. Lecture notes from the winter semester 2015/16

Fent, K.; 2013. Ökotoxikologie Umweltchemie-Toxikologie-Ökologie, Georg Thieme Verlag Stuttgart-New York

Förstner U. & Calmano, W., 1982: Bindungsformen von Schwermetallen in Baggerschlämmen. *Vom Wasser 59,* 83-92

HekaTech GmbH, unknown. Operating instructions for CHNSO Elemental Analyser

Kay, J.T.; Conklin, M.H.; Fuller, C.C. & O'Day, P., 2001. Processes of Nickel and Cobalt Uptake by a Manganese Oxide Forming Sediment in Pinal Creek, Globe Mining District, Arizona. *ENVIRONMENTAL SCIENCE & TECHNOLOGY 35,* 4719-4725

Klank, D., 2002. Partikelanalyse mit CILAS-Laserbeugung: Normgerecht von der Probenteilung bis zur Messung. *QUANTACHROME PARTIKELWELT NO 1*

Knöll, J., 2012. Ultraspurenbestimmung von Aminopolycarbonsäure-Komplexbildnern mittels inverser on-line Kopplung IC-ICP-MS. *Dissertation of the Philipps-University of Marburg*

Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2001. Chemische Untersuchungen ausgewählter Seensedimente in Schleswig-Holstein

Leipe,T., 2016. Personal communication

Marquardt, 2012. Basiswissen der ICP-Spektrometrie. Thermo Fisher Scientific, Dreieich

Meyer, A., 2017. Rostocks tickende Gift-Bombe. Article in: *Ostseezeitung,* 09.02.2017

MLS GmbH, unknown. Operating instructions for DMA-80

Nordic Yards, unknown. http://www.nordicyards.com/nordic_yards.html#facilities last date of opening 25.06.2017 11:18

Parra, S.; Bravo, M.; Quiroz, W.; Querol, X. & Paipa, C., 2015. Distribution and pollution of trace elements in marine sediments in the Quintero Bay (Chile). *Marine Pollution Bulletin 99,* 256-263

Powell, C.A., 1994. Copper-Nickel Sheathing and its Use for Ship Hulls and Offshore Structures. *International Biodeterioration & Biodegradation*, 321 331

Renberg, I.; Bindler, R. & Brännvall, M., 2001. Using historical atmospheric lead-deposition record as a chrnological marker in sediment deposits in Europe. *The Holocene 11*, 511-516

REMONDIS AG & Co. KG, 2017. Eine Anlage - viel Nutzen: insgesamt für circa 230.000 Einwohner. http://www.eurawassernord.de/geschaeftskunden/abwasser /wissenswertes/klaeranlage-rostock/einzugsgebiet/, zuletzt abgerufen am 04.01.2017 08:28 Uhr

RL 2000/60/EG (Water Framework Directive), 2000. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. http://eur-lex.europa.eu/resource.html?uri=cellar:5c835afb-2ec6-4577-bdf8-756d3d694eeb.0004.02/DOC_1&format=pdf last date of opening 27.06.2017 12:35

Schropp, S. & Windom, H., 1988. A GUIDE TO THE INTERPRETATION OF METAL CONCENTRATIONS IN ESTUARINE SEDIMENTS

Sewage Ordinance, 2012. Klärschlammverordnung vom 15. April 1992 (BGBl. I S. 912)

Sigg, L. & Stumm, W., 2016. Aquatische Chemie, ISBN 978-3-7281-3767-8, 6. Auflage, vdf Hochschulverlag AG an der ETH Zürich, S 424 ff.

