The Author

Katja Oing absolvierte nach ihrem Bachelorabschluss im Fach Georessourcenmanagement an der RWTH Aachen den Masterstudiengang Geowissenschaften mit Schwerpunkt Bodenkunde an der Universität Hamburg. In ihrer Promotion am Institut für Bodenkunde untersuchte sie die Eignung von aufbereitetem Baggergut aus dem Hamburger Hafen für den Einsatz im Deichbau. Der Fokus der Untersuchungen zur geotechnischen Eignung des Materials lag auf der Verdichtbarkeit beim Einbau, dem Schrumpfungsverhalten und dem Schadstoffemissionspotential.

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SUITABILITY OF PROCESSED DREDGED MATERIAL FROM THE HAMBURG HARBOR FOR DIKE CONSTRUCTION

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List of Abbreviations and Nomenclature

AAS	Atomic absorbtion spectroscopy
ANC	Acid neutralization capacity
ANP	Acid neutralization potential
COLE	Coefficient of linear extensibility
DBD	Dry bulk density
DC	Dike cover material
DF	Material from dewatering fields
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DW	Dry weight
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency of the United States of America
HPA	Hamburg Port Authority
I_P	Plasticity Index
L/S ratio	Liquid to solid ratio
LOQ	Limit of Quantification
METHA	Mechanical Treatment and Dewatering of Harbor Sediments
MS	Fine-grained aged marsh sediments
OD	Material from open depots
OM	Organic matter
OS	Organic Substance
PAH	Polycyclic aromatic hydrocarbons
PD	Proctor density
TC	Total carbon
TIC	Total inorganic carbon
TM	Trace metals
TOC	Total organic carbon
V_S	Volumetric shrinkage rate
w_L	Liquid limit
w_P	Plastic limit
w_S	Shrinkage Limit
WD	Wetting-drying

Abstract

In terms of the preservation of natural resources, the continuously increasing demand for dike construction material and against the backdrop of limited landfill capacities, the utilization of processed dredged material in dike construction as a substitute for traditionally used fine-grained aged marsh sediment, glacial marl or boulder clay is considered an advisable option. As a prerequisite for application, the equivalency with respect to soil physical and mechanical properties of the materials has to be verified. Furthermore, the potential leaching of contaminants has to be evaluated.

The aim of the work presented here is to assess the suitability of processed dredged materials from the area of the Port of Hamburg for use in dike construction with regard to selected properties in order to contribute to clarifying the question of the suitability of this material for dike construction. The focus of the investigations was on the one hand on the physical properties of the material, in particular compactibility and shrinkage behavior and on the examination of possible further processing options to improve the physical properties. A further focus was on the possible release of pollutants from the processed dredged material.

The results from the fundamental characterization of the inherent physical properties of the processed dredged material and fine-grained marsh sediment samples revealed, that an equivalency of these materials with respect to their compactibility and shrinkage behavior is not existing. The statistical evaluation of the results of the compaction tests and the shrinkage experiments showed that the Proctor densities achieved with the fine-grained marsh sediments were significantly higher than those of the processed dredged materials. Furthermore, the processed dredged materials showed a significantly more pronounced shrinkage behavior than the fine-grained marsh sediments.

To examine whether the compactibility of dredged material can be enhanced by further processing, i.e. pre-drying, Proctor tests were carried out at different initial water contents. Moreover, it was examined whether oven-drying at 30 and 105 °C improves the compactibility of these materials and whether ripening, i.e., the repeated drying and wetting of the dredged material under natural and laboratory conditions, can improve their compactibility. The results of the compaction tests conducted with further dried material, i.e. material which was dried to different water contents (40 % DW, 30 % DW, 20 % DW and 10 % DW) before compaction, showed a significant effect of drying on the compactibility with a drying up to a water content of 10 % DW. On the materials that had been dried to this water content, an increase in density from 45 % of the Proctor density to an average of 98 % of the Proctor density could be achieved compared with the undried material. Compared to the material dried to a water content of 40 % DW, drying to 10 % increased the density from 90 % of the Proctor density to 98 % of the Proctor density.

Oven-drying had no additional effect on the compactibility of the dredged materials. Nor ripening under laboratory neither under natural conditions led to statistically significant changes in the compactibility of the processed dredged material. From these results, it was deduced that air-drying of processed dredged material to water contents less than 10 % DW is a useful pretreatment option to improve the compaction behavior of processed dredged material and to obtain a better functional equivalency with traditionally used dike construction materials such as fine-grained aged marsh sediments.

For the comparative investigations on the shrinkage behavior of the materials, three different methods of different scales were applied. Small-scale methods conducted were the standard procedure for the determination of the shrinkage limit and the determination of the coefficient of linear extensibility ($COLE_{rod}$) according to Schafer and Singer (1976a). The large-scale shrink-swell experiments were carried out in a specially constructed test system with 90 l capacity for a period of up to 385 days. Here the specimens of layerwise compacted materials were ripened, i.e. air-dried, until shrinkage almost ceased, and a rewetting-air-drying-cycle was conducted. Shrinkage and swelling were determined by measuring the changes in volume of the specimens. The determination of the $COLE_{rod}$ on the ripened materials, i.e. materials taken from the specimens of the large-scale shrinkage tests, showed that the shrinkage behavior of the processed dredged material can be improved by ripening. $COLE_{rod}$ of the ripened materials was about 20-80 % points lower than $COLE_{rod}$ of the unripened materials. The large scale shrinkage tests showed that the volume shrinkage in the second drying cycle was less than in the first drying cycle and that the shrinkage behavior was dominated by structural and residual shrinkage in this cycle in contrast to the first drying cycle, during which a pronounced proportional shrinkage was observed. From these experiments it was concluded that ripening of processed dredged material is a useful further processing option to ameliorate the shrink-swell behavior of processed dredged material and to obtain a better functional equivalency with traditionally used dike construction materials such as fine-grained aged marsh sediments. Based on the results of the investigations on material-improving further processing options conducted in this study it was recommended to pre-dry the METHA material to water contents of less than 12 % dry prior to use in dike construction.

The aim of the investigations on the fundamental leaching behavior was to evaluate whether the use of dredged material in dike construction can pose a risk to the environment in general and to specific pathways.

One objective of the investigations on the pollutant leaching behavior was to determine the potential leaching from fresh and ripened METHA material, i.e. chemically essentially unchanged material, applying elution methods (batch-extractions and percolation column tests) prescribed by the regulations such as the BBodSchV (1999) and LAGA (2004).

Both the results from the batch-extractions and the percolation column tests revealed only occasional exceedances of the threshold value of the BBodSchV (soil-groundwater path).

Therefore, the leaching experiments carried out with fresh METHA material showed that the release of trace metals from this material is predominantly to be classified as non-critical.

Since leaching behavior and potential toxicity of trace metals are generally dependent on the chemical form in which they are present in soils and sediments, sequential extractions were carried out to determine the trace metal contents of differently available or mobilizable fractions. Overall it was found that for all trace metals investigated (Cd, Pb, Zn) and As, the proportion associated with Fe and Mn- oxides and hydroxides was the greatest. This fraction is considered to be moderately mobilizable under natural conditions. In the case of Cd and Zn, the share of the mobile to easily mobilizable fraction determined with about 20 % For As and Pb proportions of about 3 % and <1 % were determined in this fraction. In the two-stage sequential extraction of the EPA-PAH, only about 1 % of the total EPA-PAH contents were extracted in the batch-extraction with water. 99 % of the EPA-PAH were determined in the n-hexane fraction after Soxhlet digestion. The impact of laboratory ripening and partial mineralization of the organic substance on the trace metal distribution on the different fractions was overall small. In the sequential extraction of the EPA-PAH, no statistically significant effect of the mineralization of the organic substance could be observed either.

In addition to the possible leaching of pollutants from fresh and ripened material, the long-term potential maximum leaching of contaminants is also important for assessing the suitability of the processed dredged material for use in dike construction. The maximum potential release of contaminants was investigated by means of worst-case studies in order to determine the maximum pollutant emission potential in a time-lapse effect. The following scenarios were investigated: acidification, mineralization of the organic substance, destabilization of the spatial structure of the organic substance and mechanical destruction of aggregates.

After the artificial acidification of the dredged material materials in the worst-case tests, Cd, Ni and Zn leaching was significantly increased in the batch-extractions and the threshold values of the BBodSchV were exceeded. In the percolation test, however, no significant increase in the trace metal release could be determined, since the metals were re-adsorbed within the columns in areas where acidification had not taken place yet. The trace metal contents of the eluates were all below the threshold values. With regard to the effect of an acidification of METHA material installed in dikes, the results of the determination of the acid neutralization capacity and the acid neutralization potentials derived from it, showed that on average an acidification of the processed dredged material, which could lead to an initial release of Cd and Zn (pH 6), is expected to occur after more than 10000 years. An acidification, which could lead to the mobilization of As (limit pH value: 4-4.5) or Pb (limit pH value 4), may occur after about 15000 years. Accordingly, a release of trace metals due to acidification under natural conditions can be classified as uncritical in a reasonable time frame.

The destabilization of the spatial structure of the organic substance or of clay-organic complexes by applying competing complexing agents (ethylenediaminetetraacetic acid) led to a drastically increased release of trace metals from the dredged material. The treatment also led to a slightly increased release of EPA-PAH. Based on the results, the relevance of metal-organic complexes and the occlusion of pollutants within the organic substance can be demonstrated.

The mechanical destruction of the aggregate structure by ultrasonic dispersion led to a slightly increased release of Cd, Ni and Zn.

Since the conditions applied in the investigations on the effect of the destabilization of the spatial structure of the organic substance and the mechanical destruction of the aggregate structure do not occur under natural conditions, the results from these experiments were not used for a risk assessment of potential pollutant discharges from the dredged material under given and future environmental conditions.

Based on the results of the laboratory investigations carried out and the results from the leachate monitoring (Gröngröft et al., 2016) from a test field in which METHA material is installed as part of the dike cover layer, the release of pollutants from the processed dredged material can, with the exception of Cu, be classified as predominantly non-critical. The release of EPA-PAH cannot be classified as non-critical on the basis of the laboratory tests. However, the results of the leachate monitoring show that under field conditions no leaching of EPA-PAH in threshold relevant concentrations takes place. Based on the evaluation of the results of the worst-case investigations representing processes occurring under natural conditions (acidification, degradation of the organic substance), the leaching of pollutants from METHA material built into dikes is not expected to increase in the long term.

Zusammenfassung

Die Verwertung von behandeltem Baggergut als Ersatz für den üblicherweise im Deichbau verwendeten Klei oder Mergel wird, vor dem Hintergrund der Schonung von natürlichen Bodenressourcen und Deponiekapazitäten und dem steigenden Bedarf an Deichbaumaterialien, als sinnvolle Option angesehen.

Eine Grundvoraussetzung für die Verwendung von aufbereitetem Baggergut im Deichbau ist der Nachweis der funktionalen Gleichwertigkeit mit dem in Nordwestdeutschland üblicherweise für Deichabdeckungen verwendetem Klei im Hinblick auf bodenphysikalische und bodenmechanische Eigenschaften und auch im Hinblick auf eine mögliche Freisetzung von Schadstoffen.

Ziel der hier vorgestellten Arbeit ist es, die Eignung von aufbereitetem Hamburger Baggergut für den Einsatz im Deichbau zu im Hinblick auf ausgewählte Eigenschaften zu bewerten, um damit einen Beitrag zur Klärung der Frage der Eignung von aufbereitetem Hamburger Baggergut für den Einsatz im Deichbau zu leisten. Der Fokus der Untersuchungen lag zum einen auf den bodenphysikalischen Eigenschaften, insbesondere der Verdichtbarkeit und dem Schrumpfungsverhalten und der Prüfung möglicher Vorbehandlungsvarianten zur Verbesserung der physikalischen Eigenschaften. Ein weiterer Fokus lag auf der möglichen Schadstofffreisetzung aus dem behandelten Baggergut.

Hinsichtlich der Gleichwertigkeit von behandeltem Baggergut mit dem üblicherweise im Deichbau verwendeten Klei zeigten die Ergebnisse der weiteren bodenphysikalischen und bodenmechanischen Untersuchungen, dass bei dem frischen Baggergut keine Gleichwertigkeit mit den untersuchten Kleimaterialien bezüglich der Verdichtbarkeit und des Schrumpfungsverhaltens gegeben ist. So ergaben die statistische Auswertung der Ergebnisse der Verdichtungsversuche und der Versuche zum Schrumpfungsverhalten, dass die mit den Kleimaterialien erzielten Proctordichten signifikant höher waren als die der Baggergutmaterialien und, dass die Baggergutmaterialien ein deutlich ausgeprägteres Schrumpfungsverhalten zeigen.

Um zu untersuchen, ob die Verdichtbarkeit des Baggerguts durch weitere Vortrocknung verbessert werden kann, wurden Proctorversuche unterschiedlich stark vorgetrockneten Materialien durchgeführt. Darüber hinaus wurde untersucht, ob eine Ofentrocknung bei 30 und 105 °C die Verdichtbarkeit verbessert und ob die Reifung, d.h. die wiederholte Trocknung und Wiederbefeuchtung des Baggergutes unter natürlichen und labortechnischen Bedingungen dessen Verdichtbarkeit verbessern kann. Die Ergebnisse der Versuche zur Verdichtbarkeit von vorgetrocknetem Material, d.h. von Material welches vor der Verdichtung in Anlehnung an den Proctorversuch auf unterschiedliche Wassergehalte (40 % TM, 30 % TM, 20 % TM und 10 % TM) heruntergetrocknet wurde, ergaben einen signifikanten Effekt der Vortrocknung auf die Verdichtbarkeit bei einer Trocknung bis zu einem Wassergehalt von 10 % TM. Mit einem auf diesen Wassergehalt getrockneten Material konnte verglichen mit dem ungetrockneten Material eine Erhöhung der Dichte von 45 % der Proctordichte auf im Mittel 98 % der Proctordichte erzielt werden. Verglichen mit dem auf 40 % TM getrockneten Material, wurde durch

die Trocknung auf 10 % TM Wassergehalt eine Erhöhung der relativen Dichte von 90 % der Proctordichte auf 98 % der Proctordichte erreicht.

Die Ofentrocknung hatte keinen zusätzlichen Einfluss auf die Verdichtbarkeit der Baggergutproben und auch die Reifung im Labor und unter natürlichen führte nicht zu statistisch signifikanten Veränderungen in der Verdichtbarkeit. Aus diesen Ergebnissen wurde abgeleitet, dass die Lufttrocknung von aufbereitetem Baggergut auf Wassergehalte unter 10 % DW eine sinnvolle Vorbehandlungsoption ist, um das Verdichtungsverhalten von aufbereitetem Baggergut zu verbessern und eine bessere funktionale Gleichwertigkeit mit Kleimaterialien zu erreichen.

Für die vergleichenden Untersuchungen zum Schrumpfungsverhalten der Materialien wurden drei verschiedene Methoden mit unterschiedlichem Maßstab eingesetzt. Bei den Methoden mit kleinem Versuchsmaßstab handelte es sich um das Standardverfahren nach DIN 18122-2 zur Bestimmung der Schrumpfgrenze und die Methode von Schafer und Singer (1976a) zur Bestimmung der Koeffizienten der linearen Ausdehnung ($\mathrm{COLEr_{od}}$). Die Versuche zum Quellungs- und Schrumpfungsverhalten im großen Maßstab wurden über einen Zeitraum von 385 Tagen in einem eigens konstruierten Versuchssystem in PE-Wannen mit einem Volumen von 96 l durchgeführt. Hier wurden die Materialien nach lagenweise verdichtetem Einbau gereift, d.h. luftgetrocknet, bis keine weitere Schrumpfung mehr festzustellen war. Anschließen wurden die Proben wiederbefeuchtet und erneut einem Austrocknungszyklus unterzogen. Schrumpfung und Quellung der Materialien im Versuchsverlauf wurden über die Vermessung des Probenkörpers ermittelt. Die Bestimmung des $\mathrm{COLE_{rod}}$ an den gereiften, d.h. aus den Wannen für die großmaßstäbigen Schrumpfungsversuche entnommenen Materialien zeigte, dass das Schrumpfungsverhalten des vorbehandelten Baggerguts durch Reifung verbessert werden kann. So war $\mathrm{COLE_{rod}}$ der gereiften Materialien war etwa 20-80 % Punkte niedriger als der $\mathrm{COLE_{rod}}$ der ungereiften Materialien. Die großmaßstäbigen Schrumpfungsversuche zeigten, dass die Volumenschrumpfung im zweiten Trocknungszyklus geringer war als im ersten Trocknungszyklus und dass das Schrumpfungsverhalten im Gegensatz zum ersten Trocknungszyklus, bei dem eine ausgeprägte proportionale Schrumpfung beobachtet wurde, in diesem Zyklus von Struktur- und Restschrumpfung dominiert wurde.

Aus diesen Ergebnissen kann abgeleitet werden, dass die Reifung von verarbeitetem Baggergut eine nützliche Vorbehandlungsoption ist, um das Schrumpfungs- und Quellungsverhalten von aufbereitetem Baggergut zu verbessern und eine bessere funktionale Gleichwertigkeit mit traditionell verwendeten Deichbaumaterialien wie feinkörnigen Marschsedimenten zu erreichen und die Eignung für den Deichbau zu verbessern. Basierend auf den Ergebnissen der in dieser Studie durchgeführten Untersuchungen zu weiteren Vorkonditionierungsmöglichkeiten wird empfohlen, das METHA-Material vor dem Einsatz im Deichbau auf einen Wassergehalt von weniger als 12 % zu trocknen.

Bei der Frage der Verwendbarkeit von aufbereitetem Baggergut im Deichbau muss beurteilt werden, ob von den in dem Material vorhandenen Schadstoffen negative Auswirkungen für die Umwelt ausgehen können.

Ein Ziel der Untersuchungen zum Schadstoffelutionsverhalten war es, mit den nach den Regelwerken (BBodSchV, LAGA TR) vorgeschriebenen Elutionsmethoden (Schüttelversuche und Perkolationssäulenversuche) festzustellen, wie hoch die potenzielle Elution aus frischem und gereiftem, d.h. chemisch im wesentlichen unverändertem METHA-Material ist.

Die mit frischem METHA-Material durchgeführten Elutionsversuche zeigten, dass die Freisetzung von Spurenmetallen aus dem frischen behandelten Baggergut überwiegend als unkritisch einzustufen ist. So kam es sowohl in den Schüttelversuchen als auch in den Perkolationsversuchen nur vereinzelt zu Überschreitungen der zur Bewertung herangezogenen Prüfwerte der BBodSchV (Prüfwert Boden-Grundwasser).

Da das Freisetzungsverhalten und die potentielle Toxizität von Spurenmetallen im Allgemeinen von der chemischen Form abhängig sind, in der sie in Böden und Sedimenten vorliegen, wurden sequentielle Extraktionen durchgeführt, um den Spurenmetallgehalt von unterschiedlich verfügbaren oder mobilisierbaren Fraktionen zu bestimmen. Insgesamt wurde festgestellt, dass bei allen untersuchten Spurenmetallen (Cd, Pb, Zn) und As der mit Fe und Mn-Oxiden und Hydroxiden assoziierte Anteil am größten war. Diese Fraktion gilt als unter natürlichen Bedingungen mäßig mobilisierbar. Der Anteil der mobilen bis leicht mobilisierbaren Fraktion wurde für Cd und Zn mit ca. 20 % bestimmt. Bei As und Pb wurden Anteile von 3 % und < 1 % in der mobilen/mobilisierbaren Fraktion ermittelt. In der zweistufigen sequentiellen Extraktion der PAK wurde nur etwa 1 % der EPA-PAK im Schüttelversuch mit Wasser extrahiert. 99 % der PAK wurden in der n-Hexan Fraktion nach Soxhlet-Aufschluss bestimmt. Der Einfluss der Laborreifung und des teilweisen Abbaus der organischen Substanz auf die Spurenmetallverteilung auf die verschiedenen Fraktionen war insgesamt gering. Auch bei der sequentiellen Extraktion der PAK konnte kein statistisch signifikanter Effekt der Mineralisierung der organischen Substanz beobachtet werden.

Neben der Freisetzung von Schadstoffen aus frischem und gereiftem Material, ist auch die langfristig mögliche maximale potentielle Schadstofffreisetzung für eine Beurteilung der Eignung des Baggergutes für den Einsatz im Deichbau von Bedeutung. Diese wurde mittels Worst-Case-Studien untersucht, um das maximale Schadstoffemissionspotenzial im Zeitraffereffekt ermitteln zu können. Bei diesen Untersuchungen werden gegenüber den unter natürlichen Bedingungen ablaufenden Prozessen stärkere Elutionsmittel verwendet, oder drastischere Freisetzungsbedingungen eingestellt. Untersucht wurden die Szenarien Versauerung, Abbau der organischen Substanz, Destabilisierung der räumlichen Struktur der organischen Substanz und mechanische Zerstörung von Bodenaggregaten.

Nach der künstlichen Versauerung der Baggergutmaterialien in den Worst-Case-Versuchen wurden sowohl Cd und Ni als auch Zn signifikant verstärkt im Schüttelversuch freigesetzt und es kam zu Überschreitungen der Prüfwerte der BBodSchV. Im Perkolationsversuch konnte dagegen keine signifikante Erhöhung der Spurenmetallfreisetzung ermittelt werden, da die Metalle innerhalb der Säulen in Bereichen, in denen noch keine Versauerung stattgefunden hat wieder sorbiert werden. Die Spurenmetallgehalte der Eluate lagen alle unterhalb der Prüfwerte. Bezüglich des Effektes einer Versauerung von in Deichen eingebautem METHA-Material zeigten die Ergebnisse der Bestimmung der Säureneutralisationskapazität und der daraus abgeleiteten Säureneutralisationspotenziale, dass im Mittel erst nach über 10.000 Jahren eine Versauerung des vorbehandelten Baggergutes zu erwarten ist, durch die eine initiale Freisetzung von Cd und Zn eintreten könnte (pH-Wert 6). Eine Versauerung, durch die es zu einer Mobilisierung von As (Grenz-pH-Wert: 4-4,5) oder Pb (Grenz-pH-Wert 4) kommen könnte, würde nach den Berechnungen erst nach etwa 15.000 Jahren eintreten. Demnach ist eine Freisetzung von Spurenmetallanteilen durch Versauerung unter natürlichen Bedingungen in überschaubaren Zeiträumen als unkritisch einzustufen.

Nach Inkubation, d.h. dem teilweisen Abbau von im Mittel 10 % der in den Baggergutmaterialien enthaltenen organischen Substanz, wurden As, Ni und Zn im Schüttelversuch statistisch signifikant verstärkt freigesetzt. Jedoch wurde nur der Prüfwert für As nach der Inkubation vereinzelt überschritten. Ein signifikanter Effekt der Inkubation auf die Freisetzung von PAK aus den Proben konnte nicht festgestellt werden. Es ist anzunehmen, dass der Abbau der organischen Substanz unter natürlichen Bedingungen deutlich verlangsamt stattfindet, so dass dieser Prozess als unkritisch für die Schadstofffreisetzung betrachtet werden kann.

Durch die Destabilisierung der räumlichen Struktur der organischen Substanz bzw. von Ton-organischen Komplexen durch konkurrierende Komplexbildner (Ethylendiamintetraessigsäure) kam es zu einer drastisch verstärkten Freisetzung von Spurenmetallen aus den Baggergutmaterialien. Auch bei den PAK führte die Behandlung zu einer leicht verstärkten Freisetzung. Anhand der Ergebnisse lässt sich demnach die Relevanz Metall-organischer Komplexe und der Okklusion von Spurenmetallen innerhalb der organischen Substanz nachweisen.

Die mechanische Zerstörung der Aggregatstruktur durch Ultraschalldispergierung führte bei Cd, Ni und Zn zu einer leicht verstärkten Freisetzung.