Schumann, R.; Sievert, C. & Schiewer, U., 1992. Structural Compositions of Pelagic Communities in the River Warnow and their Changes. *Internationale Revue der gesamten Hydrobiologie und Hydrographie 77,* 173-185

UBA, 2005. Einträge von Kupfer, Zink und Blei in Gewässer und Böden - Analyse der Emissionspfade und möglicher Emissionsminderungsmaßnahmen. https://www.umweltbundesamt.de/publikationen/eintraege-von-kupfer-zink-blei-in-gewaesser-boeden, last date of opening 25.06.2017 11:26

UBA, 2013. Water Resource Management in Germany Part 2: Water quality. http://www.umweltbundesamt.de/publikationen/water-resource-management-in-germany-part-2, last date of opening 24.06.2017 at 11:27

Vallius, H., 2015. Quality of the surface sediments of the northern coast of the Gulf of Finland, Baltic Sea. *Marine Pollution Bulletin 99*, 250-255

Van der Voet, e.; Guinée, J.B. & de Haes, H.A.U., 2000. Heavy Metals: a problem solved?. Kluwer Academic Publishers Dordrecht/Boston/London, page 3-15

Wasser- und Schifffahrtsamt Stralsund, 2016. Personal communication

Wedepohl, K.H. & Liebau, F., 1972. Handbook of Geochemistry. *Vol. II/3 Berlin, New York, Heidelberg*

Xu, F.; Tian, X.; Yin, X.; Yan, H.; Yin, F. & Liu, Z., 2015. Trace metals in the surface sediments of the eastern continental shelf of Hainan Island: Sources and contamination. *Marine Pollution Bulletin 99,* 276-283

Zamani, N.G., 1988. Boundary Element Simulation of the Cathodic Protection System in a Prototype Ship. *Applied Mathematics and Computation 26*, 119-134

6. Attachment

Table 10: Values for the grain size analyse with the coordinates of the stations

Noth	East	Station	Clay [%]	< 20 µm[%]	Silt [%]	Sand [%]
54,083733	12,155551	UW III - 1	4,39	34,07	91,12	4,49
54,085495	12,151131	UW III - 2				
54,087937	12,153663	UW III - 3				
54,09506	12,151002	UW III - 4	3,86	30,07	89,59	6,55
54,09506	12,146196	UW III - 5				
54,09428	12,14169	UW III - 6	3,35	28,39	87,68	8,97
54,0937833	12,13765	UW III - 7	3,35	29,66	91,96	4,69
54,0937333	12,1269333	UW III - 8	3,63	34,455	94,21	2,16
54,0970667	12,1154167	UW III - 9	3,47	33,08	94,08	2,45
54,1017833	12,1084167	UW III - 10	4,085	41,205	95,09	0,825
54,1070833	12,1018833	UW III - 11	3,77	31,37	94,03	2,2
54,1127833	12,0989167	UW III - 12	4,9	39,65	93,65	1,45
54,1198	12,0965667	UW III - 13	4,42	37,15	93,76	1,82
54,1254	12,0967333	UW III - 14	5,09	34,47	91,33	3,58
54,133	12,0967333	UW III - 15	5,225	34,37	85,35	9,425
54,1406833	12,0951667	UW III - 16	6,16	32,38	84,69	9,15
54,1470333	12,0957167	UW III - 17	6,32	26,99	71,43	22,25
54,1565833	12,0964	UW III - 18	4,485	14,365	38,985	56,53
54,1605167	12,1180333	UW III - 19	5,9	36,94	86,36	7,74
54,1646167	12,1319	UW III - 20	4,74	25,25	60,395	34,865
54,1732	12,13985	UW III - 21	4,73	33,05	85,8	9,47
54,1603667	12,1113167	UW III - 22	4,49	14,835	43,36	52,15
54,1813667	12,0899	UW III - 23	6,21	26,47	74,34	19,45
54,1736	12,0952167	UW III - 24	7,415	23,68	61,045	31,54
54,1692333	12,0966833	UW III - 25	6,705	18,95	55,635	37,66
54,1559	12,0957333	UW III - 26	5,59	21,15	59,41	35