Da die in den Untersuchungen zur Destabilisierung der räumlichen Struktur der organischen Substanz und zur mechanischen Zerstörung der Aggregatstruktur keine unter natürlichen Bedingungen ablaufende Prozesse abbilden, wurden die Ergebnisse nicht für eine Gefahrenbewertung potentieller Schadstoffausträge unter gegebenen und auch zukünftigen Umweltbedingungen herangezogen.

Insgesamt kann auf Basis der Ergebnisse der durchgeführten Laborversuche und der Ergebnisse aus dem Sickerwassermonitoring (Gröngröft et al., 2016) von einem Testfeld, in das METHA Material in die Deichabdeckung eingebaut ist, die Freisetzung von Schadstoffen aus im Deichbau verwendeten aufbereiteten Hamburger Baggergut, mit Ausnahme von Kupfer, als überwiegend unkritisch eingestuft werden. Die Freisetzung von PAK kann anhand der Laborversuche nicht als unkritisch eingestuft werden. Die Ergebnisse des Sickerwassermonitoring zeigen jedoch, dass unter Feldbedingungen keine Prüfwertrelevante PAK-Freisetzung aus dem METHA Material stattfindet. Basierend auf der Bewertung der Ergebnisse der Worst-Case Versuche, die unter natürlichen Bedingungen ablaufende Prozesse abbilden (Versauerung, Abbau der organischen Substanz), ist auch langfristig nicht mit einer Verstärkung der Freisetzung von Schadstoffen aus METHA Material, welches in Deichen eingebaut ist, zu rechnen.

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Publications

Oing, K., Gröngröft, A., Eschenbach, A. (2018). Enhanced dewatering optimizes compactibility of processed dredged material. Journal of Soils and Sediments, 18(9), 3020-3030.

Oing, K., Gröngröft, A., Eschenbach, A. (2019). Ripening reduces the shrinkage of processed dredged material. Accepted for publication in the Journal of Soils and Sediments in June 2019.

1 Introduction and objectives

Global climate change is expected to cause an increase in ocean and tide water levels and additional burdens for coastal protection structures at the North Sea, caused by an intensification of westerly winds and subsequent changes in tidal current and swell (Mai et al., 2004). Precipitation increase in winter and more frequent heavy rain events may lead to an increased likelihood of inland flood events. Furthermore, there are studies that forecast higher water levels during flood events in the catchment area of the Elbe River in the future (Kropp et al., 2004). Storm surge statistics for the Elbe River indicate an increase in frequency and peak height of storm surges over the last decades (von Storch and Claussen, 2012). It is predicted that the storm surge peak water levels in the entire tidal Elbe will increase due to sea level rise (Klein et al., 2018). Therefore, climate change and its consequences necessitate an adaption of coastal and inland dikes by reinforcement and adaptation of the height and strength of the dikes and hence result in an enormous demand of dike construction materials.

German river dikes are constructed almost exclusively as multi-zone dikes, consisting of a supporting core made of sand, a sealing to reduce the infiltration of seepage and optionally a drainage body at the downstream toe (Saathoff et al., 2015). Mineral sealing's of dikes on the German North Sea and Baltic Sea coasts and along the tidal streams are constructed from materials that are easily available in the respective region. At the North Sea, fine- grained aged marsh sediments are used, which originate directly from the coastal area of the North Sea or the glacial valleys of the rivers Elbe, Weser and Ems (HTG, 2006). At the Baltic Sea glacial marl or boulder clay are predominantly used for dike construction (Saathoff et al., 2015). The exploitation of these materials is accompanied by a considerable destruction of land, and the marsh sediment deposits in inland areas, e.g. the glacial valleys of the Elbe River are limited and are no longer available without restrictions due to nature conservation laws (HTG, 2006).

In the course of the preparation of the general plan for coastal protection in Lower Saxony and Bremen, the main dikes in Lower Saxony were re-measured in 2006. Based on the data collected, it was stated that over the next 25 years more than 14 million m^3 of fine-grained-marsh sediments will be required for ensuring coastal protection in Lower Saxony which has a dike line of a length of about 610 km (Carstens, 2008). In Hamburg, the total length of the dyke line is about 100 km, thus also for Hamburg a large demand for dike construction material is to be expected.

Against the backdrop of the steadily increasing demand, the enormous land degradation accompanied with mining and the finiteness of the resources of naturally dike construction materials, the utilization of processed fine-grained dredged material in dike construction as a substitute for traditional materials is considered an advisable option (Cantré and Saathoff, 2013; Brils et al., 2014; Oing et al., 2014).

In line with maintenance measures of waterways about 41 million m³ of material are dredged every year by the German federal agencies and governmental authorities in the area of the North Sea and Baltic Sea (Köthe, 2010).

In the port of Hamburg, 11.5 million m^3 sediments were dredged for water depth maintenance in 2016 (HPA, 2016), in 2017 11.2 million m³ corresponding to 4.5 million t dry weight. The vast majority of more than 90 % of these dredged materials was relocated in the aquatic environment. However, a minor part had to be taken ashore (HPA, 2017). Before further utilization or disposal on land, processing of the dredged materials is often necessary because of its high water contents (Saathoff et al., 2015). Dredged sediments from the Hamburg harbor area of the Elbe estuary are processed in dewatering fields, where dredged sediments are naturally dewatered, or in the METHA plant (Mechanical Treatment and Dewatering of Harbor Sediments). In the METHA plant, dredged sediments are separated according to their grain-size by hydrocyclones and the fine fraction is mechanically dewatered. The dewatering is realized in two different ways. One dewatering line comprises a sieve-belt press and a high-pressure post dewatering press. The second way is the dewatering by means of membrane-chamber presses. The objective of the dewatering is to obtain an output product with a water content to approximately 45 % by weight and a sufficient shear strength (cu > 25 kN/m²) from mechanical aspects (Netzband et al., 2002a). The sand fraction is used for different construction purposes and the fine-grained fraction (i.e. METHA material) is either disposed of in landfills due to contamination levels or, when meeting specific quality criteria, used beneficially as construction material (Netzband et al., 2002b; Detzner and Knies, 2004; LAGA, 2008).

Because of its low hydraulic conductivity of less than 1×10^{-9} m s^{-1} after compaction (Rizkallah and Blümel, 1995; Blümel and Tamminga, 1987), METHA material was considered a proper substitute for natural cohesive materials used as mineral liner component in landfill cover systems since the mid-eighties (Gröngröft et al., 2001). In 2008, the fundamental aptitude of METHA material as construction material for mineral liners in landfill coverages was confirmed by the German Working Group of the Federal States on Waste (LAGA, 2008). Proceeding from this successful implementation of the processed dredged material as construction material for mineral liners in landfills, investigations on the question whether this material might be suitable for the construction of parts of dike sealing layers as well were initiated. In 2004, two test fields were constructed on a flood side of a channel closure within the Hamburg harbor. One test field was constructed from four layers of aged fine-grained marsh sediments. The second test field consisted of three layers of METHA material underlying one layer of aged marsh sediment (Gröngröft et al., 2005). Results from the investigations carried out on the test fields revealed considerable differences between METHA material and fine-grained aged marsh sediments with regard to their compactibility, shrink-swell behavior and the leaching of nutrients and contaminants and therefore demonstrated the need for further research on the equivalency of processed dredged material and traditionally used marsh sediments for the use in dike construction.

The prior aim of the presented study was the assessment of the suitability of technically processed dredged material (METHA material) for the use in dike construction with respect to soil physical and mechanical properties as well as the leaching of substances from the material. Focus was given to properties that are of importance for the impermeability and thus the stability of dikes, namely the compactibility and the shrinkage behavior.

The suitability of the material with regard to the leaching of substances was to be assessed to ascertain whether inorganic and organic contaminants and nutrients contained in the dredged material can pose an imminent or future hazard to the environment after installation in dikes.

Within the study two main objectives were followed:

Objective (1) Assessment of the functional equivalency of the processed dredged material in comparison to traditional dike construction materials with regard to chemical and physical properties especially:

a) the compactibility
b) the shrinkage behavior.

Objective (2) Assessment of the leaching behavior of contaminants from the processed dredged material especially:

a) the leaching under given conditions
b) the potential maximum leaching under worst-case conditions.

Within objective (1) the following questions should be answered:

(i) How do dredged materials from the Hamburg harbor processed in the METHA-plant differ from traditional dike construction materials – fine grained aged marsh sediments - in terms of their fundamental physical and chemical properties?
(ii) How do the materials differ in terms of their compactibility? Can the compactibility of the METHA material be improved by further processing measures?
(iii) How do the materials differ in terms of their shrinkage behavior? Is it possible to anticipate proportions of the shrinkage of the METHA material before installation in the dike and thus to achieve a better functional equivalency with the fine-gained marsh sediments?

Within objective (2) the following questions should be answered:

(i) Which pollutant emissions are to be expected after installation in the dike under given conditions i.e. from fresh METHA material and from ripened METHA material?
(ii) Which potential maximum emissions of pollutants may occur in the long-term of dike existence, i.e. after chemical changes of the dredged material?

To answer these questions, the study is composed of the following:

The legal Frameworks for the beneficial use of dredged material in Germany, current research on dredged material used in dike construction and the present knowledge on the (in-situ)-behavior of METHA material used for dike construction are given in Chapter 2 – *Dredged material in dike construction*. Processes that influence the long-term physical behavior and the possible long-term mobilization of contaminants are also described in this chapter.

A detailed description of the investigated materials and applied methods is provided in Chapter 3 – *Materials and Methods*.

In Chapter 4 – C*haracterization of the investigated materials*, the results from the determination of the inherent physical and chemical properties as well as the total pollutant contents of the investigated processed dredged materials and fine-grained marsh sediments are presented and discussed with regard to the materials' suitability for dike construction and their functional equivalency.

To assess the functional equivalency of the processed dredged material in comparison to fine grained aged marsh sediments, also comparative investigations on the materials' compactibility and shrinkage behavior were conducted. In Chapter 5 – *Compactibility of processed dredged material,* the results of the investigations on the compactibility are presented and discussed. The shrinkage behavior of the materials is described and evaluated in detail in Chapter 6 – *Shrinkage behavior of processed dredged material*. In these Chapters, recommendations for further processing options are derived and discussed.

The results of the investigations on the suitability of processed dredged material for dike construction with regard to possible pollutant emissions are presented in Chapter 7 – *Leaching behavior of contaminants*. In this chapter, the potential leaching under given conditions, determined on the basis of batch-extractions and percolation column experiments is characterized and assessed. The investigations on the potential long-term leaching behavior of contaminants followed a so-called worst-case scenario approach, in order to determine the maximum pollutant emission potential of the materials in a time-lapse effect. The results of these investigations are presented and assessed in Chapter 7 as well.

In Chapter 8 – *Assessment of the equivalency*, an overarching comparative assessment of the equivalency of the investigated processed dredged materials and fine-grained aged marsh sediments for use in dike construction based on the results obtained on material properties, compactibility, shrinkage behavior and pollutant leaching behavior is provided.

Chapter 9 - Synthesis and outlook, the results and interpretations of the previous chapters are summarized, concluding remarks are given and an outlook on further research demand is provided.

2 Dredged material in dike construction

This chapter sets the focus first on the legal framework for the use of dredged material in dike construction and the requirements applied on dike construction materials with regard to their physical and geotechnical properties as well as their contaminant contents. The second part of this chapter provides an overview over previous and current research on the issue of the use of dredged material in dike construction. Processes that influence the long-term physical behavior and the possible long-term mobilization of contaminants are described in the third part of this chapter.

2.1 Frameworks for the beneficial use of dredged material in dike construction in Germany

When dredged material has to be taken ashore an intention for disposal according to § 3 of Closed Substance Cycle Waste Management Act (KrW-/AbfG, 2012) exist. According to §1 KrW-/AbfG all movable property which the owner disposes of, wishes to dispose of or must dispose of, are defined as waste. Waste management comprises the recycling and disposal of waste. The dredged material removed from the Elbe River and taken ashore is to be assigned to the waste code 170506. Both, in the case of recovery and disposal this material requires monitoring activities. The same applies to processed dredged material after classification or dewatering when it is utilized as sealing material for landfills, as material for the backfilling of port basins, used for other comparable applications or is deposited on land.

According to KrW-/AbfG, recycling has priority over disposal. This priority applies if the utilization is technically possible and economically reasonable. The European Waste Framework Directive demands recycling rates for wastes. For dredged materials taken ashore, a recycling rate of 70 % shall be achieved by the year 2020 (Saathoff and Cantré, 2014; Saathoff et al., 2015). However, if the disposal of waste is the more environmentally friendly solution, the priority of recycling over disposal is not applicable (Heinz, 2004).

All materials used in dike construction must meet certain quality criteria. Quality requirements for traditionally used natural mineral sealing materials of river dikes are specified in regional and national standards and guidelines such as HH (1988), EAK (2002), DWA M 507 (2011), DIN 19712 (2013). Requirements that specifically apply to dredged material intended for the use in dike construction with regard to physical properties and geotechnical suitability have not yet been defined. However, as the requirements that are to be applied on this material correspond in principle to those of traditionally used materials, it is recommended that the suitability criteria and assessment methods used for traditional construction materials are also applied when assessing the suitability of dredged materials (HTG, 2006).

Criteria for the evaluation of the suitability of traditional construction materials for sea dikes and tidal river dikes with regard to their physical and geotechnical properties were elaborated by the Committee for Coastal Protection Works of the German Society for Geotechnical

Engineering (DGG) and the Hafenbautechnische Gesellschaft (HTG) and specified in the "Recommendations for the Execution of Coastal Protection Works" (EAK, 2002).

Both, the criteria specified in EAK (2002) and the quality requirements specified by the Hamburg building authority in 1988 (HH, 1988) are compiled in Table 2.1.

Table 2.1 Threshold values of properties for traditional material used in dike construction according to existing regulations.

Parameter	Threshold value	
	EAK (2002)	HH Directive (1988)
loss on ignition	< 10 %; maximum 15 %	< 10 %; maximum 15 %
sand content	< 40 %	< 40 %; >40 % if I_P >10 %
clay content	>10 %	10-40 %
liquid limit	>25 %	-
plastic limit	>15 %	-
plasticity index (I_P)	>10 %	>10 %; optimum 20-30 %
initial shear strength	>20 kN m^{-2}	-
dry density (ρ_d)	$0.85\ g\ cm^{-3} \leq \rho_d \leq 1.45$	
installation water content (w)	30 %≤w≤80 %	20 %≤w≤40 %

When it comes to the question of the suitability of processed dredged material for dike construction, it must also be assessed whether contaminants are present in the material and if these contaminants pose an environmental hazard. Within the assessment of the suitability of soil material and mineral waste for recovery, two different guidelines apply for the geochemical characterization, depending on the intended use. In Figure 2.1 an overview of the regulations for the utilization of soil material is provided.

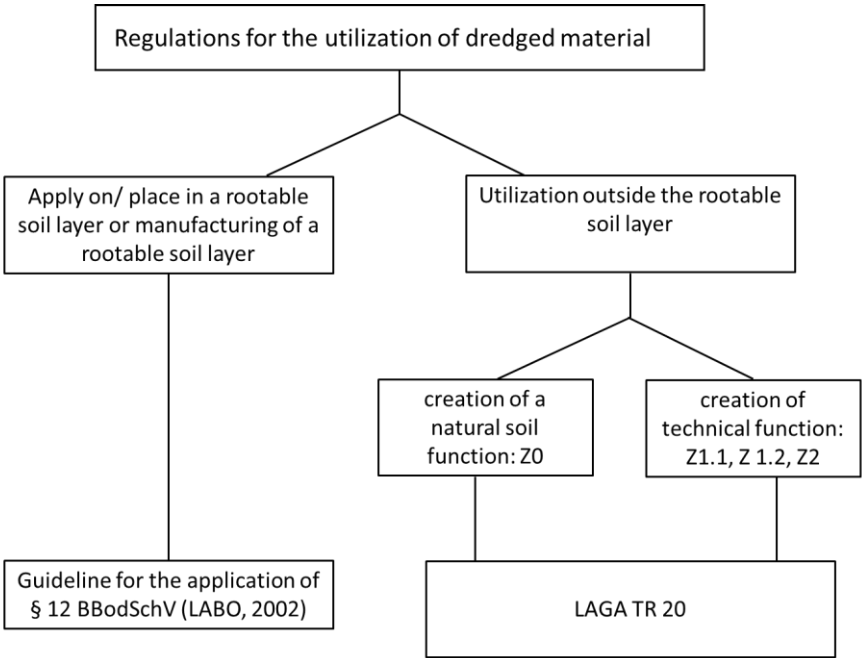

Figure 2.1 Overview of the regulations for the utilization of soil material (modified according to LAGA, 2004).

If the material is intended to be inserted in or applied on a rootable soil layer or is used for the installation of a rootable soil layer, the Federal Soil Protection Ordinance (BBodSchV, 1999) is to be applied and quality requirements specified in Annex 2 of the BBodSchV are to be met (see Figure 2.1). In the guideline for the application of §12 of the BBodSchV, regular thicknesses for the rootable soil layer for grassland use are specified with 50-150 cm, but it is also stated there that the thickness of the rootable soil layer corresponds to the root penetration depth that corresponds to the site-typical or intended vegetation (LABO, 2002). The aim of greening dikes is to promote a very dense shallow turf and to prevent deep root penetration. Therefore, the root penetration depth, i.e. the thickness of the rootable soil layer is expected to be about 30 cm. This value is also stated as rooting zone thickness in Saathoff et al. (2015).

For soil material intended for the construction of technical structures and, in the case of greened technical structures, for material intended to be inserted below the rootable soil depth, the requirements specified in the technical rules (TR) for soil material from the LAGA (LAGA, 2004) are to be applied. However, fine-grained organic dredged material is not directly subjected to the LAGA restrictions, because these restrictions are only valid for materials with a total organic carbon content of less than 5 % and a clay content of less than 10 %. Since no other requirements for materials with higher TOC and clay contents exist so far, Saathoff et al. (2015) recommend the use of LAGA for the geochemical characterization of these materials. For an open application of soil material in a technical construction, the classification limits according to LAGA with the assignment criteria Z0 or Z1 are recommended to be used. The assignment values Z0-Z2 represent upper limits of installation classes (LAGA, 2004). Materials whose pollutant contents exceed the Z1 assignment values and fall below the Z2 value are to be assigned to installation class 2 and therefore are to be installed in a sealed/encapsulated manner. If individual parameters determined in the solids are increased (> Z0), additional eluate tests are required (LAGA, 2004). For dike construction, the eluate quality is of vital importance because dikes are constructed in a not completely impermeable manner and infiltration of seepage water may cause a leaching of contaminants. The installation of materials meeting the Z0 and Z1.1 LAGA assignment for the eluates of soils, is considered uncritical. If contaminant contents in the eluates breaches these limits, the environmental harmlessness may be proven by means of a leachate prognosis according to BBodSchV (Saathoff et al. 2015). Also against the background that the LAGA are not a legally binding regulation, it is generally possible to prove the environmental harmlessness of a utilization of materials by other means (expert statement).

When evaluating the determined contaminant contents of the eluates according to BBodSchV typically knowledge about the eluate composition under in-situ conditions is missing and laboratory tests as a prognosis of eluate concentrations are applied. Here, two types of procedures are appropriate: Batch-extractions and column extractions are both used to estimate the source strength, i.e. the contaminant concentration in the leachate directly at the contaminant source. However, the trigger values of the soil-groundwater path specified in the BBodSchV apply to the site of assessment, namely to the transition zone from unsaturated to saturated soil conditions (see Figure 2.2).

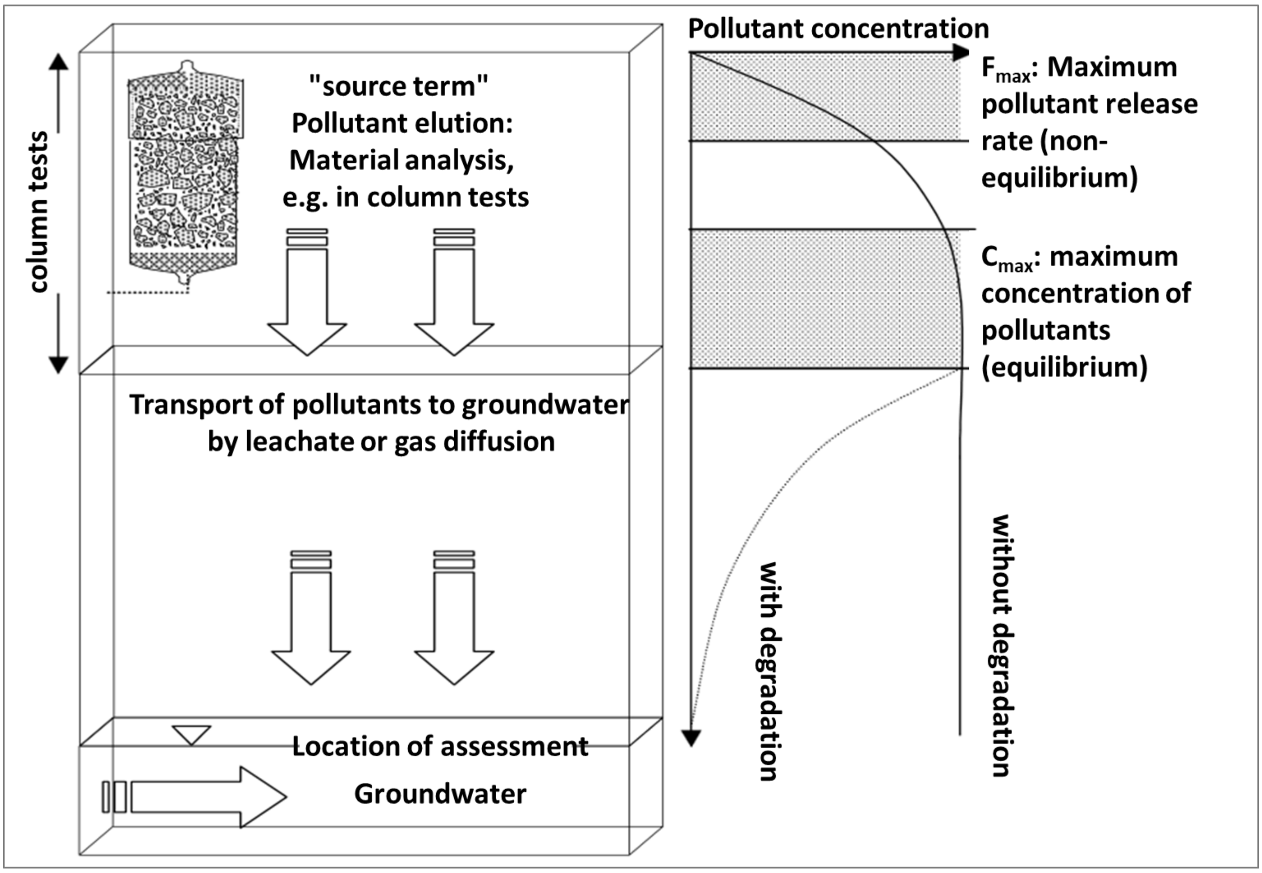

Figure 2.2 Schematic diagram for leachate prognosis (modified according to Susset, 2004).

In the case of dikes, the problem arises that the position of the transition zone that under different conditions can be equated with the groundwater level of the surrounding area, may be located in the upper layer of the dike cover in the case of high tides. The trigger values according to the BBodSchV therefore only represent an approximation to the evaluation of the eluate contents of the conducted laboratory leaching tests. According to BBodSchV (1999), the evaluation of the hazardous potential of leached contaminants to the groundwater is based on a leachate prognosis as far as no leachate data are available. In the course of the leachate prognosis, the retention and degradation capacity of the vadose zone, i.e. the decrease in concentration and load of the contaminants when the leachate percolates through the vadose zone, is estimated by means of substance- and site-specific transport considerations. For organic substances, sorption and microbial mineralization is possible during percolation, whereas sorption and precipitation processes have to be considered for trace metals.

2.2 Previous Research on processed dredged material in dike construction

Research focusing on dredged material usage in dike construction has developed rapidly over the past decade (Saathoff et al., 2015). There have been various field trials for about 20 years that have been carried out with different dredged materials. One of the first field trials was started in 2001 in Friesland (Germany). In the course of the restoration the northern dike line of the Maade River, two test fields were constructed from processed dredged materials. The materials originated from dewatering fields in Bremen Seehausen and from the METHA plant in Hamburg. In the investigations on the geochemical suitability it was shown that for all parameters except sulphate, the Z1.2 assignment criteria of the LAGA (2004) were met. The installation was performed without special preparation of the material with the installation method´s used for traditional dike construction material. The dredged material was installed and compacted with crawlers. In total, the dredged material layer thickness was 1 m. The upper part of the sealing consisted of 25 cm marsh sediment. The investigations on the physical and geochemical properties revealed that both the dredged material from Bremen and Hamburg was suitable for dike construction (HTG, 2006).

Another example for the implementation of dredged material in dike construction, described in HTG (2006) and Saathoff et al. (2015), is the Norddeich CT 4 in Bremerhaven (Germany). Here, a 900 m long dike was constructed from processed dredged material from the Bremerhaven Harbor. According to the results of the chemical analyses the processed dredged material was found to meet the Z1.2 assignment values. Only the parameters conductivity, chloride and sulphate, were found to exceed the Z 1.1 criteria. According to HTG (2006) both the investigations on the Maade River dike and the Norddeich CT 4 in Bremerhaven revealed that fine-grained dredged material is a very well-suited dike construction material equivalent in quality to the traditional used construction marsh sediments and that the dredged material can be handled and installed well even under unfavorable weather conditions, in some cases even better than the marsh sediments due to less adhesiveness.

From 2011-2015, the use of dredged material in dike construction was investigated in an international research project called DredgDikes initiated by the University of Rostock, chair of Geotechnics and Coastal Engineering and Gdansk University of Technology, department of Geotechnics, Geology and Maritime Engineering. Within this project, the application of fine-grained dredged materials as a substitute for traditional dike construction material or in homogenous dikes, as well as the use of composites of ash, dredged sand and the use of geosynthetics in dike construction was investigated. Three large-scale test dikes were built to gain deeper knowledge on installation and performance of dredged material installed. One test dike was built up in Rostock. At this test dike investigations on various research topics such as construction, stability, deformation, vegetation, erosion stability, desiccation cracking, water infiltration and seepage were carried out. A second test dike installed in the area of Gdansk was installed to investigate the suitability of a composite of ash and dredged sand for dike construction. The third large-scale test dike was constructed near Rostock to examine the long-term performance of ripened dredged material from the Baltic Sea area. Research results from the projects showed that the dredged materials investigated had a high potential for use as cover layer material in sea dike construction. By means of laboratory tests and infiltration tests in the field it was shown that cover layers built from dredged material exhibit sufficiently low hydraulic conductivities. The investigations on the test dikes revealed a good manageability of the materials during construction and a high stability against erosion due to a rapidly developing dense turf after construction. The often-mentioned tendency of dredged material to form shrinkage cracks, was confirmed within the project. Therefore, materials investigated in the DredgDikes project are yet not recommended as construction material for sealing layer in river dikes without further treatment or additional barrier (Saathoff et al., 2014).

Concerning the suitability of processed dredged material from the Hamburg area for dike construction, different investigations have been carried out in recent years on behalf of the Hamburg Port Authority (HPA). To investigate the long-term physical behavior and the possible mobilization and elution of contaminants of the METHA material, two test fields were constructed on a flood side of a channel closure within the Hamburg harbor in 2004. One test field was constructed from four layers of natural aged marsh sediments (MS). The second test field consisted of three layers of METHA material underlying one layer of aged marsh sediment (Gröngröft et al., 2005). Compaction was performed in layers of about 20-25 cm by using a small sheep-foot compactor. Due to the high water content of the METHA material (mean 61 % DW) in comparison to the aged marsh sediments (40 % DW), the bulk densities of the layer constructed from METHA material were considerably lower (0.93–0.97 g cm^{-3}) than the dry bulk densities obtained for the layers constructed from the aged marsh sediments (1.34–1.38 g cm^{-3}). In 2012, soil excavations have shown pronounced differences between the dredged material and the marsh sediments regarding the structure development of the materials. In contrast to the MS layers, where desiccation had led to the development of a relative dense sub-polyedric structure in the depth, the layers constructed from METHA material showed a rough prismatic structure, which is characteristic for soils with pronounced swelling and shrink behavior (Blume et al. 2015). The width of the vertical cracks ranged between 1 and 2 cm and extended to the bottom of the fine-grained dike cover layer (about 125 cm below surface level). In another test dike (Drewer Hauptdeich) build from METHA Material in 2006, comparable desiccation cracking behavior was observed during excavations in 2016 (Oing et al., 2016). Investigations on the hydraulic conductivity of the test fields under hydraulic pressure during high tides have shown that in the test field constructed from MS the first flooding period led to swelling to an extend that the following flooding period did result in less and in the case of the third flooding period even in no seepage. The seepage of the test field constructed partly from dredged material was almost constant over the three periods of flooding. The explanation for the differences in the hydraulic system behavior was related to disparate shrinking and swelling capacities of the MS and the processed dredged material (METHA material) (Gröngröft et al., 2014). Laboratory experiments on the desiccation behavior of cover layers constructed from MS and METHA material also revealed considerable differences between the desiccation cracking of these materials (Beyer et al., 2012). The results of these laboratory investigations indicated that desiccation cracking in the METHA Material occurs at lower water contents but also that the cracks reach a greater depth than in the aged marsh sediment. Furthermore, the investigations showed that cracks in the METHA material are less reversible due to swelling than in the aged marsh sediments. These findings are in a good in agreement with the results of the above-mentioned field investigations on the test fields and the test dike.

According to the results of the leachate monitoring on the test fields, the mobilization of pollutants from the METHA material installed occurred according to the redox dynamics recognized by the redox-sensitive speciation of the main elements (Gebert and Gröngröft, 2010). The elemental contents of the pore water as well as of the leachate showed that the sulphidically precipitated trace metals (e. g. cadmium, zinc, nickel) were released intermittently with the oxidation to sulphate. After their release the trace metals were fixed again by sorption or association with iron (hydr)oxides due to the prevailing neutral pH value in the case of continuing oxidative conditions, or precipitation in the case of reoccurring reducing conditions. Elements bound to iron and manganese oxides, such as arsenic, were released initially under reducing conditions and occasionally during the transition to reducing conditions. The analysis of the composition of the test field seepage (2004-2016) showed that the total dissolved trace element content was low (Gröngröft et al., 2016). For the elements copper, nickel and arsenic, occasional exceedances of the BBodSchV (1999) threshold values for soil groundwater path were detected. Exceedances of the Ni an As values occurred during the first test phase (2004-2006) in which reducing conditions prevailed in the dike cover layer. The maximum values were determined with 69 µg/l (Ni) and 36 µg/l (As). The maximum copper content in the leachate was determined in 2016 with 96 µg/l. Lead was found only exceptionally and in very low concentrations in the leachates. The cadmium content of leachate decreased continuously from initial values of up to 1 µg/l, so that after 2009 no contents above the determination limit of 0.3 µg/l were determined. After a maximum content of 300 µg/l in the transition phase from reduced to oxidized conditions (2005), zinc was determined always in contents below 50 µg/l in the leachate. An exceeding of the EPA-PAH (without naphthalene) threshold value of 0.2 µg/l was determined in the leachate of both test fields only in April 2008. However, the temporal parallelism and singularity of this measurement suggest a methodological artifact. In the period 2013-2015, the average EPA-PAH content of leachate was < 0.032 µg/l and therefore continuously below the threshold value of the BBodSchV.

2.3 Ripening of dredged material and its consequences for physical properties and contaminant leaching

After disposal of dredged material on land, de-watering, settling and consolidation of particles and suspended matter takes place. The transformation of the soft anaerobic sediment into an aerated soil with structure is referred to as ˈripeningˈ (Vermeulen et al., 2003). According to Saathoff et al. (2015) the terms ˈripeningˈ and ˈripening processˈ are used for the drying of dredged material, associated with mineralization and the occurrence of soil genesis effects. According to Pons and van der Molen (1973), the process of ripening may be subdivided into three in part simultaneously ongoing processes: physical, chemical and biological ripening. During physical ripening, the consistency of the sediment changes from soft to friable or hard. On land disposal sites, the progress of the physical ripening can be observed directly as the subsidence of the surface results in the formation of soil prisms separated by shrinkage cracks (Pons and van der Molen, 1973). The physical ripening stimulates the process of chemical ripening because it improves aeration of the sediment which, in turn, causes the oxidation of sediment compounds. Biological ripening consists of changes in the composition of microorganisms and the structure of organic matter during oxidation and after aerobic conditions are reached.

In the following the processes of physical and chemical ripening are described in more detail and discussed against the background of how these processes may influence properties of processed dredged material used in dike construction.

Rijniersce (1983) defined **physical ripening** as a soil forming process, by which a sediment that is exposed to drier hydrological conditions than those with which it can maintain equilibrium is practically irreversibly converted into more compact, aerated, more permeable material, the physical properties of which depend on the new hydrological conditions and which can be designated by the name soil. According to Kim et al. (1993a) physical ripening is regarded as an initial soil-forming process caused by drying and wetting. After a series of drying/shrinkage and wetting/swelling events, land disposed sediments exhibit a physically ripened state with a marked improvement of the soil structure (Bronswijk, 1989), amended aggregate stability and enhanced permeability (Kim et al., 1993b).

When a swelling and shrinking soil or sediment dries out, the following four shrinkage stages are distinguished (Haines, 1923; Stirk, 1954; Bronswijk, 1990, see Figure 2.3):

(1) structural shrinkage

(2) normal shrinkage

(3) residual shrinkage

(4) zero shrinkage

Figure 2.3 shows the relationship between moisture ratio (ratio of water volume to solids volume) and void ratio (ratio of void volume to solids volume) for two different materials and the corresponding shrinkage stages.

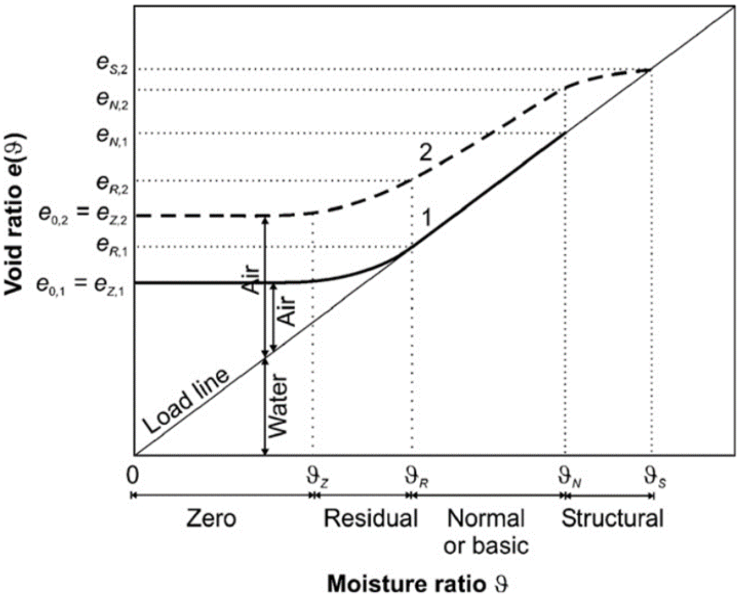

Figure 2.3 Shrinkage stages occurring during the shrinkage of materials with varying physical ripening stages (modified according to Cornelis, 2006).

Samples of moist, homogeneous, non-structured materials behave in accordance with the continuous line (line 1, see Figure 2.3). If the water content of such a material decreases, the internal tension forces of the water at first pull the particles more closely together. Surface cracks appear while the inside of the sample remains saturated with water. The changes in porosity or void ratio respectively, are proportional to the decrease of the water content. This part of the shrinkage is called **normal shrinkage**. This process changes when the particles are packed so tightly that they are able to absorb the increasing internal tension forces. Then air penetrates into the specimens and the volumetric shrinkage is less than the loss of water. Volume changes occurring in this phase are referred to as **residual shrinkage**. As soon as the soil particles have reached their densest packing, no further decrease in volume occurs at further dewatering. This is the **zero-shrinkage** phase.

Samples of structured materials, on the other hand, behave according to the dashed line (line 2, see Figure 2.3). Starting from saturated conditions at which all pores are completely filled with water, dewatering at first leads to a penetration of air into cracks and the gaps between the aggregates, with little volume changes. This phase is called **structural shrinkage**. As soon as cracks and interaggregate spaces are filled with air, further water loss can only occur when water from inside the aggregates is released. Due to the increasing tension forces inside the aggregates, their volume decreases proportionally to the loss of water ("normal shrinkage"), afterwards air penetrates into the aggregates ("residual shrinkage") and at the end no further volume change occurs upon dewatering ("zero shrinkage").

A re-saturation of dried soil or sediment with water leads to a swelling of the aggregates as, in turn, the components that are capable of swelling adsorb or store water. The volumetric change of the aggregates initially leads to a reduction of the interaggregate gaps and cracks, while the ˈexternal ˈ volume of the specimen remains constant. Only when the cracks are closed and the swelling forces are exceeding the superimposed load of the layers overlying the layer can there be an increase in volume. While the change in volume during the normal shrinkage phase is predominantly irreversible, the changes in volume described by structural shrinkage are reversible, i.e. they occur with all changes in water content.

Fresh sediments, such as marine mudflat sediments after embankment or filled up fine-grained dredged material, initially behave in accordance with the above-mentioned processes of homogeneous materials (Pons and Zoneveld, 1965; Rijniersce, 1983). The materials respond to the tension forces generated during initial drying by irreversible normal shrinkage. This irreversible normal shrinkage leads to the formation of a rough column structure. As soon as this phase is exceeded, reversible swelling and shrinking processes form aggregates within the columns without being able to close the primary cracks again.

The major **chemical ripening** process concerning land disposed sediments, is the oxidation of reduced sulfur compounds (Vermeulen et al., 2007). As in anoxic sediments the partitioning of trace metals is generally dominated by the formation of metal sulfides such as sphalerite (ZnS), galena (PbS) and different Fe-sulfides (FeS, FeS_2) (Caille et al., 2003), oxidation can lead to increased metal leachability (Gambrell, 1994) and hence the release of considerable amounts of trace metals, in particular for some elements like Zn and Cd (Caille et al., 2003; Isaure et al., 2005; Lors et al., 2004; Stephens et al., 2001; Tack et al., 1996). At neutral pH conditions, released trace metals can be retained by rapid re-adsorption onto the surface of clay minerals and organic matter (Calmano et al., 1993; Tack et al., 1995; Du Laing et al., 2009). Furthermore, reduced iron becomes suddenly oxidized to Fe(hydr)oxides under oxic conditions. Fe- as well as Mn-(hydr)oxides exhibit large specific surfaces and are therefore capable to adsorb trace metals from soil solution as well (O’Day et al., 1998; Panfili et al., 2005; Piou et al., 2009). Besides hydroxides, sulphates and phosphates are secondary phases at which trace metals can precipitate under oxic conditions (Lions et al., 2010). However, the redistributed contaminants are potentially more mobile than the original reduced sulfide form (Tack et al., 1996; Hartley et al., 2010). Apart from the release of trace metals, oxidation of sulfides can lead to a mobilization of trace metals by causing a fundamental change in a major fate controlling parameter – the pH. This is because during the oxidation of sulfides, protons are produced leading to an acidification of the oxidized sediment. This especially applies for soils and sediments with low carbonate contents and low acid neutralization capacities (Calmano, 1993; von Lührte, 1997). If the concentration of H^+ ions in the soil solution increases, the negative charge of the surfaces of the organic substance, clay minerals and Fe and Mn oxides decreases, thus increasing the solubility and mobility of the heavy metals bound to these substances (Du Laing et al., 2009). This is particularly applies for trace metals with lower affinity to specific bonding such as Cd and Zn. The proportion of specifically bound trace metals is determined by the stability of the trace metal´s hydroxocomplexes. The order of stability is Cd < Ni < Zn < Cu < Pb (Scheffer and Schachtschabel, 2010).

According to Cappuyns et al. (2003), the leaching of metals upon acidification is the result of desorption of cationic trace metals from cation exchange sites and the dissolution of solid soil compounds such as oxides, clay minerals and carbonates. Ca^{2+} released into soil solution due to the dissolution of $CaCO_3$ can enhance the mobilization of trace metals such as Cd (Christensen, 1984, Wang et al., 1997) Zn (Wang et al., 1997) and Pb (Griffin and Au, 1977). According to Christensen et al. (1984), the mobilizing effect of Ca^{2+} is due to its competition with Cd for sorption sides. Bicarbonate, which is also released during the dissolution of $CaCO_3$, forms complexes with Cu. According to Scheffer and Schachtschabel (2010), in the presence of HCO_3^-, Cu is present in soil solutions of soils with a pH value > 6 with about 80 % in the form of carbonato-complexes.

The oxidation and mineralization of organic matter (OM) may also lead to a release of metals bound to oxidizable fractions (Schulin et al., 1995; Stephens et al., 2001). During the oxidation of OM, protons are released, which can contribute to acidification. Mineralization of organic matter and the resulting possible conversion into dissolved organic matter (DOM) can lead to the mobilization of trace metals bound to OM (Savric, 2001). Dissolved organic matter can increase the release of metals bound to the sediment. This is especially true for copper, which is known to have a high affinity for organic matter (Salomons, 1995; Lager et al., 2005). The formation of potential mobile metal organic carbon complexes under oxidizing conditions prevents copper from co-precipitation with or adsorbing onto Fe (hydr)oxides (Rinklebe and Shaheen, 2014). According to Herms and Brümmer (1984), mobilization of heavy metals by soluble organic complexing agents can occur in the series Cu > Cd > Zn > Pb.

Arsenic mobility clearly differs to that of trace metals. Under oxic conditions, the most common As species in soils and sediments is Arsenate, which is immobilized by sorption to iron oxides (Fitz and Wenzel, 2002; Wenzel et al., 2002). Therefore, Arsenic mobilization from sediments is mainly related to changes in redox conditions (Hartley et al., 2004, 2009), with moderately reducing conditions being conducive for As release from sediments (Xie et al., 2009). Regarding the pH, As in contrast to the trace metals, becomes more mobile at high pH values of about 7 (Scheffer and Schachtschabel, 2010).

The behavior of organic pollutants such as polycyclic aromatic hydrocarbons and the effect of chemical ripening on the behavior and fate of these compounds in sediments also differs from that of the trace metals. The substance-group of polycyclic aromatic hydrocarbons (PAH) includes several hundred individual compounds with a broad spectrum of physicochemical properties and biological effects. Due to their low solubility in water and high affinity to hydrophobic organic substances and surfaces, they accumulate in the environment, especially in terrestrial soils and aquatic sediments. Although PAHs are strongly sorbed to soil organic matter, they were found at greater soil depth indicating that PAH can at least partially be leached out with seepage water (Wild and Jones, 1995; Wilcke et al., 1996).

In addition to toxicity, potential mutagenicity and other hazardous effects, the further fate of these substances in the environment is important for the assessment of a potential risk posed by these substances. Since degradation is slow or incomplete for many PAH, especially higher condensed PAH such as Benzo(a)pyrene, reversible and irreversible sorption processes in soil and sediments are of paramount importance for their fate and hence, for the assessment (Marschner, 1999). Sorption and desorption are crucial processes not only for PAH bioavailability but also for PAH transport in soil (Wilcke, 2000). In soils and sediments two phases of PAH sorption occur. The first rapid phase leads to a relatively stable distribution of the respective substance between solution and sorbent within a few minutes, hours, or days (Pignatello, 1989). This phase probably corresponds to the sorption to sites near the surface of organic macromolecules (Wilcke, 2000). The second phase of sorption is slow and may be caused by sorption to carbonaceous OM fractions (Cornelissen et al., 2005) or may be explained by a diffusion to more surface-distant binding sites, the so-called aging (Weissenfels et al., 1992; Eschenbach, 1995).

For hydrophobic compounds such as PAH the organic substance is the most important sorbent (Chiou et al., 1998; Litz, 1990). Different models are used to explain the binding tendency. Decisive factors are the high specific surface area and the multitude of functional groups of the binding partners as well as the possibility of the formation of chelates (Schleuß and Wu, 1996). Covalent bonds, hydrophobic interactions and diffusion-controlled distribution processes are also relevant (Marschner, 1999). For hydrophobic organic environmental chemicals, such as PAH, the essential element of sorption is "hydrophobic bonding" (Förstner and Grathwohl, 2007; Kleineidam, 1998). In contrast to trace metals, binding does not take place via functional groups of humic and fulvic acids, but mainly in the hydrophobic areas of organic matter (Kördel et al., 2011), inner hydrophobic structures and via complexation (Eschenbach et al., 1998). Consequently, the composition and quality of the organic substance contained in soils and sediments influences PAH behavior. Therefore, as for the trace metals, oxidation and mineralization of OM taking place after the deposition of dredged material on land may have an impact on the mobility of PAH. The conversion of organic matter in dissolved organic matter is one of the most important processes for the mobilization of PAH because desorption of PAH from soils and sediments may be enhanced by dissolved organic matter serving as PAH carrier (Wilcke, 2000). The association of PAH with dissolved organic matter depends on the polarity, molecular size, configuration, and chemical composition of the carrier molecule (Marschner, 1999). It has been shown that large molecules that contain nonpolar domains such as humic acids exhibit a higher capacity to bind organic contaminants than more polar fulvic acids (Chiou et al., 1983, 1986). Especially the leaching of higher molecular PAH may be caused by association with DOM (Gauthier et al., 1987; Maxin and Kögel-Knabner, 1995; Chin et al., 1997), as these PAH are more hydrophobic. In investigations of Jones et al. (1989) it was shown that the leaching rate did not decrease with increasing molecular weight to an extent that was expected based on the water solubility of the different compounds. The authors regarded this as an indicator for particle-associated transport of the high molecular weight PAH mediated by the dissolved organic carbon. However, Totsche et al. (1997) reported of a mobility decreasing influence of dissolved organic matter and attributed it to co-sorption of PAH associated with DOM. According to the authors, subsoil horizons containing high amounts of Fe-oxides may act as barrier for PAH transport because DOM is strongly retained by these oxides (Totsche et al., 1997).

The sorption characteristics of both solid and dissolved organic matter can be modified by the chemical environment such as pH and ionic composition/electrolyte content of the soil solution (Marschner, 1999). These parameters also may promote or inhibit the formation of DOM. As described above, chemical ripening, especially oxidation of anoxic sediments can cause a change in pH particularly with sediments that contain little carbonate contents. In a column experiment, Marschner (1998) investigated the effect of varying pH values on the leaching of benzo(a)pyrene from a trickle- field soil. It was found that acidification from a pH of about 6 to a pH of 3.3 increased DOM but reduced benzo(a)pyrene leaching. The authors ascribed this phenomenon to the composition of the DOM that consisted mainly of hydrophilic acids with a low affinity for PAHs.