Table 11: TIC, TOC and TC values in %

Station	TIC (%)	TC (%)	TOC (%)
UW III - 1	1.76	16.03	14.26
UW III - 2	1.41	14.58	13.17
UW III - 3	1.15	15.18	14.03
UW III - 4	1.23	13.74	12.51
UW III - 5	0.94	11.95	11.00
UW III - 6	1.33	17.58	16.25
UW III - 7	1.37	15.08	13.71
UW III - 8	1.34	12.76	11.43
UW III - 9	1.67	11.36	9.69
UW III - 10	1.78	10.16	8.38
UW III - 11	2.02	9.88	7.86
UW III - 12	1.65	8.81	7.15
UW III - 13	1.75	7.15	5.40
UW III - 14	1.69	6.50	4.81
UW III - 15	1.21	4.73	3.52
UW III - 16	1.55	4.28	2.72
UW III - 17	1.12	2.94	1.82
UW III - 18	0.65	1.13	0.48
UW III - 19	1.55	5.34	3.79
UW III - 20	0.63	1.80	1.17
UW III - 21	0.95	6.65	5.71
UW III - 22	0.90	1.82	0.92
UW III - 23	1.59	3.49	1.90
UW III - 24	1.37	2.42	1.05
UW III - 25	1.15	1.81	0.66
UW III - 26	1.09	2.91	1.82

Table 12: Original concentrations of the Unterwarnow sampling campaign

Sample	Al [%]	Fe [%]	As [mg/kg]	Cd [mg/kg]	Cr [mg/kg]	Cu [mg/kg]	Hg [µg/kg]	Ni [mg/kg]	Pb [mg/kg]	Sb [mg/kg]	Zn [mg/kg]	Mn [mg/kg]
UWIII_1	2.94	4.39	13.15	1.26	53.62	70.58	773.6	19.23	183.78	1.67	477.33	471.96
UWIII_2	1.86	2.49	9.28	0.36	32.20	25.95	131.7	10.13	41.61	1.07	126.88	776.50
UWIII_3	1.81	2.54	11.28	0.38	26.52	35.84	178.6	9.18	27.55	0.64	161.59	662.45
UWIII_4	2.40	3.19	10.32	0.58	36.64	36.58	245.6	13.34	38.78	0.73	231.71	819.77
UWIII_5	1.88	2.58	10.23	0.37	35.49	27.34	175.9	14.46	29.31	0.67	192.22	411.10
UWIII_6	2.27	4.00	13.09	0.78	43.54	45.30	444.9	16.62	39.44	0.65	265.72	1176.00
UWIII_7	2.82	4.23	13.81	1.04	46.71	62.43	795.5	18.75	55.06	0.88	357.37	1081.40
UWIII_8	2.88	4.24	13.49	1.28	58.49	100.73	1190.6	20.67	66.61	1.30	440.80	845.34
UWIII_9	2.86	4.09	11.95	1.32	52.33	104.31	2124.0	19.97	73.54	1.12	428.84	731.00
UWIII_10	2.89	3.86	11.84	1.04	48.36	88.92	1560.8	21.10	62.33	0.96	328.99	679.47
UWIII_11	3.24	4.17	11.32	1.03	46.77	127.56	1064.0	20.57	57.74	1.16	288.21	657.68
UWIII_12	3.16	3.74	11.64	0.90	49.04	78.02	797.3	21.55	50.40	0.87	247.69	603.89
UWIII_13	3.21	3.04	10.43	0.72	46.41	63.37	431.1	19.01	39.31	0.79	199.81	543.21
UWIII_14	3.36	3.00	10.51	0.71	50.11	58.06	414.3	19.35	37.66	0.87	187.85	544.00
UWIII_15	3.15	2.78	10.82	0.45	46.85	34.15	142.2	16.98	23.62	0.72	110.79	494.23
UWIII_16	3.23	2.65	9.74	0.57	57.10	49.87	197.5	16.92	29.04	0.80	137.90	532.11
UWIII_17	2.56	1.67	5.99	0.31	28.90	19.94	82.9	11.02	17.34	0.35	69.83	352.07
UWIII_18	2.10	0.77	1.06	0.13	7.67	7.83	23.1	6.43	9.36	0.17	28.70	174.93
UWIII_19	4.13	3.01	9.40	0.59	54.40	41.52	161.8	22.53	29.95	0.61	138.42	396.07
UWIII_20	2.31	0.94	2.20	0.27	18.41	13.28	63.9	7.53	13.85	0.29	54.10	153.30
UWIII_21	3.41	2.86	9.29	0.63	44.09	35.17	252.6	18.07	27.68	0.48	165.08	367.08
UWIII_22	2.20	0.96	2.25	0.18	28.36	8.80	22.4	9.10	11.07	0.24	32.12	205.55
UWIII_23	3.22	1.75	5.07	0.38	38.13	20.27	66.7	14.64	18.88	0.38	70.07	282.15
UWIII_24	2.99	1.44	5.66	0.84	85.93	26.55	418.8	11.37	199.57	1.14	1215.96	260.78

UWIII_25	2.67	1.20	3.40	0.33	35.55	14.28	116.8	10.05	20.26	0.37	65.81	199.45
UWIII_26	2.61	1.48	3.92	0.28	28.36	15.82	74.4	10.51	15.25	0.32	58.17	314.97

Table 13: Results without sand content

Station	Al [%]	Fe [%]	Mn [mg/kg]	As [mg/kg]	Cd [mg/kg]	Cr [mg/kg]	Cu [mg/kg]	Hg [µg/kg]	Ni [mg/kg]	Pb [mg/kg]	Sb [mg/kg]	Zn [mg/kg]	TOC [%]
UWIII_1	3.03	4.50	494.15	13.76	1.32	56.14	73.90	809.97	20.13	192.42	1.74	499.77	14.93
UWIII_2	1.91	2.65	830.37	9.71	0.38	33.69	27.14	137.76	10.60	43.53	1.12	132.72	13.78
UWIII_3	1.89	2.66	692.94	11.80	0.39	27.75	37.49	186.82	9.60	28.81	0.67	169.02	14.68
UWIII_4	2.56	3.42	877.23	11.04	0.62	39.21	39.14	262.81	14.27	41.50	0.79	247.95	13.39
UWIII_5	2.70	3.13	430.03	10.70	0.39	37.12	28.60	184.00	15.12	30.66	0.70	201.07	11.51
UWIII_6	2.49	4.39	1291.88	14.38	0.86	47.83	49.76	488.74	18.26	43.32	0.71	291.90	17.86
UWIII_7	2.96	4.44	1134.62	14.49	1.09	49.01	65.50	834.64	19.68	57.77	0.93	374.95	14.38
UWIII_8	2.94	4.33	864.00	13.79	1.31	59.78	102.95	1216.88	21.12	68.08	1.33	450.53	11.68
UWIII_9	2.93	4.20	749.36	12.25	1.35	53.64	106.93	2177.34	20.47	75.38	1.15	439.61	9.93
UWIII_10	2.92	3.89	685.12	11.94	1.05	48.76	89.66	1573.78	21.28	62.85	0.97	331.73	8.45
UWIII_11	3.31	4.27	672.47	11.57	1.06	47.83	130.43	1087.93	21.03	59.04	1.19	294.69	8.04
UWIII_12	3.21	3.80	612.78	11.81	0.91	49.77	79.17	809.03	21.87	51.14	0.88	251.33	7.26
UWIII_13	3.27	3.10	553.28	10.62	0.73	47.27	64.55	439.09	19.36	40.04	0.80	203.51	5.50
UWIII_14	3.48	3.11	564.20	10.90	0.73	51.97	60.21	429.68	20.07	39.06	0.90	194.83	4.99
UWIII_15	3.48	3.07	545.66	11.95	0.50	51.72	37.70	157.00	18.74	26.08	0.80	122.32	3.89
UWIII_16	3.55	2.91	585.70	10.72	0.62	62.85	54.89	217.39	18.62	31.96	0.88	151.79	3.00
UWIII_17	3.29	2.15	452.82	7.71	0.40	37.17	25.65	106.62	14.18	22.30	0.45	89.81	2.35
UWIII_18	4.83	1.76	402.41	2.44	0.29	17.65	18.01	53.14	14.80	21.54	0.39	66.01	1.10