With increasing residence-time of PAHs in soils their extractability, degradability, and toxicity decrease due to aging (Hatzinger and Alexander, 1995; Beck et al., 1996, Eschenbach et al., 1998). The degradability and extractability of organic environmental chemicals can decrease sharply over weeks, months and even years without chemically a verifiable chemical altering of the substances (Pignatello, 1989; Hance and Führ, 1993). The phenomenon that PAH are less extractable from soils with increasing residence time can be attributed to various binding processes such as slow sorption processes, physical entrapment, biogenic fixation and also mineralization and formation of metabolites (Eschenbach, 1995; Eschenbach and Oing, 2013). Mahro and Kästner (1993) stated that the formation of non-extractable residues (NER) of PAH is controlled by incorporation into humic substances via covalent bonds.

Depending on the process of the formation of the NER or the binding type respectively, NER are potentially remobilizable and therefore can pose a risk to the environment. NER fixated by covalent bonding may be considered to be irreversibly bound to the soil. A release of these NER and NER that are included in microbial biomass and biogenically bound can be considered as unlikely. Heavily sorbed or physically entrapped NER, i.e. in hydrophobic cavities of the organic substance or in the intermediate layers of clay minerals are considered as potentially remobilizable (Eschenbach and Oing, 2013). Potentially remobilizable NER represent a possible hazard and should therefore be taken into account in risk assessment (Eschenbach et al., 2000).

3 Material and methods

3.1 Material selection and sampling

For the investigations, samples of processed dredged material (n=21) and of fine-grained aged marsh sediment (MS, n=4) were analyzed. The dredged materials can be divided into different groups according to the type of material processing and the (chemical/ripening) status of the material. An overview over the material groups is given in Table 3.1.

Recently produced (fresh) technically processed dredged material (METHA, n=9) was obtained directly from the METHA plant. These samples were taken in the period from March to July 2014. In order to cover the entire spectrum of material properties of processed dredged material from the METHA, criteria for material selection were defined in advance. These criteria were determined on the basis of the statistical evaluation of analysis data of METHA output material (n=104) produced between May 2009-December 2012. Although the METHA samples produced in the sampling period differed in part from the predefined criteria with regard to their sand contents and loss on ignition values, the materials chosen for the investigations cover a broad spectrum for both parameters. Sand contents vary between 21 and 47% by weight and loss on ignition values between 5.5 and 9.9 % DW. Therefore, the chosen materials can be regarded as representative for dredged material processed in the METHA plant (Eschenbach et al., 2013).

Samples of ripened processed dredged material originated from an open depot (OD, n=3) where METHA material was able to ripe for about one year and the lower part of a dike cover layer (DC, n=6) which was partly constructed from METHA material in 2006.

Material of the group of naturally processed dredged material was obtained from open dewatering fields in Hamburg-Moorburg (DF, n=3), where the dredged material was naturally dewatered for about one year.

The samples of the fine-grained aged marsh sediments originated from two sediment depots of the Hamburg Port Authority, one depot of the Schleswig-Holstein Agency for Coastal Defence, National Park and Marine Conservation (LKN SH) in Nordstrand and a depot of the Artlenburger dike association near the city of Lüneburg. All materials from the depots serve for dike construction and maintenance exclusively.

Table 3.1 Overview of the tested materials. OD= open depot, DC= dike cover, MS= marsh sediment, HPA= Hamburg Port Authority, LKN SH= Landesbetrieb für Küstenschutz, Nationalpark und Meeresschutz Schleswig Holstein.

Material group		Sample	Origin
Technically processed dredged material	Fresh from the METHA plant	METHA 1	Direct output of METHA plant
		METHA 2	
		METHA 3	
		METHA 4	
		METHA 5	
		METHA 6	
		METHA 7	
		METHA 8	
		METHA 9	
	METHA material ripened under natural conditions	OD 1	Interim depot Dradenau since May 2014, sampling depth: 10-30 cm
		OD 2	Interim depot Dradenau since June 2014, sampling depth: 10-30 cm
		OD 3	Interim depot Dradenau since July 2014, sampling depth: 10-30 cm
		DC 1	Dike top, sampling depth: 85-100 cm
		DC 2	Dike top, sampling depth: 130-1170 cm
		DC 3	Outer slope, sampling depth: 100-130 cm
		DC 4	Outer slope, sampling depth: 130-190 cm
		DC 5	Inner slope, sampling depth: 45-65 cm
		DC 6	Inner slope, sampling depth: 80-185 cm
Naturally processed dredged material	Dewatering fields	DF 1	Dewatering field 2 Moorburg-Mitte (middle)
		DF 2	Dewatering field 2 Moorburg-Mitte (end)
		DF 3	Dewatering field 6 Moorburg-Mitte (end)
Traditionally used dike construction material	Fine-grained aged marsh sediments	MS 1	Depot Finkenwerder Sand, HPA
		MS 2	Depot Trudel Op, HPA
		MS 3	Depot in Nordstrand, LKN SH
		MS4	Depot near Lüneburg, Artlenburger Dike Association

3.2 Methods

3.2.1 Basic characterization of the materials

The first step was to characterize the basic physical and chemical properties of the materials. Samples were homogenized, air-dried and sieved to pass a 2 mm screen. A part of the sieved material was milled using a disc mill with an inlet made of tungsten carbide and oven-dried at 105°C before use.

The following basic **physical properties** were analyzed:

- Water content was examined in accordance with DIN ISO 11465.
- Grain-size distribution was analyzed by a combination of sieving and sedimentation according to DIN ISO 11277 after removal of organic matter and carbonates using a sedimat device (Sedimat 4–12, UGT GmbH, Müncheberg, Germany).
- The determination of the liquid limit and plastic limit was conducted according to DIN 18122-1.
- Particle density was measured by helium gas pycnometry (AccuPyc II 1340, Micromeritics GmbH, Aachen, Germany) according to DIN 19683.

Basic characterization of the **chemical properties** of the materials consisted of the following parameters:

- pH values were determined according to DIN EN 15933.
- Specific electrical conductivity was examined in accordance with DIN ISO 11265.
- Total carbon and nitrogen content was determined according to DIN EN 15936 using an elemental analyzer (VarioMAX, Elementar GmbH, Hanau, Germany).
- Inorganic carbon content was examined by gas chromatography analysis (7890 GC System, Agilent Technologies, Santa Clara, USA). Prior to analysis, milled soil samples were processed with phosphoric acid (43 %) to transform inorganic carbon into CO_2 (Luther-Mosebach, 2016).
- Organic carbon content was calculated from total and inorganic carbon content.

3.2.2 Characterization of compactibility and shrinkage behavior

One focus of the geotechnical characterization of the samples was given on their **compactibility**. The Standard Proctor compaction test was used to determine the maximum bulk density (in the following: Proctor density PD) and the corresponding optimum moisture content (w_{opt}). The tests were carried out according to German Standard DIN 18127 with a compacting energy of 586 kNm m^{-3} and materials, which were air-dried and passed through a 2 mm sieve. Each compaction test was conducted at a minimum of five water contents. For every compaction cycle the same material was used and the water content was increased by 2 % DW for each cycle. Based on the measured relationship between water content (% DW) and bulk density (g cm^{-3}) two linear regressions were calculated, one each for the ascending and descending section. The values of PD and w_{opt} were calculated from the intersection of both regression lines. Besides Proctor densities, the initial densities of the materials were determined. For this purpose, compaction tests based on the standard Proctor test procedure were carried out with materials at their initial water contents i.e. without any pre-drying.

The concept for the investigations on the **shrink and swell behavior** of the materials consisted of two parts:

1. Determination of the shrink capacities in small-scale experiments (shrinkage limit and volumetric shrinkage rate according to German DIN 18122-2 (2000), Coefficient of linear extensibility in accordance with the method described by Schafer & Singer (1976a))
2. Determination of the shrink and swell behavior in large-scale experiments.

The determination of the shrinkage limit was performed according to DIN 18122-2. The volumetric shrinkage rate was calculated from the initial sample volume and the sample volume at the end of the test. Coefficient of linear extensibility (COLE) was determined on remolded samples according to Schafer & Singer (1976a) and is referred to as $COLE_{rod}$.

The large-scale experiments were carried out in polyethylene tubs of 60x41 cm base area and a volume of 96 l. In Figure 3.1, the experimental set-up of the large-scale swelling and shrinkage investigations is shown schematically.

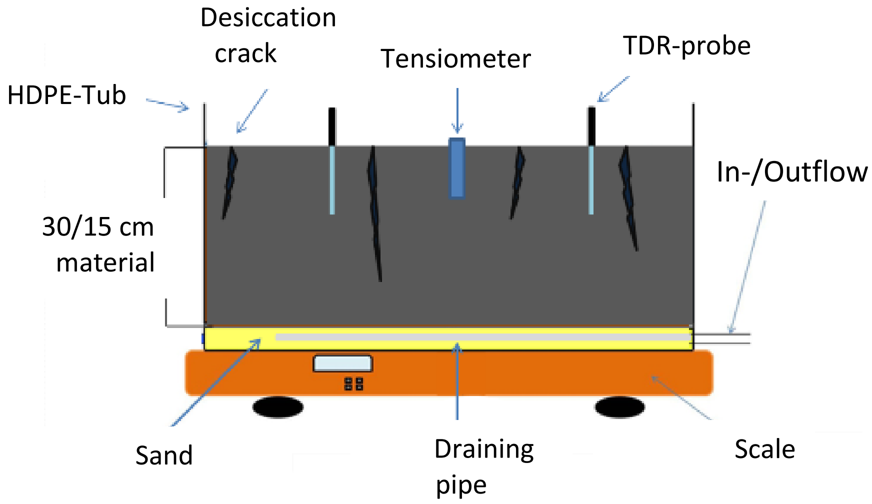

Figure 3.1 Schematic illustration of the experimental set-up of the swell and shrinkage investigations in the large-scale experimental approach.

About 75 l of the samples were compacted into the tubs in three layers. Each layer was compacted with 346 kNm m^{-3} by using a construction stamp. This compaction procedure is based on the Standard Compaction Method for METHA material developed at the University of Hanover (IGBE 1993). The installation took place at initial water contents of the samples (dredged materials: 50-62 Vol.%, MS: 28-31 Vol.%). In the first test series, in which five samples (METHA 1, 2, 3, 4, 6) were analyzed, the height of the specimens after compaction was about 30 cm. In the following test series (METHA 7, 8, 9, DF 1, 2, 3, MS 1, 2, 3) the height of the specimens was reduced to 15 cm to accelerate the drying process. To enable a steady saturation, the tubs were equipped with a sand layer at the bottom which contains a draining pipe that was connected to a feed line for saturation of the samples (see Figure 3.1). For the investigation of the shrink and swell behavior, the samples were dried out for about 20 weeks (first test series) and 15 weeks (second test series).

The evaporative water loss was determined by weighing the tubs (KPZ 51E-9-1, K-PZ Waagen, maximum load 300 kg). In the first test series, the specimens were equipped with Tensiometers and TDR-probes to determine the water content decrease during the drying process in detail. For saturation, the specimens were filled up with water gradually from the bottom to the top. The water level was increased slowly over a period of 10 days to prevent air inclusions in the pores. After saturation, the water was let out and the specimens were dried for 20 (test series 1) to 30 (test series 2) weeks again. Although base area of the samples was high, samples reacted with monolithic shrinkage and visible cracks occurred exclusively along the outer walls. Therefore, the volume of the specimens could be determined by measuring the height, length and width of the specimens at the beginning and every second week during the whole time of the experiment.

For the determination of height loss, the space between sample surface and tub edge was measured in a grid pattern. The distance between side margin and sample was approximately determined by assuming a trapezoidal shape of the gap. Solid, void, water, shrinking and swelling volumes as well as dry bulk densities (DBD), moisture ratio and void ratio were calculated from the measurements of specimen’s volume and weight.

3.2.3 Investigation of further processing methods

One subquestion in the investigation of compactibility and shrinkage behavior was whether it is possible to improve the behavior of METHA materials with regard to these properties by means of further processing methods. Since both compactibility and shrinkage behavior strongly depend on the installation moisture content, it was hypothesized that drying and ripening (repeated drying and swelling) would be useful pre-treatment options.

The concept for the investigation on the effect of further processing of the dredged material on its compactibility consisted of three processing approaches:

1. Air-drying of the materials to four different initial water contents (10 % DW, 20 % DW, 30 % DW, 40 % DW)
2. Oven-drying at 30 °C and 105 °C until weight constancy
3. Ripening of the materials under laboratory conditions.

Ripening (repeated drying and swelling) under laboratory conditions was performed in line with the large-scale shrinkage experiments described above. Compactibility of the differently further processed materials was then assessed using the Standard Proctor test according to DIN 18127 (2008).

For the investigation on the effect of further processing of the dredged material on its shrinkage behavior the coefficient of linear extensibility ($COLE_{rod}$) according to Schafer and Singer (1976a) was determined on ripened dredged materials.

3.2.4 Characterization of the total pollutant contents

The extraction of **total trace metals amounts** was performed using microwave-assisted aqua regia digestion. About 0.5 g of milled material was weighed in Teflon-PFA microwave vessels and 13.5 ml of aqua regia (37 % HCl and 65 % HNO_3; 3:1) were added. Digestion was performed in a Microwave Accelerated Reaction System (MarsXPress, CEM GmbH, Kamp-Lintfort, Germany) with a heat and temperature program recommended for mineral soils by the manufacturer (10 min heating to 160 °C, 15 min holding at 160 °C, 15 min cooling). Extracts were then transferred to 50 ml volumetric flasks, which were filled up to the mark with double demineralized water afterwards. In the next step, the extracts were filtered through blue ribbon filters (Whatman, Buckinghamshire, United Kingdom) into 50 ml PE flasks. Trace metal and arsenic contents of the extracts were determined by graphite tube atomic adsorption spectroscopy (AAS, Varian AA280Z, Santa Clara, USA) - or flame AAS (Varian AA280FS, Santa Clara, USA). Ignoring that certain silicate bound amounts of trace metals may remain in the residuum, the contents extracted with aqua regia digestion are referred to as total trace metal content.

The contents of **polycyclic aromatic hydrocarbons** (PAH), **polychlorinated biphenyls** (PCB) and **organochlorine pesticides** (OCP) were determined by Soxhlet Extraction in accordance with DIN ISO 18287. Approximately 7 g of undried homogenized sample (< 2mm) were mixed with anhydrous sodium sulfate. The dried samples were filled into cellulose extraction tubes and covered with glass wool to prevent loss of material during extraction. 500 µl of deuterated PAH (Nap D8, Ant D10, Chr D12, Per D12) and PCB standard solution (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) were added. The extraction was carried out for 2 hours at 130°C in a Soxhlet apparatus using n-hexane as solvent. After extraction, the extracts were allowed to cool down. Afterwards, the extracts were transferred into volumetric flasks which were filled up to the mark with n-hexane. 1 ml of the extracts were then transferred into a crimp neck vial and stored in a freezer. The determination of the 16 EPA-PAH, PCB and OCP (Pentachlorbenzole, Hexachlorbenzole, alpha-HCH, beta-HCH, gamma-HCH, p,p-DDE, p,p-DDD, p,p-DDT) was carried out by means of gas chromatography mass spectrometry (Agilent GC7890 MS5975C Quadrupole, Agilent Technologies, Santa Clara, USA).

The determination of **mineral oil hydrocarbons (MOH)** was conducted based on DIN EN ISO 9377-2 (H53). 20 g of homogenized undried material were weighed into 100 ml half round flasks, 40 ml acetone were added, and the mixtures were shaken by hand. 20 ml of n-hexane marked with decane (C_{10}), eicosan (C_{20}) and tetracontane (C_{40}) were added. The mixture was agitated for 30 min at 200 rot min^{-1} in a horizontal shaker. In the next step the hexane phase with the solved MOH was separated by adding distilled water, shaking and taking the buoyant phase of by using a one-way glass pipette. This procedure was repeated. Afterwards, the extract was cleaned up by column filtration. Columns were filled with glass wool, 2 g magnesium silicate gel (Florisil®) and 2 g sodium sulfate. In the last step, the cleaned extracts were transferred to 1.5 ml crimp neck vials and stored in a freezer until analysis. The determination of the MKW contents was carried out by means of GC-FID (GC-2010, Shimadzu, Duisburg, Germany).

The contents of organotin cations as well as dioxins and furanes were analyzed in a commercial laboratory.

3.2.5 Characterization of the pollutant leaching behavior

Leaching from fresh and ripened materials

The release of soluble constituents upon contact with water is regarded as a main mechanism of release, which results in a potential risk to the environment during the re-use or disposal of materials.

To assess the potential risk of the release of contaminants from the materials, the **leaching** of pollutants was analyzed. Leaching from fresh (unripened) and ripened, i.e. chemically unchanged METHA material was determined using elution methods provided in relevant regulations /legislative standards (BBodSchV, 1999; LAGA, 2004).
The following elution methods were applied:

1. Ammonium nitrate extraction for the determination of the mobile trace metal contents available to plants according to DIN ISO 19730
2. Batch extractions for the investigation of the leaching behavior of inorganic and organic substances according to DIN 19529 and DIN 12457-4
3. Percolation column test for the joint investigation of the leaching behavior of inorganic and organic substances according to DIN 19528
4. Water impoundment column method for the investigation of the elution behavior of pollutants on undisturbed soil samples according to Gerth (2007).

The extraction of mobile, readily available fractions of trace metals was carried out according to DIN ISO 19730 (2009) and is referred to as **ammonium nitrate (AN) extraction** in the following. In Germany, this method is used to estimate the transfer of heavy metals and arsenic from soils to plants (BBodSchV 1999). 10 g air-dried, homogenized and sieved (<2 mm) soil sample were weighed into 50 ml PE-vessels and 25 ml 1 M NH_4NO_3 were added. The suspension was shaken for 2 h and centrifuged (3000 rot min^{-1}) for 10 min. After centrifugation the obtained solution was filtered through a membrane cellulose acetate filter (45 µm, VE 100) under vacuum, and collected in polyethylene carboys. Afterwards, the filtered solution was preserved by adding of $HN0_3$ (1 % from the extracted solution volume).

The batch extraction according to DIN 19529 is recommended in the Substitute Building Materials and Soil Protection Umbrella Ordinance (UmbrellaO, Draft 2018) for the preparation of eluates with water and is used to estimate the leachate concentration directly at the pollutant source. This extraction was conducted to investigate the elution behavior of inorganic and organic substances with a liquid to solid (L/S) ratio of 2 l: 1 kg dry mass (L/S=2) according to DIN 19529. Due to problems in the applicability of the formula for calculating the eluate volume to METHA materials (because of the high initial water content negative quantities were produced), the method was modified and a ratio of 2 l water: 1 kg wet weight (< 2mm sieved material) was adjusted for extraction.

The **10:1 batch extraction** was performed according to DIN 12457-4. The fresh material was sieved (< 2 mm) and the water content was determined according to DIN ISO 11465. For the extraction with a L/S ratio of 10, an amount of 50 g of the samples were weighed into bulkhead bottles and 500 ml of double demineralized water were added. The shaking was carried out for 24 hours at 15 rot min^{-1} in an overhead shaker (3040, GFL, Burgwedel, Germany) at room temperature. The bottles were removed from the shaker and the mixture was allowed to rest for 15 minutes so that the supernatant could be transferred into centrifuge tubes without rinsing larger amounts of material. After centrifugation for about 30 minutes at 1942 g, the eluates were prepared for pollutant analysis (Trace metals (TM): negative pressure filtration via 0.45 µm cellulose acetate filter, PAH: liquid/liquid extraction with n-hexane) and the target

The **percolation column test** according to DIN 19528 is carried out in upward-flow and is used for the joint examination of the leaching behavior of inorganic and organic substances. Glass columns with an internal diameter 10 cm and a filling height of about 40 cm were fitted with glass wool in bottom and top section. Additionally, a layer of about 5 cm of fine-grained quartz sand was applied in the top and bottom sections of the columns to ensure proper water flow over the width of the column. The < 2 mm sieved material was filled in the columns in 5 cm steps. Each layer was slightly compacted by using the net weight of a small construction stamp (approx. weight 1.5 kg, 9 cm diameter). The quantity of material was determined by weighing. Water content of the material was determined in three replicates according to DIN ISO 11465. The flow rate per time unit was calculated in accordance with DIN 19528 depending on the dry matter, the void ratio or particle density of the materials respectively as well as the column properties (filling height, diameter). After a saturation time of 2 hours, the flow rate was set to a speed that enables a water to solid contact time of 5 hours. The eluates were collected in 10 l glass bottles. For the purpose of a better manageability, sampling of the eluates took place every 24 hours instead of at defined L/S ratios. After sampling the eluates were prepared according to the respective analytics (TM: negative pressure filtration through 0.45 µm cellulose acetate filter, PAH: liquid/liquid extraction with n-hexane). As for comparison purposes and the assessment according to legislative standards the determination of the pollutant leaching at defined ratios is needed, the cumulated loads determined were fitted by a second-degree polynomial and the function was used to calculate the leaching at defined L/S ratios.

The percolation column tests were conducted with the unripened materials (METHA 2, METHA 3, METHA 5, METHA 8 and DF 1). These materials were homogenized and sieved to pass a 2 mm screen in their originally moist conditions. In addition to the tests with the unripened material, the column leaching tests were carried out with ripened material. For this purpose, material from the large-scale-shrink swell experiments was also homogenized and sieved to pass a 2 mm screen before installation into the columns. The tests were carried out in two parallels for all materials and treatment variants.

In contrast to the percolation column test in which homogenized material is packed into column and therefore the leaching from disturbed soil samples is investigated, the method of the **water impoundment column** according to Gerth (2007) enables the investigation of the pollutant leaching from undisturbed soil samples. With this method, comparative investigations on unripened and ripened processed dredged materials were conducted. The column consists of a sampling ring (12 cm x 10 cm; length x diameter). > 2mm sieved, unripened material was packed in layers in the column and compacted with an installation punch to remove cavities. Furthermore, undisturbed soil samples were taken from the soil specimens of the large-scale shrink swell experiments, were the material had been ripened. For sampling of the ripened material, the sampling ring was hammered into the material dissected out afterwards. Then, the samples were saturated by pumping in demineralized water from below until a closed water film formed on the sample surfaces. After a saturation time of 24 hours, the eluates were drawn off by applying a vacuum. The eluates were then prepared according to the respective analytics (TM: negative pressure filtration through 0.45 µm cellulose acetate filter, PAH: liquid/liquid extraction with n-hexane) and analyzed for selected pollutants. Afterwards the samples were saturated again. A total of four elutions (on four consecutive days) were performed on each sample.

Within the scope of the investigations on potential maximum leaching of pollutants from the dredged materials, the first step was to determine the trace metal contents of differently available or mobilizable fractions by means of **sequential extractions**. Sequential extractions are used to characterize the binding behavior of trace metals in soils and sediments and to provide information on the mobility and mobilizability of trace metals. Speciation is carried out by the gradual application of selective extraction agents of increasing strength and the quantitative determination of the contaminant contents in the extracts of the individual fractions. For comparison purposes, the sequential extractions were performed with unripened materials, ripened and incubated materials (METHA 2, METHA 3, METHA 5, METHA 8, DF 1) in three replicates.

The modified BCR procedure, used for the sequential extraction of trace metals from the dredged material samples, represents an improvement on the standardized BCR procedure introduced in 1993 by the former European Community Bureau of References (now European Standards, Measurements and Testing Programme, SM&T). The BCR procedure was introduced to standardize the sequential extraction of trace metals from soil and sediments throughout Europe and to make data collected in this field comparable (Lopez-Sanchez, 2002).

The BCR procedure has been further modified in this study and extended by another extraction step. Ammonium nitrate extraction according to DIN ISO 19730, which is used for the determination of mobile or plant-available trace metal fractions, was conducted before the actual BCR procedure. Table 3.2 provides an overview of the extraction steps, binding forms and mobilizability of the fractions of the sequential extraction.

Table 3.2 Extraction steps, binding forms and mobilizability of the fractions determined by the sequential extraction

	Fraction	extraction agents	binding form	mobilizability
F1	exchangeable / plant available	1 M Ammonium nitrate	Unspecific adsorbed	mobile/easy to mobilize
F2	exchangeable carbonatic	0,11 M acetic acid; pH 7	Unspecific adsorbed, bound to carbonates	mobile/easy to mobilize
F3	reducible	0,5 M Hydroxylamine hydrochloride; pH 1.5	bound to Fe and Mn oxides and hydroxides	moderate mobilizability
F4	oxidizable	pre-treatment: 8,8 M H_2O_2; 1M Ammonium acetate; pH 2	bound to soil organic substance and sulphides	difficult to mobilize
F5	aqua regia soluble	HCl / HNO_3	Residual fraction, part of the crystal lattice of minerals	not mobilizable under natural conditions

The sequential extraction was performed as follows:

Fraction 1: Ammonium nitrate extraction was carried out according to DIN 19730. 10.00 g (± 0.01 g) air-dried and <2 mm sieved sample material was weighed into a 100 ml centrifuge vessel and mixed with 25 ml of 1 M ammonium nitrate solution (80.04 g/l NH_4NO_3, Merck). Afterwards, the centrifuge cups were shaken for 2 hours in an overhead shaker with 15 rpm^{-1} at room temperature then the solid phase was separated by 20 minutes of centrifugation at 1942 g. The supernatant was filtered by means of vacuum filtration via a 45 µm cellulose acetate filter (Sartorius, Goettingen, Germany) and filled in 50 ml polyethylene (PE) bottles. To stabilize the extract, nitric acid (conc. 1:2) was added to the extract in a volume of about 2 % of the extract volume and the PE bottles were stored in the refrigerator. The sample residue was mixed with 20 ml of bi-distilled water, shaken for 15 minutes and centrifuged for 20 minutes at 1942 g. The decanted washing solution was discarded. The washed material was air-dried for 3 days and then homogenized before further use.

Fraction 2: 1.0 g of air-dried soil was weighed into a 100 ml centrifuge vessel, mixed with 40 ml 0.11 M of acetic acid and shaken in an overhead shaker with 15 rpm^{-1} at room temperature for 16 hours. Then the mixture was centrifuged at 1942 g for 20 min. The supernatant was decanted and filtered into a 50 ml PE bottle via an ashless filter (MN 640 d, Macherey-Nagel).

The extraction step was followed by a washing step in which the residue was washed with 20 ml dist. H_2O by overhead shaking for 15 min and centrifugation for 20 min. The washing solution was discarded.

Fraction 3: 40 ml of 0.5 M NH_2OH-HCl solution (adjusted to a pH of 1.5 by adding 25 ml 2 M HNO_3) was added to the residue from the first extraction step. Then the sample was shaken, centrifuged, filtered into a PE bottle and the residue washed as in the first step.

Fraction 4: The sample residue was dropwise processed with 10 ml 8.8 M H2O2 and left to rest for 1 hour at room temperature under multiple manual shaking, heated in a water bath for another hour at 85 °C and then reduced to 3 ml by further heating in an oven (105 °C). After adding of another 10 ml of H_2O_2, the sample was heated again for 1 hour in the water bath at 85 °C. Afterwards, the volume was reduced to 1 ml by oven heating. The cooled down sample residue was mixed with 50 ml 1 M NH_4OAC solution (77.08 g/l NH_4OAc, Merck; adjusted to pH 2 with conc. HNO_3), shaken for 16 hours and centrifuged at 1942 g for 20 min. The extract obtained in this step was also filtered into a PE bottle, the residue was washed with 20 ml dist. water, dried at 105°C and homogenized.

Fraction 4: As a final step, an aqua regia digestion was carried out with the dried sample residue in order to determine the heavy metal content of the residual fraction. This step is not part of the modified BCR extraction scheme but was carried out in order to be able to carry out a balancing of the heavy metal contents.

The sequential extraction scheme for the **EPA-PAH** used here consisted of a batch test (L/S=10), followed by a Soxhlet extraction with n-hexane as solvent (conducted as described above).

Potential maximum release of contaminants under worst-case conditions

The aim of the further investigations on the potential maximum release of contaminants was to determine the potential maximum release of pollutants under the most unfavorable conditions possible. The investigations followed a so-called **worst-case** scenario approach, in order to determine the potential maximum pollutant emission from the materials in a time-lapse effect (Eschenbach et al. 1998, 2001).

The following pollutant-releasing processes/ scenarios were investigated:

1. Acidification
2. Mineralization of soil organic substance
3. Destabilization of soil organic substance
4. Destabilization of soil aggregates.

In order to assess the potential release of trace metals by **acidification**, the following analyses were carried out:

a. Determination of the acid neutralization capacity (ANC) of dredged material samples
b. Analysis of trace metal leaching in batch tests with reduced pH
c. Analysis of trace metal contents in the eluates of column leaching experiments with acidified water.

The determination of the **ANC** of dredged material samples was carried out in a titration test. For this purpose, 10 g of air-dried < 2 mm sieved material was weighed into beakers and mixed with 100 ml of demineralized water. Over a period of 124 days, the pH value of the continuously stirred samples was determined daily and gradually adjusted to the respective target pH value by adding 0.1 M HCl (target pH values: 6, 5, 4). The ANC was calculated from the amount of protons added.

For the analysis of the trace metal leaching in batch tests with reduced pH, the samples were mixed with the respective amount of acid calculated from the results of the ANC determination to set a target pH value of 5. Afterwards, the samples were shaken for 24 hours (L/S=10) with 15 rot min-1 in an overhead shaker (3040, GFL, Burgwedel, Germany) at room temperature. In the first experimental approach (approach 1), the samples were immediately filtrated after shaking and the eluates obtained were examined for the trace metals As, Cd, Cu, Ni, Pb and Zn. In a further experimental approach (approach 2) the samples were left to rest for 2 weeks after shaking. During this time, the samples were shaken up manually every day. After 2 weeks the samples were centrifuged, the pH values in the supernatants were determined and the trace metal contents of the eluates were analyzed.

Before the start of the column leaching tests, a pre-test was carried out on the buffering behavior of the materials in the columns. The aim was to simulate the buffering behavior in the column leaching tests on the basis of the results of the ANC determination. To this end, the buffering speed in the columns was first estimated, assuming an exponential relationship of ANC and pH value as well as the buffering speed with the addition of protons and the pH value in the columns, and the pH value was calculated in layers (1.5 cm thick). A test run with the METHA 2 sample was then carried out. A column was filled with the material and percolated with acidified double demineralized water (pH 2.9 adjusted with conc. HCl) over a period of 2 weeks. pH values were documented daily. After the test, the material from the column was sampled layer by layer (thickness 1.5 cm) and the pH value of the material was determined according to DIN EN 15933.

The analysis of trace metal contents in the eluates of the METHA 2 sample was carried out in a second leaching test in two replicates. The material was percolated over a period of two weeks with double demineralized water adjusted to pH 2.9. The eluates were sampled every 24 hours, the pH value in the eluates was measured and after vacuum filtration via 0.45 µm cellulose acetate filters and acidification for stabilization, the trace metal contents were determined. After completion of the column leaching test, the material of the two columns was sampled in layers, the pH value of each layer was determined and the total trace metal contents were determined by means of microwave-assisted aqua regia digestion in order to draw conclusions about a possible relocation of trace metal contents within the columns.

To estimate the **period of time** during which acidification relevant to mobilization occurs in processed dredged material installed in dikes, further calculations were carried out on the basis of the data from the ANC determination. According to the "Arbeitshilfe Sickerwasserprognose bei Detailuntersuchungen" of the Altlastenausschuss (ALA) of the German Soil Protection Association (LABO, 2008), the acid neutralization potential (time until a certain pH value is reached in the soil due to supply of protons) can be calculated using the following formula:

$$ANP_{pH}^{t} = ANC_{pH}^{t} * BD * LT * 1000/AA$$

ANP_{pH}^{t} = acid neutralizing potential [a]

ANC_{pH}^{t} = acid neutralizing capacity [meq * kg^{-1}]

BD = bulk density [g DW *cm^{-3}]

LT = layer thickness [m]

AA = acid amount [meq * m^{-2} * a-1] deposited yearly on m^{-2} soil

The total deposition of nitrate, ammonium, sulphate and chloride minus the bases calcium, Magnesium and potassium (non-saline components) introduced via precipitation, total acid input in the field was 0.8 kmol ha^{-1} a^{-1} in Schleswig-Holstein (MELUR 2016) in 2015 and between 0.5 and 0.8 kmol ha^{-1} a^{-1} in Lower Saxony (NMELV 2016b). In the absence of available data on total acid depositions in Hamburg, a total acid deposition of 0.8 kmol ha^{-1} a^{-1} was assumed as an approximate value. This corresponds to an acid amount (AA) of 80 meq m^{-2} a^{-1}. The average bulk density of the dredged material installed in the test field in the Ellerholz canal was 0.95 g cm^{-3}, the average thickness of the dredged material layer was 0.7 m (Gröngröft et al., 2016).

To investigate the potential impact of the release of adsorbed or organically bound pollutants (trace metals and PAHs) by **mineralization of organic matter** the change in the available pollutant fractions after accelerated mineralization of the organic substance (incubation at 30°C for about 11 weeks) was examined by means of sequential extractions and the leaching of pollutants from the incubated materials was determined in 10:1 batch-extractions.

The incubation was conducted under aerobic conditions in two experimental approaches. One approach was used exclusively to quantify degradation rates. In this approach, the samples (15 g DW), which had previously been adjusted to a water content of 55 % of the maximum water holding capacity (MWHC), were incubated in 1 l laboratory glass bottles in an oven at 30 °C for 11 weeks. The quantification of the degradation rates was carried out by determination of the CO_2 release by means of gas chromatography.

The second experimental approach was used to obtain incubated material for the investigations on the effect of the mineralization of OS on the leaching of contaminants (sequential extractions and batch extractions). For this purpose, 500 g DW of the samples were adjusted to a water content of 55 % of the MWHC, filled into 2.5 l glass reagent bottles and incubated at 30°C in an oven for about 11 weeks. To ensure optimal oxygen supply, the bottles were ventilated daily. After incubation, batch extractions (L/S=10) were carried out with the samples. For this purpose, 50 g DW of the samples were mixed with 500 ml of double demineralized water and shaken for 24 hours at room temperature. The eluates were prepared with respect to the different contaminants examined (TM: vacuum filtration via 45 µm cellulose acetate filter, PAH: liquid/liquid extraction with n-hexane) and analyzed. All samples were examined in three replicates.

The influence of the **destabilization of the organic substance** on the pollutant release from the dredged material was investigated by the use of competing complexing agents. The extraction was conducted in accordance with Eschenbach et al. (1998) with 0.05 M Na_2-EDTA solution and a solid to solution ratio of 6:1. The pH value of the solution was adjusted to 4.6 with ammonia. The mixture was shaken for 90 min at 15 rot min^{-1} in an overhead shaker (3040, GFL, Burgwedel, Germany), centrifuged and the supernatant was decanted. A part of the solution was acidified for stabilization and the contents of As, Cd, Pb and Zn were determined on the graphite tube or flame AAS. The other part of the solution was prepared by liquid/liquid extraction with n-hexane and the PAH contents in the eluates were determined by means of GC-MS.

Aggregation and occlusion may prevent the mobilization of certain amounts of pollutants in soils (Eschenbach et al., 2000; Eschenbach et al., 2001). In order to examine the importance of the effect of the **destabilization of aggregates** on the leaching behavior of pollutants, investigations were carried out in which the aggregate structure of the samples was mechanically destroyed by ultrasonic treatment and the release of trace metals and PAH was determined in batch extractions (L/S=10). For this purpose, the samples were prepared in accordance with Mascher et al. (2000) with water (50 g DW, 500 ml double demineralized water) and processed with an ultrasound probe (UW 200, Bandelin electronic, Berlin, Germany). The ultrasound treatment took place in 1 l laboratory glass bottles and was carried out for 30 minutes at maximum performance. After completion of the ultrasonic treatment, the suspensions were shaken for 24 hours in an overhead shaker (3040, GFL, Burgwedel, Germany) with 15 rot min^{-1} at room temperature. The samples were then centrifuged and the supernatant was decanted. The treatment of the eluates obtained was carried out according to the respective pollutants (TM: vacuum filtration via 45 µm cellulose acetate filter, PAH: liquid-liquid extraction with n-hexane).

3.2.6 Data analyses and statistics

Correlations between inherent material properties (particle size distribution, inorganic and organic carbon content, etc.) and physical as well as chemical characteristics and the relationship between the physical and chemical characteristics, were examined using correlation or regression analyses. As results of the correlation calculations, both the correlation coefficient r as a measure of the strength and direction of the correlation and the p-value for the significance are given. A value of 5 % ($p \leq 0.05$) was chosen as significance level (error probability p). According to Fahrmeir et al (2004), the strength of the correlation between two characteristics can be classified by r as follows: $r < 0.5$ weak correlation, $0.5 \leq r > 0.8$ average correlation < $0.8 < r$ strong correlation. As a measure for the quality of determined regression functions the degree of determination R^2 is given, which represents the proportion of the variance jointly explained by the predictors. The strength of the influence of different predictors in multiple regression is estimated using the standardized regression coefficient ß. The independent variable with the strongest positive or negative ß has the greatest influence on the dependent variable.

For testing whether there are significant differences in soil properties between different materials and different treatment/processing variants, the t-test was used for normally distributed data. For data not normally distributed, the Mann-Whitney U test (independent samples) or the Wilcoxon sign-rank test (dependent samples) were performed. Here, an error probability of 5 % was assumed as well.

4 Characterization of the investigated materials

4.1 Fundamental properties and pollutant contents

The first step to examine the suitability of processed dredged material from the Hamburg harbor for the use in dike construction and its functional equivalency with traditionally used fine-grained aged marsh sediments was to characterize the fundamental physical and chemical properties and the total pollutant contents of the materials.

In the following chapter, the results of this characterization of the investigated materials are presented. In the discussion provided in this chapter, the results from the fundamental chemical and physical characterization of the materials are assessed with regard to the threshold values for the evaluation of the suitability of dike construction materials specified in EAK (2002). The results from the determination of the total pollutant contents of the materials are assessed on the basis of the assignment criteria specified in the requirements for the utilization of mineral waste (LAGA, 2004).

4.1.1 Characterization of the fundamental physical and chemical properties

The results of the chemical and physical characterization are compiled in Table A1 in the Appendix.

The **water content** of the METHA materials ranged from 47 % DW to 73 % DW, the dewatering field samples showed lower values of 46 % DW to 59 % DW. Water contents of 50 % DW on average were determined on the DC samples. The OD samples were significantly drier with a water content of 27.7-32.5 % DW. In the marsh sediment samples examined, the moisture varied over a wide range (19-56 % DW).

The **pH** value of both the METHA and OD materials determined in $CaCl_2$ solution was predominantly in the neutral to very weakly acidic range (6.7-7.3). For the DC samples, higher pH values (7.3-7.7 in $CaCl_2$) were determined. Three of the four investigated fine-grained aged marsh sediments exhibited pH values similar to those of the dredged materials (6.4-7.1). With a pH value of 4, sample MS 4 was classified as strongly acidic.

The **conductivities** determined varied between the different sample collectives and also within the sample collectives. Values between 279 µS cm^{-1} (METHA 3) and 1009 µS cm^{-1} (METHA 9), on average about 630 µS cm^{-1} were determined for the METHA material. The conductivity of the DF and DC samples was in the upper range of this value range (704-932 µS cm^{-1}). The OD samples exhibited lower conductivities (on average 364 µS cm^{-1}). Three of the four examined aged marsh sediment samples showed significantly lower conductivities (32 µS cm^{-1}- 89 µS cm^{-1}) than the dredged material samples. One MS sample (MS 3) exhibited a conductivity (524 µS cm^{-1}) comparable to those of the processed dredged materials.

In Figure 4.1 and Figure 4.2, the grading curves determined for the different materials are presented.

The **clay** contents of the dredged material samples covered a range of 14-29 %. The average clay content of the sample collective of the dredged materials was 22 %. The METHA samples covered almost the entire range, but the average clay content was slightly higher at 25 % by weight. The dewatering field samples exhibited clay contents of 15-24 % by weight. The clay contents of the aged marsh sediments varied in a wide range from about 14 % up to 64 % by weight.

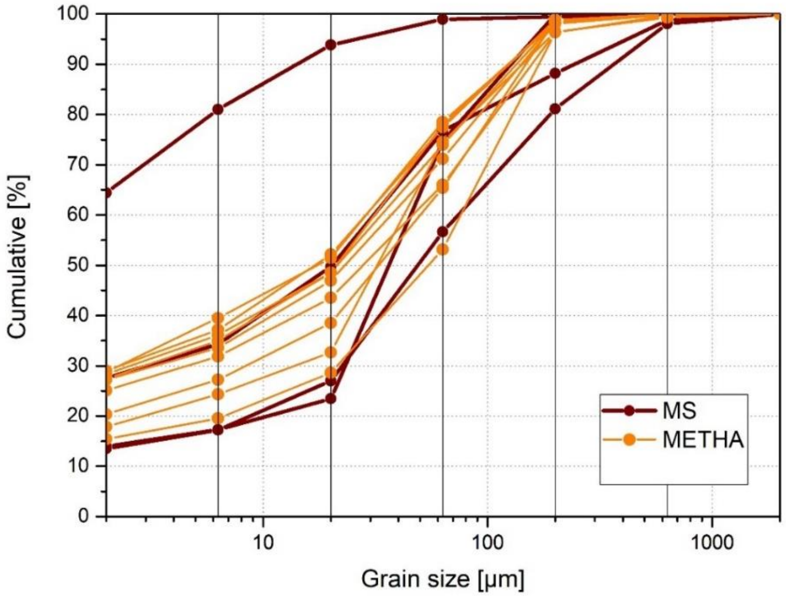

Figure 4.1 Grading curve fine-grained marsh sediments (MS) and METHA materials.

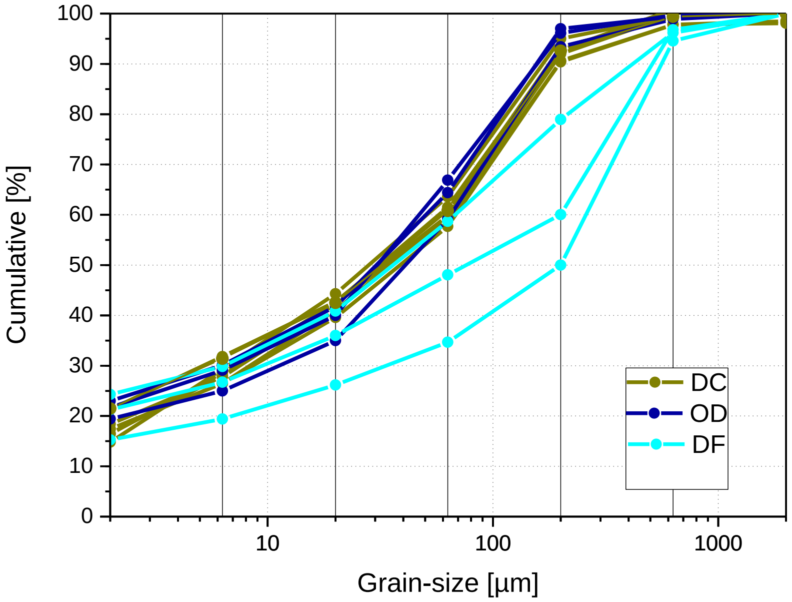

Figure 4.2 Grading curve dike cover (DC), open depot (OD) and dewatering field (DF) materials.

The **silt** contents of the dredged material samples varied from 19 % (DF 2) to 51 % (METHA 5). Within the silt fraction, the highest percentage shares were determined in the coarse fraction (on average 57 %). As the clay content, the silt content of the aged marsh sediments also varied within a wide range (36 %-60 % by weight).

The **sand** content of the dredged material samples is controlled by the processing technology. Although there were still between 21 and 47 % sand in the METHA samples, this fraction consisted almost exclusively (on average 93 %) of fine sand. In contrast, the dredged material samples from the dewatering fields, where the sand fraction is not separated due to processing, contained on average 53 % sand and significant proportions of medium sand. In the aged marsh sediments, sand contents between 1 % and 43 % were determined. The sample from the North Sea contains very well sorted fine sand, the sample from the area of Lüneburg was nearly sand-free.

Total carbon contents (TC) of 2.96 % DW (DF 2) to 4.95 % DW (METHA 5) were determined on the dredged material samples. As intended with the material selection, the TC content of the fresh METHA samples was found to scatter relatively strongly, while the total carbon contents determined on the dewatering field samples are more uniform and lower overall (2.96-3.73 % DW). The TC contents of the DC samples do not differ significantly from that of the METHA samples. The OD samples exhibited relatively low total carbon contents with 3.95% DW on average. On the fine grained aged marsh sediment samples TC contents of 1.39 % DW (MS 3) to 3.57 % DW (MS 4) were determined.

The organic and inorganic carbon contents of the investigated materials are presented in Figure 4.3.

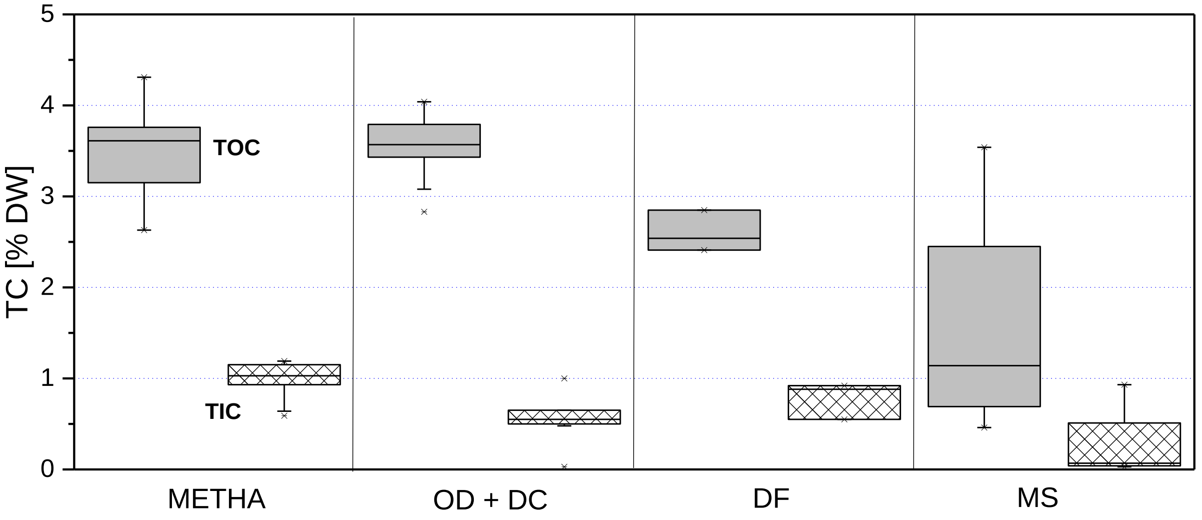

Figure 4.3 Organic and inorganic carbon contents of the investigated materials. METHA= METHA materials, OD= open depot materials, DC= dike cover materials, DF= dewatering field materials, MS= marsh sediments.

The **inorganic carbon (TIC) contents** within the dredged material samples vary between 0.48 % DW (DC 5) and 1.19 % DW (METHA 5). With an average of 0.98% DW, the fresh METHA samples contain significantly ($p < 0.05$) more inorganic carbon than the DC samples (mean 0.56% DW). The inorganic carbon contents of the DF and OD vary relatively strongly. For the MS samples TIC contents of < 0.1 % DW (MS 4) to 0.93 % DW (MS 3) were determined. By means of Mann-Whitney U Tests it was shown that the TIC content of the MS samples differs significantly ($p < 0.05$) from that of the METHA materials.