UWIII_19	4.48	3.26	429.30	10.18	0.64	58.97	45.00	175.37	24.42	32.46	0.66	150.04	4.11
UWIII_20	3.54	1.45	235.36	3.38	0.41	28.27	20.39	98.10	11.56	21.27	0.44	83.06	1.80
UWIII_21	3.76	3.16	405.48	10.27	0.70	48.70	38.85	279.02	19.97	30.58	0.53	182.35	6.30
UWIII_22	4.59	2.00	440.95	4.70	0.37	59.26	18.40	46.81	19.02	23.14	0.50	67.12	1.92
UWIII_23	4.00	2.17	350.28	6.29	0.47	47.33	25.16	82.81	18.17	23.43	0.47	86.99	2.36
UWIII_24	4.37	2.10	380.92	8.27	1.23	125.52	38.78	611.74	16.60	291.51	1.66	1776.16	1.53
UWIII_25	4.32	1.95	311.12	5.45	0.54	57.02	22.91	187.36	16.12	32.51	0.59	105.56	1.06
UWIII_26	4.02	2.27	484.57	6.03	0.42	43.63	24.33	114.46	16.17	23.46	0.50	89.49	2.80

Table 14: Concentrations without the content of particles >20 µm

Station	Content <20 µm [%]	Faktor	As [mg/kg]	Cd [mg/kg]	Cr [mg/kg]	Cu [mg/kg]	Hg [mg/kg]	Ni [mg/kg]	Pb [mg/kg]	Zn [mg/kg]
UWIII_1	50,18	2,01	56,44	16,55	67,50	3784,21	365,11	1357,13	3533,84	87722,77
UWIII_2	50,18	2,01	23,15	3,34	7,77	703,51	104,55	374,81	685,31	7645,80
UWIII_3	50,18	2,01	28,65	4,23	9,95	950,58	118,31	329,08	252,94	4451,17
UWIII_4	56,02	2,27	32,96	6,03	21,40	1340,24	201,34	487,75	517,16	8986,06
UWIII_5	50,18	2,01	30,57	3,79	13,15	970,34	72,31	395,30	423,79	5635,04
UWIII_6	59,18	2,45	52,35	10,24	34,06	1972,23	523,20	752,93	655,49	10478,49
UWIII_7	57,65	2,36	58,40	14,38	48,61	2915,84	860,26	1170,68	1032,46	19675,34
UWIII_8	51,08	2,04	57,14	17,28	74,92	5891,06	1006,46	2081,55	1376,59	29362,83
UWIII_9	53,56	2,15	48,92	15,74	68,93	5458,27	1552,65	2083,07	1468,47	31535,33
UWIII_10	42,23	1,73	45,70	12,33	50,37	4300,37	1060,52	1876,48	1315,28	20505,75
UWIII_11	54,98	2,22	47,21	11,69	48,34	5966,65	699,77	2623,58	1187,62	16642,27
UWIII_12	41,80	1,72	43,56	10,49	44,21	3826,64	481,48	1681,49	1086,18	12483,58
UWIII_13	46,42	1,87	31,73	7,50	33,39	2941,39	234,18	1204,75	747,29	7854,30
UWIII_14	47,65	1,91	31,53	7,43	35,46	2909,14	225,38	1123,55	728,82	7074,66
UWIII_15	47,38	1,90	30,08	4,88	21,13	1599,80	70,28	579,73	400,94	2616,70
UWIII_16	47,88	1,92	25,77	5,52	32,39	2847,54	105,09	843,84	491,32	4004,10
UWIII_17	53,03	2,13	10,03	1,88	9,07	576,37	29,19	219,83	191,11	1210,50
UWIII_18	72,70	3,66	0,81	0,14	0,98	60,06	4,04	50,35	60,21	268,65
UWIII_19	42,35	1,73	28,24	5,57	32,25	2258,60	64,08	935,46	674,89	4146,00
UWIII_20	59,07	2,44	2,08	0,58	4,89	244,50	9,80	99,95	104,25	749,32
UWIII_21	49,60	1,98	26,58	5,87	27,86	1550,58	92,73	635,65	500,38	4570,05
UWIII_22	72,39	3,62	1,93	0,36	5,69	302,80	4,73	106,74	115,05	317,07
UWIII_23	54,93	2,22	8,84	1,93	14,50	772,68	18,82	296,65	276,29	1322,60
UWIII_24	54,89	2,22	8,16	4,75	72,08	2281,56	109,21	301,82	2268,60	242667,32
UWIII_25	63,21	2,72	4,01	1,24	11,41	442,91	22,65	149,70	255,57	2085,84
UWIII_26	62,82	2,69	5,79	1,08	7,81	448,54	23,43	166,24	160,27	887,05