The **organic carbon contents (TOC)** were calculated from the TC and TIC contents. They vary between 2.63% DW (METHA 3) and 4.31% DW (METHA 8) for fresh METHA samples. The TOC contents of the DC samples were in the same range. The DF samples exhibited lower TOC contents. The samples OD samples also showed lower TOC contents than the fresh METHA samples. On the MS TOC contents in the range of 0.46 % DW (MS 3) to 3.57 % DW (MS 4) were determined.

The METHA material is characterized by high liquid limits (91.9 % on average) and moderately high plastic limits (49.5 % on average) and thus shows a high plasticity Index (I_p: 0.42 on average). The DF samples, like the DC samples, are less plastic (I_p on average 0.34 and 0.35), the OD samples show the least plasticity Index within the dredged material collectives (I_p on average 0.25).

The plasticity index of the MS samples with their wide grain size distribution spectrum varies greatly. I_p is only 0.08-0.16 for the clay-poor MS samples, 0.67 for the sand-free and clay-rich sample MS 4.

The particle density of the dredged material samples examined is on average 2.51 g cm $^{-3}$ and varies between 2.48 g cm $^{-3}$ (METHA 8) and 2.57 g cm ^{3} (DHD 3). The particle density of the MS samples varies between 2.51 g cm $^{-3}$ and 2.62 g cm $^{-3}$.

By means of the Mann-Whitney U tests, it was it was examined whether the physical and chemical properties of the materials (METHA materials and the marsh sediments) differ significantly from each other. The tests revealed only for the TIC statistically significant differences between the METHA samples and the fine-grained aged marsh sediments. The TIC content of the MS was significantly lower. For all other tested parameters (clay content, sand content, fines content, TOC) no significant differences could be determined. This is due to the relatively small set of samples (both dredged material and marsh sediment samples) analyzed. In addition, the marsh sediments exhibit a very wide range in their inherent soil properties. Even though statistically not verifiable, there are still differences between the organic carbon contents and the particle size distribution between the marsh sediments and the dredged material. Two of four investigated fine-grained marsh sediments exhibited markedly lower TOC than the METHA samples. Also with regard to the sand content differences can be stated. The sand fraction of the METHA material was shown to consist mainly of fine sand (93 %), while up to 17 % of the sand contained in the marsh sediments is to be classified as medium sand. One of the marsh sediment samples contained almost no sand.

By means of linear correlation analyses, the statistical relationships between the physical and chemical characteristics of the dredged materials (METHA 1-9 and DF 1-3) were tested. The results are compiled in Table 4.1.
Linear regression analyses revealed that:

- With r =0.789 there is a positive (with an increase in one parameter there is also an increase in the other) correlation between the silt content and organic carbon content (TOC).
- The parameters loss on ignition (LOI) and TOC are less correlated (r =0.792) than assumed. The reason for this can be seen in, the limited range of TOC contents, resulting in a stronger effect of scattering of the properties of the organic substance. Another reason may be seen in uncertainties regarding the inorganic carbon content of some samples, which have a significant effect on the content of organic carbon which is calculated by substraction (TOC = TC - TIC).
- The liquid limit and plastic limit show a strong positive correlation with TOC.
- The particle density correlates most strongly with LOI (r=-0.830).

Table 4.1 Linear correlation coefficients (Pearson r) between selected properties of dredged material samples (METHA and DF materials, n=12, italic: $p < 0.05$).

	Clay	**Silt**	**Sand**	**TOC**	**LOI**	**Plastic limit**	**Liquid limit**	**Particle density**
Clay		*0.744*	*-0.881*	*0.789*	*0.835*	*0.765*	*0.904*	*-0.765*
Silt	*0.744*		*-0.972*	0.798	0.568	*0.833*	*0.779*	-0.569
Sand	*-0.881*	*-0.972*		*-0.845*	*-0.697*	*-0.861*	*-0.886*	*0.673*
TOC	*0.789*	*0.798*	*-0.845*		*0.792*	*0.765*	*0.897*	*-0.788*
LOI	*0.835*	0.568	*-0.697*	*0.792*		*0.668*	*0.894*	*-0.830*
Plastic limit	*0.765*	*0.833*	*-0.861*	*0.765*	*0.668*		*0.864*	*-0.551*
Liquid limit	*0.904*	*0.799*	*-0.886*	*0.897*	*0.894*	*0.864*		*-0.816*
Particle density	*-0.765*	-0.569	*0.673*	*-0.788*	*-0.83*	*-0.551*	*-0.816*	

4.1.2 Characterization of the total pollutant contents

Total **trace metal** contents of the dredged material and fine-grained aged marsh sediment samples are compiled in Table A2 in the Appendix and shown in Figure 4.4. Trace metal contents were determined for all samples. Organic pollutant contents were determined exclusively for the dredged materials.

The highest average As content was determined on the DC samples with 38.28 mg/kg DW (compare Figure 4.4). With average contents of 724.36 mg/kg DW (Zn) and 3.96 mg/kg DW (Hg), this material group also showed the highest Zn and Hg contents. Compared to the METHA, DF and DC samples, higher average Cu (198.03 mg/kg DW), Ni (64.35 mg/kg DW) and Pb contents (124.99 mg/kg DW) were determined on the OD samples. The comparison of the determined trace metal contents with test results from the years 2009 to 2012 provided by the Hamburg Port Authority shows a good agreement (Oing et al., 2018a). This means that the trace metal contents determined in the current dredged material samples were within the concentration range to be expected for processed dredged material from the Hamburg harbor.

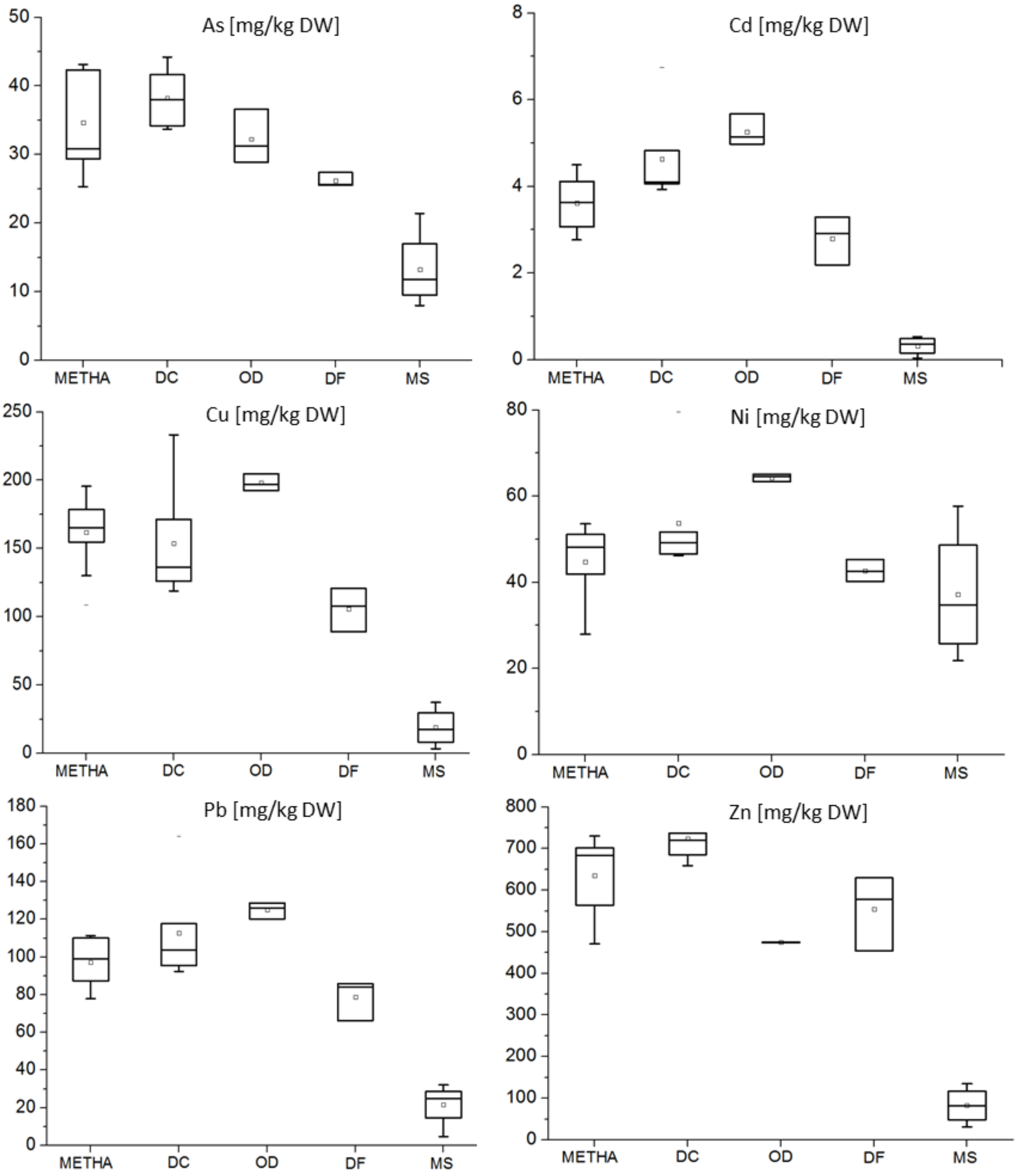

Figure 4.4 Trace metal contents of the materials. METHA=METHA material, DC=dike cover material, OD=open depot material, DF=dewatering field material.

The mean trace metal contents of the MS samples were determined with 13.24 mg/kg DW (As), 0.33 mg/kg DW (Cd), 18.91 mg/kg DW (Cu), 37.24 mg/kg DW (Ni), 21.62 mg/kg DW (Pb), 82.68 mg/kg DW (Zn) and 0.11 mg/kg DW (Hg).

The results from the determination of the **EPA- PAH** contents are compiled in Table A3 in the Appendix and Figure 4.5.

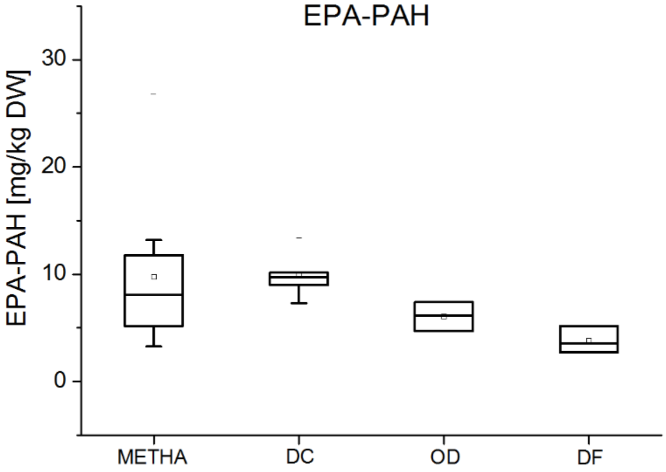

Figure 4.5 EPA-PAH contents of the materials. METHA=METHA material, DC=dike cover material, OD=open depot material, DF=dewatering field material.

The EPA-PAH contents determined in the METHA samples ranged from 4.9 mg/kg DW (METHA 4) to 26.8 mg/kg DW (METHA 1) and therefore partly exceeded the mean value of 6.2 mg/kg DW determined in the period from 2009 to 2012 and also the maximum value of 14.2 mg/kg DW of this period. On average, the PAH content of the investigated METHA materials was 10.4 mg/kg DW. The dewatering field materials exhibited lower PAH contents ranging from 2.7 mg/kg DW (DF 3) to 3.6 mg/kg DW (DF 1). The mean EPA-PAH content of the DC samples was 9.9 mg/kg DW. On the OD samples an average EPA-PAH content of 6.1 mg/kg DW (OD) was determined.

The **PCB** contents (sum of the 6 PCB congeners 28, 52, 101, 138, 153, 180) of the METHA samples are 1-3 times higher than the contents determined in the period 2009 to 2012. However, the determined maximum value of 0.2 mg/kg (METHA 2) is below the maximum PCB content of 0.26 mg/kg DMW determined in the years 2009 to 2012. The PCB contents of the dewatering field materials range from 0.042 mg/kg DW (DF 2) to 0.068 mg/kg DW (DF 3) (comp. Table A4 in the Appendix).

The contents of **organochlorine pesticides** (OCP; pentachlorobenzene, alpha-HCH, hexachlorobenzene, beta-HCH, gamma-HCH, p,p-DDE, p,p-DDD, p,p-DDT) are shown in Table A5 in the Appendix. The OCP contents of the samples analyzed first (METHA 1 to METHA 3) were all below the detection limit of 0.01 mg/kg DW. By concentrating the Soxhlet extracts, a reduction of the limit of quantification was achieved in the analysis of the other samples. The OCP contents of the samples METHA 4 to METHA 9 range from 0.051 to 0.291 mg/kg DW. The dewatering field samples from 0.040 to 0.058 mg/kg DW.

The METHA dredged material samples showed **mineral oil hydrocarbons (MOH)** contents (C10-C40) of 456 to 1950 mg/kg DW (see Table A6 in the Appendix). With an average value of 1200 mg/kg DW, the METHA batches investigated are significantly higher polluted with MOH than the batches produced in the period 2009-2012 (average MOH contents 354 mg/kg or 380 mg/kg DW). The DC samples showed contents of 396-894 mg/kg DW, the OD materials contents between 272 and 618 mg/kg DW.

The average **tributyltin (TBT)** content of METHA samples and dewatering field materials was 411 µg OZK/kg DW. The maximum TBT content of the tested material batches was determined for METHA 6 with 910 µg OZK/kg DW (see Table A7 in the Appendix). On the DC samples, an average TBT content of 277 mg/kg DW was determined. The TBT contents of the OD samples were determined with values between 170-650 mg/kg DW. The other organotin compounds contained in the samples amounted in total less than half of the TBT content on average.

The content of dioxins (PCDD/PCDF) expressed as a weighted sum (I-TEQ-NATO) of the contents of the 17 toxicologically relevant individual compounds ranged from 36 ng I TEQ/kg DW (DF 3) to 103 ng/kg DW (METHA 8) (see Table A8 in the Appendix).

4.2 Discussion

4.2.1 Physical and chemical properties

In this chapter, the results from the fundamental chemical and physical characterization of the materials are assessed with regard to the threshold values for the evaluation of the suitability of dike construction materials specified in EAK (2002).

A further detailed assessment of the suitability of METHA material for dike construction and its equivalency with fine-grained marsh sediments is presented in Chapter 8 as a superordinate evaluation based on all results, in particular the results from the investigations on compactibility, shrinkage behavior and pollutant leaching behavior.

Table 4.2 Threshold values specified for dike construction materials and values determined on the METHA materials and fine-grained aged marsh sediments

Parameter	Threshold value		METHA materials	Marsh sediments
	EAK (2002)	HH Directive (1988)		
loss on ignition	< 10 %; maximum 15 %	< 10 %; maximum 15 %	5.1-10.8 %	0.8 – 6.1% [1]
sand content	< 40 %	< 40 %; >40 % if I_P >10 %	21.4-46.9 %	1.0-43.4 %
clay content	>10 %	10-40 %	15.4-29.0 %	13.5-64.4 %
liquid limit	>25 %	-	62.5-104.3 %	31.6-112.0 %
plastic limit	>15 %	-	41.0-57.8 %	22.0-45.2 %
plasticity index (I_P)	>10 %	>10 %; optimum 20-30 %	21-51 %	8-67 %
installation water content (w)	30 %≤w≤80 %	20 %≤w≤40 %	47.5-72.9 %	18.7-56.0 %

[1] Calculated from organic carbon content by multiplication with a factor of 1.72

The comparison of the values determined for the METHA materials and aged marsh sediment and the threshold values shows that:

- With regard to the loss on ignition, the METHA materials can be rated as suitable for dike construction. For the marsh sediment, the loss on ignition values are also in a range that also complies with the threshold values listed in Table 4.2.
- The criterion of a sand content of < 40 % is not met for both METHA materials and marsh sediments for some samples. Taking into account the additional criterion mentioned in the HH Directive, all METHA materials and three of the four marsh sediments examined are to be classified as suitable.
- One sample of the marsh sediments (MS 4) has to be classified as unsuitable for dike construction due to its high clay content (64 %, comp Table A1 in the Appendix).
- With regard to the parameters liquid limit, plastic limit and plasticity index all materials of the METHA materials and marsh sediment can be regarded as suitable for dike construction.
- The criterion of an installation content of 20 %≤w≤40 % specified in the HH directive is not met for both METHA materials and marsh sediments for some samples. According to the threshold values specified by EAK, both the all of METHA materials and the marsh can be regarded as suitable.

The comparison of the properties of the materials with the criteria for the suitability of materials for construction of dike cover layers reveals that the processed dredged material from the Hamburg harbor is generally suitable for dike construction. For some materials, there are limitations of the suitability due to their sand or water contents. However, since the criteria are recommendations, non-compliance is not an exclusion criterion for the materials to be used in dike construction. In addition, both the water and the sand contents of the METHA material could be adjusted via the processing technology applied in the METHA plant. Furthermore, the water content can be adjusted after the processing in the METHA plant, for example when the material is stored in roofed depots and left to dry before use.

4.2.2 Total pollutant contents

The total trace metal and EPA-PAH contents were assessed on the basis of the assignment criteria specified in the requirements for the utilization of soil material (LAGA, 2004). However, fine-grained organic dredged material such as the METHA material is not directly subjected to the LAGA restrictions, because these restrictions are only valid for materials with a total organic carbon content of less than 5 % and a clay content of less than 10 %. Since no other requirements for materials with higher TOC and clay contents exist so far, the LAGA assessment criteria were used as a makeshift for the geochemical characterization of the materials.

An evaluation of the pollutant contents of the material on the basis of the precautionary values specified in the BBodSchV (1999) was not carried out, since it is not intended to utilize the processed dredged material within the rootable soil layer. It is planned to substitute only a part of the marsh sediment of the dike cover layer with METHA material and to cover it with a layer of marsh sediment of about 50 cm thickness. The major proportion of the root mass (>80 %) of the grass species typically contained in seed mixtures for dikes along the German North Sea coast and for tidal river dikes (Poa pratensis, Lolium perenne, Festuca rubra; EAK 2002) is expected to be located in the uppermost 10-30 cm and thus in the layer of marsh sediments. According to Elsäßer et al. (2004), the root density below 30 cm is generally low, so that pollutant contents from this depth range are usually nor or only to a limited extend relevant for the assessment.

The LAGA (2004) assignment criteria for selected contaminants are compiled in Table 4.3.

Table 4.3 LAGA (2004) assignment criteria for selected pollutants.

	LAGA assignment criteria [mg/kg]			
	Z0	Z 1.1	Z 1.2	Z 2
As	20	30	50	150
Cd	0.6	1	3	10
Cu	40	100	200	600
Ni	40	100	200	600
Pb	100	200	300	1000
Zn	120	300	500	1500
EPA-PAH	1	5	15	20

The comparison of the total pollutant contents determined on the METHA materials and the marsh sediments with the LAGA assignment values shows, that:

- The As contents determined for the METHA materials (mean 35 mg/kg) do not breach the Z 1.2 assignment criteria, while the mean As content of the MS samples (12 mg/kg) complies with the Z0 assignment criteria (compare Table 4.3).
- The contents of Cd (on average 4.3 mg/kg) determined for the METHA material breaches the Z 1.2 criteria. The marsh sediments (average Cd content of 0.3 mg/kg) comply with the Z0 criteria.
- The Cu contents of the METHA material (162 mg/kg on average) are below the Z 1.2 limit. For the marsh sediments Cu content were determined that comply with the Z0 criteria (average 16 mg/kg).
- Total contents of Ni determined for the METHA materials (on average 51 mg/kg) do not breach the Z1.1 criteria. For the marsh sediments the average Ni content (34 mg/kg) was found to be below the Z0 criteria.
- The Pb content (average 106 mg/kg) was slightly higher than the Z0 criteria for the METHA samples. With an average Pb content of 18 mg/kg the marsh sediments comply to the Z0 criteria.
- The Zn content of the METHA materials (on average 623 mg/kg) breaches the Z1.2 assignment criteria, while the Zn content (average 71 mg/kg) of the marsh sediments comply to the Z0 citeria
- The EPA-PAH contents of the METHA material (average 8.9 mg/kg) comply to the Z1.2 assignment criteria. For the marsh sediments the total PAH contents have not been determined.

Overall the results from the determination of the total pollutant contents show, that the METHA materials contain higher pollutant amounts than the marsh sediments. In terms of the total pollutant contents, the METHA material is therefore not equivalent to the marsh sediments. However, depending on the origin of aged marsh sediments (foreland of river dikes) these materials may also contain higher contaminant contents, than the marsh sediments examined in the present study (Oing et al., 2018a).

With regard to the suitability of the materials for the use as construction material for dike cover layers, the comparison with the LAGA criteria values (LAGA, 2004) showed that, the marsh sediments can be rated as suitable for dike construction. Since the Cd and Zn contents of the METHA material breached the Z1.2 assignment criteria, this material can according to LAGA (2004) be utilized for the construction of technical buildings when it is planned to install it in a sealed/encapsulated manner (compare Chapter 2.1). However, since the technical rules of the LAGA (LAGA, 2004) are not actually applicable to dredged material with a fine grain content (<63 µm) of more than 10 % by weight, the assessment made on the basis of the LAGA is not legally binding and it remains to be examined by means of expert opinions and construction site specific plan approval procedures in which manner the material can possibly be built into dikes.

Furthermore, the leaching behavior of the contaminants has to be evaluated for a comprehensive assessment of the suitability of the METHA material for dike construction. The final assessment is therefore given in Chapters 7 and 8 on the basis of the results of the detailed investigations on leaching behavior of contaminants and taking into account the findings from field tests on dikes in which METHA material is installed.

5 Compactibility of processed dredged material

As described in Chapter 2.2, previous investigations on the compactibility of dredged materials used for dike construction had shown that the bulk densities of these materials after installation were considerably lower than bulk densities of aged marsh sediments (Gröngröft et al., 2005). The aim of the investigations presented in this Chapter was to analyze whether the compactibility of the processed dredged material could be improved by enhanced dewatering of the material prior to construction. It was hypothesized that a decreased water content of the material would allow higher bulk densities to be achieved during construction and hence the soil physical properties would become more comparable to those of the aged marsh sediments.

The first step was to characterize the initial densities (bulk density determined in the Proctor test with original moist material) and Proctor densities of the different materials. Afterwards, further processing options were tested.
The investigation concept consisted of three further processing approaches:

1. Air-drying of the materials to four different initial water contents (10 % DW, 20 % DW, 30 % DW, 40 % DW)
2. Oven-drying at 30 °C and 105 °C until weight constancy
3. Ripening of the materials under laboratory conditions.

The ripened material was obtained from the large-scale shrinkage tests.

5.1 Results

5.1.1 Characterization of the compactibility of the materials

The results of the determination of the initial density and the Proctor density of the different materials are compiled in Table 5.1. The initial densities determined on the materials were found to differ significantly from each other. For the METHA materials, values between 0.4 g cm^{-3} (METHA 5) and 0.84 g cm^{-3} (METHA 3) were determined. On the dewatering field samples, initial densities of 0.72 g cm^{-3} to 0.95 g cm^{-3} were determined. The samples MS 1, MS 2 and MS 3 exhibit an initial density of 1.46 - 1.60 g cm$^{-3,}$ while the clay rich sample MS 4 could be compacted much less (0.71 g cm^{-3}). By means of Mann-Whitney U Test it was found that the initial densities of the METHA material were significantly lower than the initial densities achieved with the MS ($p < 0.05$).

Table 5.1 Results from the characterization of the compactibility (METHA=METHA material, OD=open depot material, DC=dike cover material, DF=dewatering field material, MS=aged marsh sediments, SD=standard deviation, PD=Proctor density acc. to Standard Proctor test, w_{opt}=optimum water content, DW=dry weight), * Proctor test failed because of the very high clay content of the sample..

Material group	Sample	Initial density	PD	w_{opt}
		[g cm^{-3}]	[g cm^{-3}]	[% DW]
Technically processed dredged material (fresh)	METHA 1	0,50	1.19	35.58
	METHA 2	0,41	1.15	39.23
	METHA 3	0,84	1.38	28.11
	METHA 4	0,72	1.35	32.27
	METHA 5	0,40	1.14	35.09
	METHA 6	0,52	1.25	35.06
	METHA 7	0,63	1.16	37.71
	METHA 8	0,51	1.23	39.86
	METHA 9	0,50	1.3	31.82
	Mean	**0.57**	**1.24**	**34.97**
	SD	**0.14**	**0.08**	**3.56**
Technically processed dredged material (ripened under natural conditions)	OD 1		1.35	30.82
	OD 2		1.25	32.57
	OD 3		1.38	26.85
	Mean		**1.33**	**30.08**
	SD		**0.06**	**2.4**
	DC 1		1.28	30.68
	DC 2		1.29	31.35
	DC 3		1.15	32.92
	DC 4		1.27	33.08
	DC 5		1.27	34.28
	DC 6		1.22	35.32
	Mean		**1.25**	**32.94**
	SD		**0.05**	**1.59**
Naturally processed dredged material (dewatering fields)	DF 1	0,72	1.35	32.81
	DF 2	0,95	1.36	29.82
	DF 3	0,75	1.37	32.26
	Mean	**0.80**	**1.36**	**31.63**
	SD	**0.12**	**0.01**	**1.3**
Fine-grained aged marsh sediments	MS 1	1,46	1.59	17.26
	MS 2	1,60	1.69	18.63
	MS 3	1,50	1.65	19.25
	MS4	0,71	-*	-
	Mean	**1.32**	**1.64**	**18.38**
	SD	**0.41**	**0.04**	**0.83**

Figure 5.1 shows the Proctor density PD and the corresponding w_{opt} determined for the various material groups.

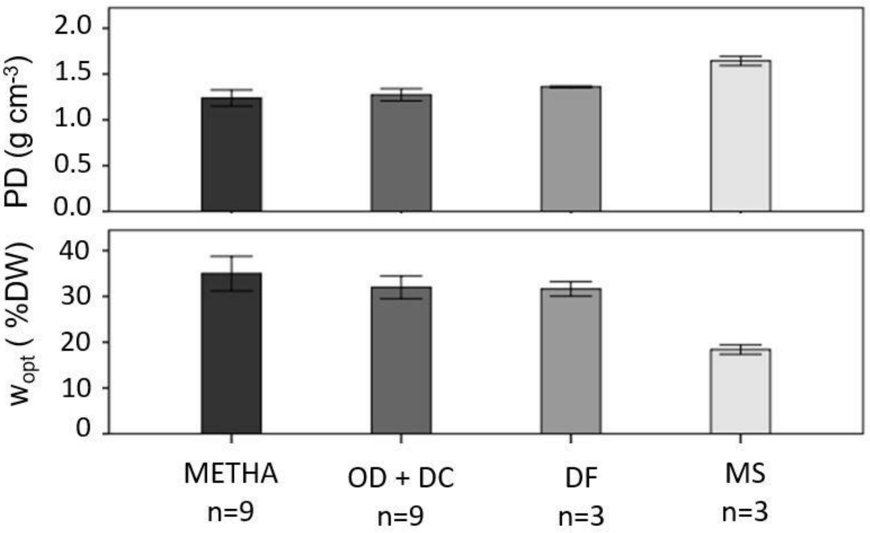

Figure 5.1 Average Proctor density (PD) and optimum water content (wopt) of the material groups. Error bar= Standard deviation.

The PD of MS samples ranged between 1.59-1.69 g cm^{-3}. The corresponding values for w_{opt} were between 17.7 and 19.3 % DW (see Table 5.1). The investigated METHA material samples exhibited lower PD between 1.15 g cm^{-3} (METHA 2) and 1.38 g cm^{-3} (METHA 3). Corresponding optimum moisture contents were between 39.2 % DW and 28.1 % DW. The PD of the OD and DC samples were found to be in the range of the densities examined for the METHA material samples. PD obtained on the DF samples did not differ from those of the METHA materials either. The evaluation of measurement results of the Standard Proctor test based upon the pairwise Mann-Whitney U Test showed no significant differences between the PD of the groups of processed dredged materials, but between the groups processed dredged materials and the aged marsh sediments.

To examine whether the Proctor densities achieved in the compaction tests can be explained on the basis of the soil properties determined on the individual samples, correlation analyses were carried out with the data from all samples (dredged materials and marsh sediments). As a result, the TOC content was shown to be most important for the compactibility (r=-0.88). High TOC contents affect the compactibility negatively. The clay content and TIC content were shown to have an (negative)influence on the compactibility as well (clay: r=-0.40; TIC: r=0.468). However, the relationship between these parameters and the achieved Proctor densities could not be verified statistically ($p > 0.05$). In further linear correlation analyses, the statistical relationships between selected soil properties and the initial densities, Proctor densities and optimum water contents were tested based on the data of the dredged materials (METHA 1-9 and DF 1-3) exclusively to examine the effect of soil properties on the compactibility of this particular material in more detail. The results are compiled in Table 5.2.

Table 5.2 Linear correlation coefficients (Pearson r) between selected properties and compactibility of dredged material samples (METHA and DF materials, n=12).

	Initial density	Proctor density	w_{opt}
Clay	-0.865	-0.738	0.731
Fines	-0.805	-0.634	0.577
Sand	0.876	0.71	-0.667
TOC	-0.786	-0.701	0.72
TIC	-0.501	-0.201	0.216
LOI	-0.788	-0.825	0.835
Plastic limit	-0.964	-0.885	-0.688
Liquid limit	-0.943	-0.872	-0.863
Particle density	0.736	0.78	-0.949
Initial density		0.86	-0.792
Proctor density	0.86		-0.822
w_{opt}	-0.792	-0.822	

Linear regression analyses revealed that:

- All tested correlations are statistically significant ($p < 0.05$),
- there is a strong positive correlation (r=0.876) between the proportion of sand and initial density (bulk density determined in the Proctor test with original moist material). The sand content correlates negatively with LOI (r=-0.697), but this relationship is less close than with the initial density,
- the correlation coefficient between the intitial density and Proctor density is high (r=0.856),
- the LOI has a strong and negative effect on the Proctor density (r =-0.825) and a strong positive correlation (r =0.835) with the optimum water content (wopt). These correlations are similarly close as those determined for the relationship between LOI and the parameters sand and clay,
- both plastic limit and liquid limit correlate strongly and inversely with initial density and Proctor density.

To also examine the effect of soil properties on the compactibility of the fine-grained marsh sediments in more detail, linear correlation analyses were examined with the data from the marsh sediments exclusively. By means of these analyses, no significant correlations between soil texture, TOC or TIC and the results of the Standard Proctor test could be determined (results not shown). The results of the statistical data analyses indicate, that clay content is the parameter with the strongest (inverse) effect on the compactibility of these materials (results not shown). The problem of relationships that cannot be verified statistically is probably due to the small set of marsh sediment samples investigated and the wide range of values covered for the individual parameters. However, it is assumed that, as with dredged materials, the parameters of grain size distribution, TOC and TIC have a strong influence on the compactibility of these materials.

Based on the relationships between compactibility and soil properties the significant differences in the Proctor densities achieved with the marsh sediments and the dredged materials can be attributed to the differences in both the TIC and TOC contents of the materials. Two marsh sediments (MS 1 and MS 2) contain almost no inorganic carbon, one sample (MS 3) reveals a TIC content of the same order of magnitude as the dredged materials. For all tested marsh sediments, however, the proportion of TOC is significantly lower than in all dredged materials examined. Therefore, with the marsh sediments higher Proctor densities could be achieved.

5.1.2 Effect of further processing on compactibility

The Proctor densities obtained for the partially dried materials are referred to as “Proctor density partially dried” ($PD_{\_PD}$). The results of the determination of $PD_{\_PD}$ are shown in Figure 5.2. The highest values for $PD_{\_PD}$ were determined with the materials that had been air-dried to 10 % DW water content, i.e. which had been dewatered to the highest extent.

In comparison the values for $PD_{\_PD}$ measured on the samples that had been dried to a residual water content of 40 % DW were about 0.04 g cm^{-3} (METHA 5) to 0.13 g cm^{-3} (METHA 3) lower (see Figure 5.2). The optimal water contents decreased with increasing intensity of drying. For the samples METHA 1 ($r= -0.985$, $p < 0.05$) and METHA 3 ($r= -1$, $p < 0.01$) regression analysis resulted in inverse linear relationships between initial water content and $PD_{\_PD.}$ The relationship determined for the other samples was found to be strong with r values in the range between -0.884 and -0.920, but not significant. A strong linear relationship was determined between initial water content and w_{opt} regarding the samples METHA 5 ($r= 0.990$, $p < 0.01$) and DF 3 ($r= 0.980$, $p < 0.05$). For the other samples, no statistically significant, but also strong relationships between initial moisture content and w_{opt} were found.

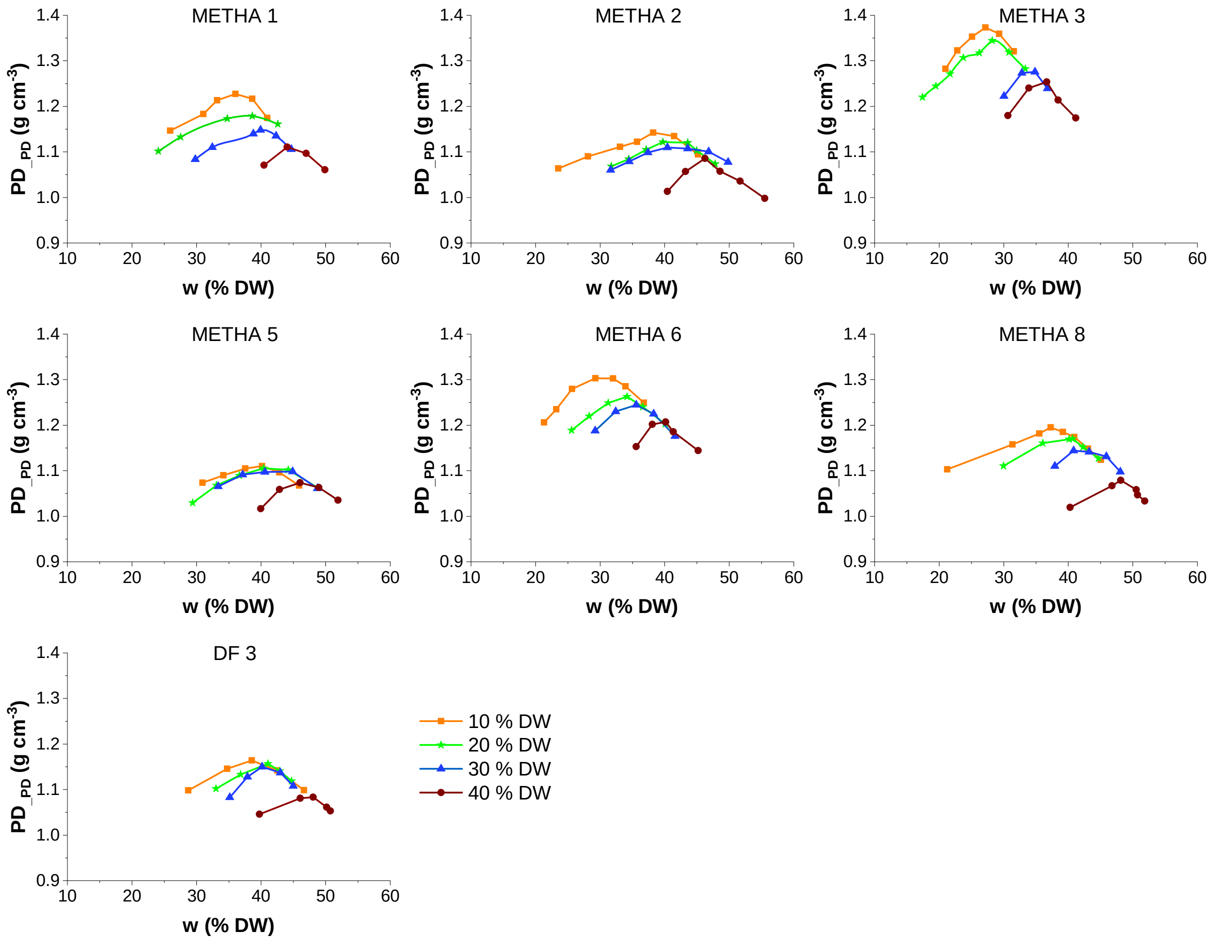

Figure 5.2 Results of the compaction test (PD_PD = Proctor density partially dried, w = water content, DW= dry weight) conducted with material air-dried to initial water contents of 10% DW (circle signature), 20% DW (triangle signature), 30% DW (asterisk signature), and 40% DW (square signature).

To examine whether the PD_$_{PD}$ of the samples with different initial water contents differed from the PD in the Standard Proctor test with air-dried material and also between each other, Wilcoxon signed-rank tests were conducted. The differences between the results of the Standard Proctor tests and the PD_$_{PD}$ reached with the materials which were air-dried to a water content of 10 % DW, were found to be not significant. However, the values for PD_$_{PD}$ of the materials dried to water contents of 20 % DW, 30 % DW and 40 % DW differed significantly ($p < 0.05$) from the PD of the Standard Proctor test. The test also showed that the PD_$_{PD}$ of the samples with different initial water contents differed significantly from each other (p= 0.02-0.03). By means of correlation analysis, the increase in Proctor density was shown to be significantly correlated with sand content (r= 0.88; $p < 0.01$), silt content (inverse, r= -0.81; $p < 0.05$) and clay content (r= 0.80; $p < 0.05$). By means of multiple regression analyses, no significant relationships between further material properties and the changes in compactibility of the partially dried materials could be found.

To investigate the effect of ripening on the compactibility of the processed dredged materials, Proctor tests were carried out with METHA material that had ripened in the laboratory large-scale shrink and swell experiments and METHA material that had ripened under natural conditions (OD and DC samples). The results of the Proctor tests with the laboratory ripened materials are presented in Figure 5.3.

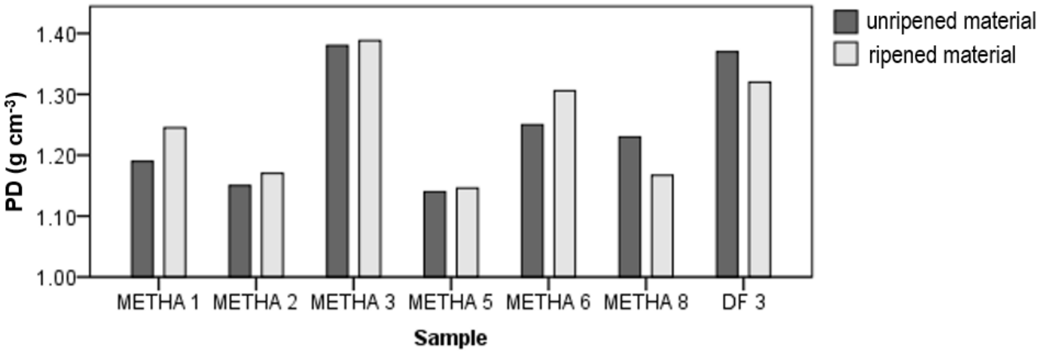

Figure 5.3 Proctor densities (PD) obtained with unripened and ripened materials.

The Proctor test showed higher PD for five of the seven studied samples after ripening. Compared to the results from the Proctor tests conducted with unripened materials, the PD of most of the ripened materials were higher by 0.01 to 0.05 g cm^{-3}. However, for the samples METHA 8 and DF 3 the measured PD of the ripened materials were lower by about 0.06 and 0.04 g cm^{-3} than for the unripened materials, respectively. The effect of ripening on w_{opt} was inconsistent either. For three of the seven investigated samples lower optimal water contents were determined after ripening.

The results of the Wilcoxon signed-rank test showed that the differences between the PD of the ripened and unripened materials were not significant (p= 0.74).

The comparison of the results of the Standard Proctor tests conducted with METHA material and the OC and DC samples showed that ripening under natural conditions had no significant effect on the PD either (p= 0.366, results not shown).

It was hypothesized that different drying temperatures would affect the resulting aggregate stability and hence the compactibility. In order to investigate this, the Proctor compaction test was conducted on processed dredged material that had been oven-dried at 30 °C and 105 °C as well as on ripened material that had been dried at 105 °C. The results are presented in Figure 5.4.

Despite slightly lower water contents before compaction (Standard Proctor test: 4.9 % DW; 30 °C dried: 3.33 % DW), the PD obtained with unripened materials dried at 30 °C were below the PD yielded with air-dried material in the Standard Proctor test. PD obtained with unripened 30 °C dried materials were between 1.12 g cm^{-3} and 1.28 g cm^{-3} and therefore at the same level of PD_$_{\mathrm{PD}}$ with the materials which were air-dried to a water contents of 20 % DW (see Fig. 1). The w_{opt} of the 30 °C dried materials were found to be higher with values in the range of 40.7 % DW (METHA 8) and 45.3 % DW (METHA 6).

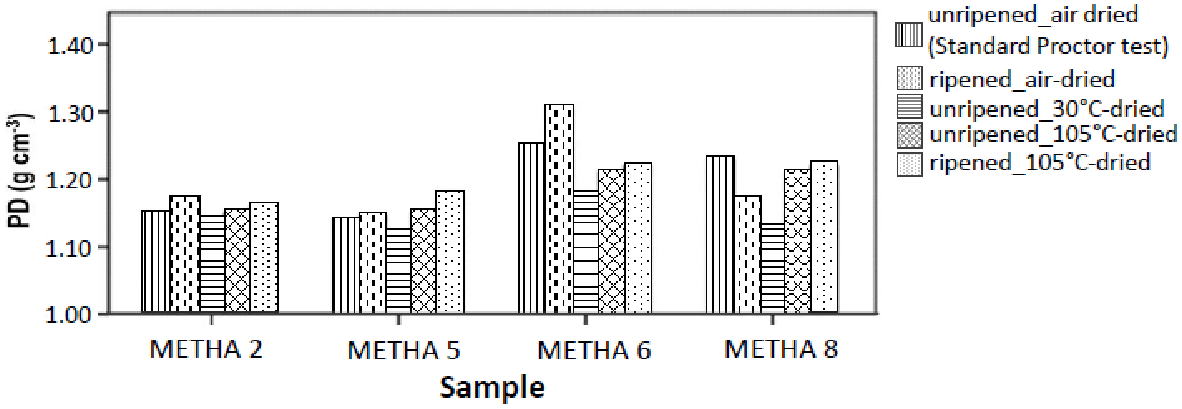

Figure 5.4 Proctor densities (PD) obtained with air-dried, unripened oven-dried and ripened and subsequently oven-dried materials.

The Wilcoxon signed-rank test showed that the differences between the PD obtained in the Standard Proctor test and the PD obtained after drying at 30 °C are not significant (p= 0.068). PD obtained with unripened 105°C-dried materials were not significantly different from those determined in the Standard Proctor test either (p= 0.715). On two samples higher bulk densities were obtained after 105 °C-drying. The Proctor densities of the other 105°C-dried materials were lower than the bulk densities obtained with the air-dried material in the Standard Proctor tests. Compared to drying at 30 °C, drying at 105 °C yielded higher, but statistically not significantly different (p= 0.66) Proctor densities. The corresponding optimum water contents were found to be lower.

5.2 Discussion

The physical characterization of the aged marsh sediments (MS) and the different groups of processed dredged materials revealed considerable differences between the four material groups (compare Chapter 4). In the investigations on the compactibility of the materials, generally, the aged marsh sediment samples show the highest compactibility. However, one sample could not be analyzed because of its high clay content (64 %). All samples of dredged materials irrespective of the type of processing and further laboratory processing showed lower values for the Proctor density (PD) than the MS samples. The corresponding optimum moisture of the aged marsh sediments was much lower (17-19 % DW) than of the processed dredged materials (28-40 % DW). By means of the Mann-Whitney U test only the parameter TIC was shown to differ significantly between the METHA samples and the MS. However, no significant correlation between TIC and the PD of the MS samples could be found.

Ball et al. (2000) stated that compactibility properties are correlated with both the liquid and plastic limit. Based on the entire set of samples (dredged material and aged marsh sediments), PD was found to correlate inversely and significantly with plasticity and liquid limit. Farooq et al. (2016) found a similar relationship. Their investigations on the compactibility of fine-grained soils implied that the maximum dry unit weight had a decreasing trend with increasing liquid limit.

The backwards multiple linear regressions indicated that of all tested parameters the organic carbon content was the variable with the strongest (negative) correlation with the compactibility of the METHA material. These findings correspond well with results of Díaz-Zorita and Grosso (2000) which showed that a higher TOC level reduce PD of natural soils. Paradelo and Barral (2013) examined the same effect by the addition of increasing rates of compost to technosols. Soane (1975) showed that organic carbon was the parameter with the strongest correlation with bulk densities obtained on 58 Scottish soils. An increase in organic carbon content of 1 % was found to result in a decrease in PD of 0.094 g cm^{-3}. Soane (1990) reviewed the effects of soil organic matter on soil compactibility and concluded that organic matter reduces the compactibility of soils because it leads to an increase in resistance to deformation and/or an increase in the elasticity of the soils. According to Blanco-Canqui et al. (2013), soil organic matter improves soil aggregation and increases the stability of soil aggregates and therefore reduces the soils compactibility. Like the dredged materials, some of the aged marsh sediments showed relatively high organic carbon contents, but higher Proctor densities and lower LL and PL. This may be traced back to the composition of organic matter. According to Zang and Hartge (1992) the stabilizing effect organic matter on aggregates is more pronounced the more humified the organic matter is. The organic matter of the dredged material from the Hamburg harbor area is known to consist primary of highly humified compounds and less degradable TOC (Gröngröft and Eschenbach, 2015) and probably stable clay humus complexes. The composition of the organic matter of the MS samples was not investigated.

For the aged marsh sediment, the clay content was identified as the most important of the investigated variables that influenced the compactibility. Regarding the processed dredged materials, the influence of the clay content could not be ascertained with statistical significance, as the range of the clay contents was quite small and the number of samples was small. However, it is generally acknowledged from other studies that grain-size distribution has an effect on compactibility. Smith et al. (1997) assessed the compaction susceptibility of South African forestry soils of various soil textures (8-66 % clay) and organic carbon contents (0.3-5.8 %) and came to the conclusion that indices of compaction susceptibility of the investigated soils were affected more by particle size distribution than by organic carbon content and that the effect of organic carbon content on the compaction behavior was only evident for soils with a clay content less than 25 %. Aragón et al. (2000) found that the compactibility of soils showed a high negative correlation with the organic carbon content and the silt content. The increase in silt content reduced the compactibility of soils with the same organic matter contents, so that a combined effect of the soils silt content and organic carbon content was assumed. In this study, no combined effect of the particle size distribution and TOC could be found.

Große and Saathoff (2014) investigated the effect of various drying temperatures (oven- and air-drying) and drying modes (complete- or partial air-drying) and came to the result that the drying mode has a considerable effect on the compactibility of fine-grained, organic dredged material from the Baltic Sea area. Although their investigations were carried out with materials of comparable soil texture to the materials in this study, higher Proctor densities coupled with lower optimum water contents were observed when the samples were oven-dried. In the investigations of Große and Saathoff oven drying down to mass constancy before performing the Proctor test was compared to air-drying to a water content of approximately 25 % DW, a much higher water content than in the present study. Therefore, these results are not directly comparable to the results obtained in the present study. However, the authors attributed the phenomenon of higher Proctor densities after oven-drying to enhanced aggregation of fine particles among each other and with organic compounds at higher drying temperatures, which leads to larger grain-sizes. Other authors (Sunil and Deepa 2016) investigated the influence of drying temperature on the physical properties of lateritic soil, lithomargic clay and a commercial bentonite. They tested the compactibility of the lateritic soil and the lithomargic clay in four conditions: air-dried and oven-dried at 50 °C, 75 °C and 110 °C. The results of the Proctor compaction tests showed similar results to those of Große and Saathoff (2014). They showed that compared to air-drying, oven-drying of the soils in general caused an increase in the bulk densities and a decrease in the optimum moisture contents and that the successively increased drying temperature additionally caused a small increase in the maximum dry density and a decrease in the optimum moisture content. The authors suggested that the changes in the compaction characteristics brought about by drying at elevated temperatures were partly due to aggregation effects, which had also been demonstrated by previous studies on the influence of drying temperatures on index properties of lateritic soils (Sunil and Krishnappa 2012).

The results of the investigations on the effect of different drying temperatures presented in this paper indicate that a thermal pre-treatment of the processed dredged materials does not improve the compactibility of these particular materials. The effect of temperature drying on bulk densities obtained in the Proctor compaction test was inconsistent and not statistically significant. This may be due to the fact that the water contents of the materials in the standard proctor test were very low either. The results indicate that a drying below a water content of 10 % DW does not have an additional effect on compactibility.

The results from the Proctor tests conducted with material which had ripened under laboratory and natural conditions, i.e. material that had been repeatedly dried over a longer period of time, showed that for this particular material the effect of ripening is inconsistent and not significant either.

By drying to water contents from more than 60 % DW down to 10 % DW the compactibility increased linearly with decreasing water content. Overall, an increase in Proctor density of 8-11 % compared to bulk densities of undried processed dredged materials could be achieved by air-drying of the materials to water contents of about 10 % DW. In parallel, the optimum water content decreased. It appears, that partial air-drying of the processed dredged material causes an aggregation of soil particles in a way that enhances compactibility.

Based on these findings, it can be recommended to air-dry the material intended for dike construction for example in large roofed depots where the material is regularly restacked to accelerate the drying process. However, the feasibility of options for the air-drying of large quantities of the processed dredged materials has to be examined in future investigations.

6 Shrinkage behavior of processed dredged material

Past studies have shown that the discharge of water from the METHA material during the primary shrinking process after installation in a dike cover layer causes formation of rather large and continuous cracks (comp. Chapter 2.2, Gröngröft et al., 2014). Cracking in dike covers increases permeability in the event of flooding. This can impair the stability of the dikes and increases the risk of dike failure.

Therefore, key objective of the investigations presented in this paper was to analyze whether the shrinkage behavior of the processed dredged material from the METHA plant could be ameliorated by enhanced dewatering and ripening of the material prior to construction. It was hypothesized that a decreased water content of the material would allow higher bulk densities to be achieved during construction, that desiccation cracking during primary shrinking would be reduced and thus the soil physical properties of the METHA material become more comparable to those of the aged marsh sediments. For this purpose, comparative examinations on the shrinkage behavior of the materials were conducted.

Small-scale methods conducted were the standard procedure for the determination of the shrinkage limit and shrinkage rate according to DIN 18122-2 (2000) and the determination of the coefficient of linear extensibility ($\mathrm{COLE}_{\mathrm{rod}}$) according to Schafer and Singer (1976a). Large-scale shrink-swell experiments were carried out in a specially constructed test system with 90 l capacity for a period of up to 385 days. Here the materials were ripened, i.e. air-dried, until shrinkage almost ceased (first drying cycle), saturated with water, and air-dried again (second drying cycle). Shrinkage and swelling were determined during the processes by measuring the changes in volume. On the ripened materials $\mathrm{COLEr}_{\mathrm{od}}$ was determined.

6.1 Results

6.1.1 Shrinkage limit and volumetric shrinkage rate

The results of the small-scale shrink experiment on the shrinkage limit and the volumetric shrinkage rate are presented in Table 6.1 and Figure 6.1.

Table 6.1 Shrinkage limit (w_S) and Shrinkage rates (V_S) of the METHA material (METHA), open depot material (OD), dike construction material (DC), dewatering field material (DF), fine grained aged marsh sediments (MS). SD=Standard deviation.

Sample	**Shrinkage limit** w_S % DW	**Shrinkage rate** V_S %
METHA 1	41.44	41.67
METHA 2	43.64	45.38
METHA 3	37.52	27.51
METHA 4	42.38	36.08
METHA 5	44.83	44.41
METHA 6	44.39	41.96
METHA 7	44.08	40.75
METHA 8	42.71	43.82
METHA 9	41.85	42.25
Mean	42.54	40.43
SD	2.21	5.53
OD 1	34.83	19.16
OD 2	33.42	25.85
OD 3	31.79	19.69
Mean	33.35	21.57
SD	1.52	3.72
DC 1	29.82	32.25
DC 2	31.55	32.35
DC 3	32.86	34.65
DC 4	32.6	36.2
DC 5	33.5	30.8
DC 3	31.8	36.7
Mean	32.02	33.83
SD	1.29	2.38
DF 1	38.2	35.88
DF 2	34.25	29.99
DF 3	39.06	33.02
Mean	37.17	32.96
SD	2.57	2.95
MS 1	18.95	39.14
MS 2	20.51	28.37
MS 3	25.51	13.31
MS 4	55.48	26.71
Mean	30.11	26.88
SD	17.14	10.59

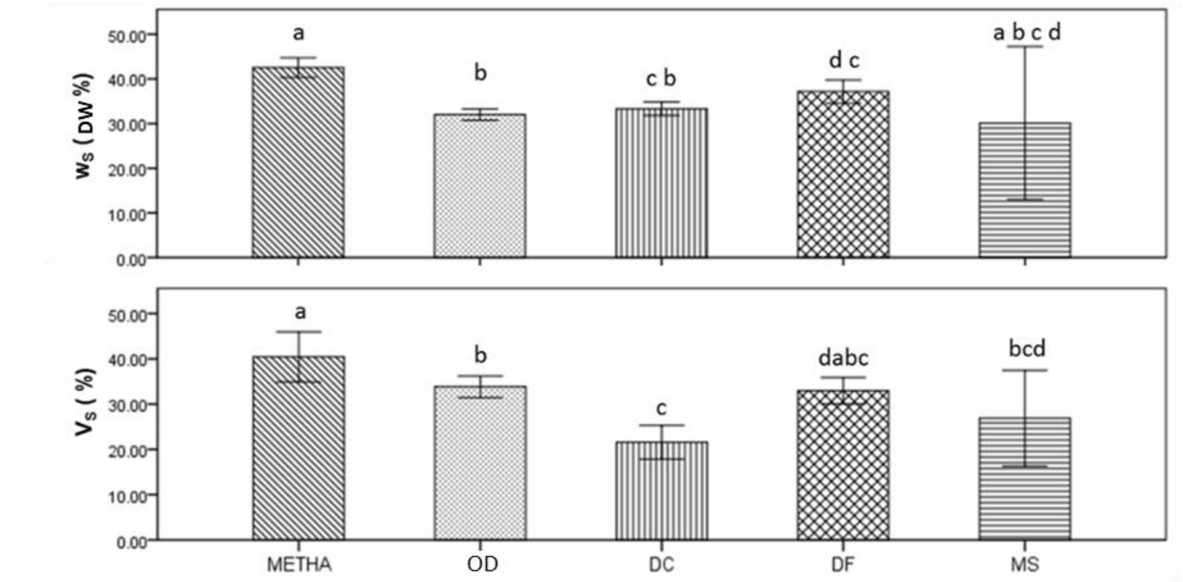

Figure 6.1 Mean shrinkage limit w_S and Volumetric shrinkage rate V_S of METHA material (METHA, n=9), open depot material (OD, n=3), dike construction material (DC, n=6), dewatering field material (DF, n=3), fine grained aged marsh sediments (MS, n=4). Error bars=standard deviation. Differences between means that share a letter are not statistically significant.

The mean shrinkage limit of the fresh METHA samples was about 43 % DW and was found to differ significantly from the w_S of the OD, DC and DF samples ($p < 0.05$). On these samples shrinkage limits were lower with a mean of 33 % DW (OD), 32 % DW (DC) and 37 % DW (DF). The mean w_S of the MS samples were found to be not significantly different to the mean of the other material groups. This is probably due to the fact that the shrinkage limits of the aged marsh sediments varied in a very wide range. Also, the volumetric shrinkage rate (V_S) of the METHA samples differed significantly compared to V_S of the OD, DC and MS samples with average values of 40 % (METHA), 22 % (OD) and 34 % (DC). For the MS samples, an average V_S of 27 % was determined. Unlike w_S, V_S of the OD and DC samples differed significantly from each other ($p < 0.05$) as well.
To examine which material properties are responsible for the specific differences in V_s and w_s of the different materials, statistical investigations were carried out.

By means of Mann-Whitney U test it was shown that clay content, sand content and TIC content of the METHA samples and the DC samples differed significantly ($p < 0.05$). The grain size distribution of the OD samples did not differ significantly from that of the METHA samples, however, the w_S, and V_S were found to be significantly lower. Regarding the OD and DC samples, clay and TOC content were found to be significantly different. Correlation analyses conducted separately for each material group showed that regarding the METHA samples ($r=-0.822$, $p < 0.01$) and the DC samples ($r=-0,841$, $p < 0.05$), the shrinkage limit was closest and inversely correlated with the sand content, while the volumetric shrinkage rate shows the highest correlation with clay content (METHA: $r=0.933$, $p < 0,01$). The correlation coefficient for the relationship between V_S of the METHA samples and TOC content was determined with r= 0.777 ($p < 0.05$). For the OD and DC samples, no significant relationship between TOC content and V_S was found. These findings were substantiated by the results of the multiple regression analyses, by which sand content was shown to be the dominant soil property influencing w_S and clay content to be the most predicting parameter for V_S. The influence of other tested soil properties like silt and TIC content, was found to be statistically not significant ($p > 0.05$) for the shrinkage limit and the shrinkage rate. The dewatering field samples showed volumetric shrinkage rates comparable (V_s) to the METHA samples, w_S of the DF samples differed significantly from those of the METHA samples ($p < 0.05$). This is consistent with the results of the Mann-Whitney U test by which no significant differences between the clay content of these material groups, but between the sand content of these two materials could be found. Shrinkage limit of the aged marsh sediments was found to be in the range of 19 % (MS 1) up to 55 % (MS 4) and did not differ significantly from the shrinkage limits of the processed dredged materials (METHA, OD/DC and DF as one set). Volumetric shrinkage rates of the MS were found to be lower than V_S of most of the processed dredged materials and to differ significantly from the volumetric shrinkage rates determined on the METHA materials ($p < 0.05$). By means of the Mann-Whitney U test only the parameter TIC was shown to differ significantly between the METHA materials and the MS. However, no significant correlation between TIC and V_S of the METHA samples or the MS samples could be found. Beside the correlation of shrinkage limit and volumetric shrinkage rate with grain-size fractions, correlations between shrinkage limit and liquid limit (r=0.873, $p < 0.01$) were found regarding the METHA materials.

For the METHA and MS materials, correlations between shrinkage limit and plastic limit (METHA: r=0.786, $p < 0.05$; MS: r=0.986, $p < 0.05$) were determined. The volumetric shrinkage rate was found to correlate with liquid limit (METHA: r=0.979, p < 0.**; OD and DC: r=0.758, $p < 0.05$; DF: r=0.999, $p < 0.05$) and plastic limit (METHA: r=0.731, $p < 0.05$; OD and DC: r=0.773, $p < 0.05$).

6.1.2 Coefficient of linear extension (COLE)

The results of the $COLE_{rod}$ determination on the unripened i.e. not laboratory ripened materials ($COLE_{rod\_u}$) are illustrated in Figure 6.2 and compiled in Table 6.2.

The $COLE_{rod\_u}$ values of the METHA samples ranged between 0.05 and 0.13. For the OD materials and the DC materials, $COLE_{rod\_u}$ was determined in the range of 0.03-0.05 and 0.05-0.07. $COLE_{rod\_u}$ values of the DF samples were found to be in the range of 0.07 up to 0.09. For the MS, $COLE_{rod\_u}$ was determined with values between 0.01-0.2.

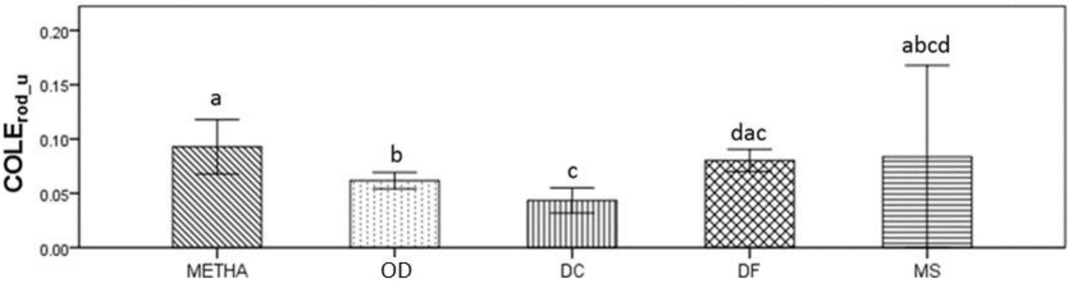

Figure 6.2 Mean $COLE_{rod\_u}$ of the METHA material (METHA, n=9), open depot material (OD, n=3), dike construction material (DC, n=6), dewatering field material (DF, n=3), fine-grained aged marsh sediment (MS, n=4). Error bars=standard deviation. Differences between means that share a letter are not statistically significant.

According to the Mann-Whitney U test the mean $COLE_{rod}$ for the groups METHA, OD and DC differed significantly between each other, whereas the DF and MS had almost overlapping shrinkage rates. This is consistent with the results of the statistical analysis of the volumetric shrinkage rates. To examine which material properties are responsible for the specific differences in the shrinkage of the different materials multiple regressions were carried out.

Regarding the METHA material, sand (r=-0.793, $p < 0.05$) and clay content (r=0.777, $p < 0.05$) were shown to be the most important of the tested soil properties influencing $COLE_{rod\_u}$. This means that the higher the clay content of the samples, the more pronounced the shrinkage and the higher the sand content, the less shrinkage was observed. Also with regard to the shrinkage of the MS samples in the COLE test, it could be shown that a higher sand content reduces shrinkage. For the relationship of $COLE_{rod\_u}$ of the MS samples and soil properties, a very strong correlation with TOC content (r=0.997, $p < 0.01$) and clay content (r=0.974, $p < 0.05$) was determined.

$COLE_{rod\_u}$ of the other material groups was found to be correlated with plastic limit (METHA: r=0.824, $p < 0.01$; OD/DC: r=0.874, $p < 0.01$; MS: r=0.957, $p < 0.05$) and liquid limit (METHA: r=0.805, $p < 0.05$; MS: r=0.991, $p < 0.01$). Regarding the METHA materials, a strong relationship (r=0.930, $p < 0.01$) between $COLE_{rod\_u}$ and shrinkage limit could be determined.

Table 6.2 and Figure 6.3 compile a comparison of $COLE_{rod}$ determined on the ripened materials ($COLE_{rod\_r}$) and unripened materials ($COLE_{rod\_u}$). Ripening had a significant ($p < 0.01$) influence on the shrinkage behavior of all investigated materials: all ripened samples showed a lower shrinkage capacity than the corresponding unripened samples. In comparison to $COLE_{rod\_u}$, $COLE_{rod\_r}$ was about 30 % (METHA 1) – 80 % (METHA 4, METHA 6) lower. Regarding the DF samples, $COLE_{rod\_r}$ was 54 % (DF 3) - 63 % (DF 1) lower. $COLE_{rod\_r}$ values determined on the MS were found to be 37 % (MS 2) – 88 % (MS 3) lower than $COLE_{rod\_u}$.

Table 6.2 Coefficient of linear extensibility of the unripened ($\text{COLE}_{\text{rod\_u}}$) and ripened materials ($\text{COLE}_{\text{rod\_r}}$). METHA=METHA material, OD=open depot material, DC=dike construction material, DF=dewatering field material, MS=fine grained aged marsh sediments, SD=Standard deviation.

Sample	**$\text{COLE}_{\text{rod\_u}}$** -	**$\text{COLE}_{\text{rod\_r}}$** -
METHA 1	0.07	0.05
METHA 2	0.11	0.03
METHA 3	0.05	0.02
METHA 4	0.09	0.02
METHA 5	0.11	0.03
METHA 6	0.13	0.02
METHA 7	0.1	0.02
METHA 8	0.1	0.04
METHA 9	0.09	0.03
Mean	0.09	0.03
SD	0.02	0.01
OD 1	0.03	-
OD 2	0.05	-
OD 3	0.05	-
Mean	0.04	-
SD	0.01	
DC 1	0.06	-
DC 2	0.05	-
DC 3	0.05	-
DC 4	0.07	-
DC 5	0.07	-
DC 3	0.06	-
Mean	0.06	-
SD	0.01	
DF 1	0.09	0.03
DF 2	0.08	0.01
DF 3	0.07	0.03
Mean	0.08	0.02
SD	0.01	0.01
MS 1	0.07	0.02
MS 2	0.05	0.03
MS 3	0.01	0.001
MS 4	0.2	-
Mean	0.08	0.02
SD	0.08	0.01

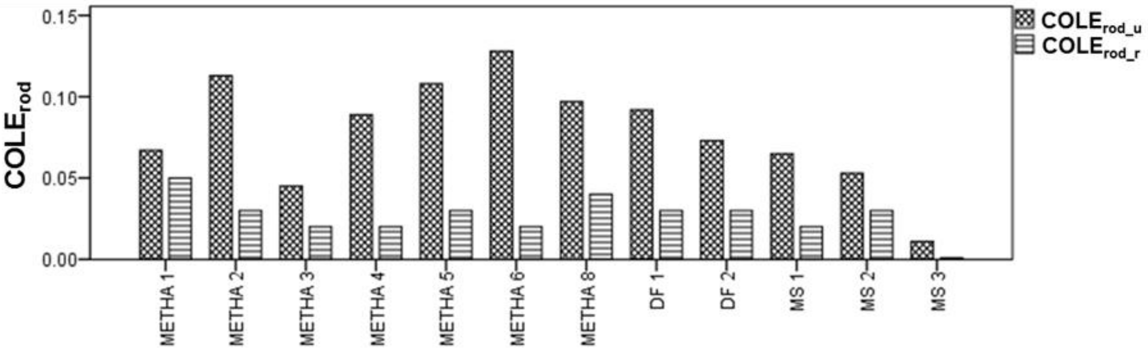

Figure 6.3 Comparison of values for $COLE_{rod}$ of the unripened ($COLE_{rod\_u}$) and ripened materials ($COLE_{rod\_r}$). METHA material (METHA), dewatering field material (DF), fine grained aged marsh sediment (MS).

For the relationship between $COLE_{rod\_r}$ and soil properties no significant correlation could be found. The decrease in $COLE_{rod\_r}$ compared to $COLE_{rod\_u}$ was found to be correlated significantly, but not very strong with clay content ($r=0.677$, $p < 0.05$). For samples with a higher clay content, the shrinkage-reducing effect of ripening was therefore more pronounced.

6.1.3 Large-scale shrink and swell experiment

The large-scale shrink and swell experiments were conducted to comparatively investigate the shrinkage behavior of the materials on a larger test scale in a more realistic approach, i.e. layerwise compacted installation and in order to be able to investigate the structure development of the materials and their shrinkage behavior after structure/aggregate formation as observed in the field trials.

The large-scale experiments were carried out in newly designed approaches using PE tubs with a volume of 96 l. About 75 l of the samples were compacted into the tubs in three layers. Each layer was compacted with 346 kNm m^{-3}. For the investigation of the shrink and swell behavior, the samples were dried out for about 20 weeks (first drying cycle). Afterwards, the specimens were filled up with water gradually from the bottom to the top for saturation. The water level was increased slowly over a period of 10 days to prevent air inclusions in the pores. After saturation, the surplus of water was let out and the specimens were dried about 30 (second drying cycle) weeks again.

Solid, void, water, shrinking and swelling volumes as well as dry bulk densities (DBD), moisture ratio and void ratio were calculated from the measurements of specimens' volume and weight.

The initial water contents of the dredged materials ranged from 44-72 % DW corresponding to volumetric water contents of 50-62 Vol. %. The initial water contents of the MS samples were much lower (19-22 % DW; 28-31 Vol. %).

During the first drying cycle an average decrease of water contents of about 36 Vol. % was observed on the METHA samples. Referred to the initial water content, the decrease in water content was about 66 %. On the fine grained aged marsh sediments, the decrease in water content was determined with an average of 70 %.

After saturation of the specimens for about 10 days the volumetric water contents of the samples METHA 1 and 6 were lower (3-11 Vol. %) than their initial water contents. The volumetric water contents of the other METHA samples after saturation were 1-5 Vol. % higher than their initial water contents. The increase in volumetric water content of the DF samples was between 3-18 Vol.%. On the MS samples water contents after saturation were by a mean of 30 Vol.% higher than their initial water contents.

Volumetric water contents achieved at the end of the second drying cycle were slightly higher (1-3 Vol. %) than after the first cycle for the samples METHA 2, 8 and DF 3. On the other samples lower volumetric water contents (0.1-8 Vol. %) than at the end of the first drying cycle were obtained.

In all large-scale-experiments, with the exception of sample METHA 7 and METHA 9, no cracks on the specimens' surfaces were observed. As a result of shrinkage, the specimens detached from the margin of the tubs. The volume of these "cracks" (distance between specimen and tub margin) as well as the shrinkage in height was determined during the entire trial period. Because of the surface cracks developed on sample METHA 7 and METHA 9, it was expected that suction stresses and drying behavior and thereby the shrink and swell behavior of these specimens would be not comparable to those of the other samples. Therefore, the results of these samples were excluded from statistical analysis.

Dry bulk densities (DBD) of the specimens were calculated from solid dry weight and volume. Initial DBD ranged between 0.83-0.93 g cm^{-3} (METHA samples), 1-1.08 g cm^{-3} (DF samples) and 1.27-1.43 g cm^{-3} (MS samples). By means of the Mann-Whitney U test it was shown that the DBD of the METHA samples and the DF samples were not significantly different from each other, while the DBD of the processed dredged materials and the MS samples differed significantly ($p < 0.05$).

During the first drying cycle DBD of the processed dredged materials increased about 0.04 g cm^{-3} (DF 2) - 0.23 g cm^{-3} (METHA 6). The average DBD increase of the MS samples was 0.03 g cm^{-3}. Referred to the initial DBD the DBD increase was determined with 11-22 % (METHA samples), 4-10 % (DF samples) and 2-9 % (MS samples).

In the course of swelling DBD decreased about 0.04-0.08 g cm^{-3} (METHA samples), 0.04-0.06 g cm^{-3} (DF samples) and 0.01 – 0.04 g cm^{-3} (MS samples). During the second drying cycle DBD increased similarly strong as during the first drying cycle. At the end of this drying cycle DBD of the METHA materials were determined with 0.95 g cm^{-3} (METHA 9) - 1.18 g cm^{-3} (METHA 4 and METHA 6). The dewatering field samples showed dry bulk densities of 1.10-1.20 g cm^{-3}. Dry bulk densities of the MS samples were found to be in the range of 1.32 g cm^{-3} (MS 1) and 1.29 g cm^{-3} (MS 2). The results revealed that the second drying cycle did not lead to a further increase in DBD of the specimens, even if lower water contents than in the first drying cycle were obtained on some samples.

To examine whether the changes in DBD, caused by shrinking and swelling were significant or not, the Wilcoxon signed-rank test was conducted with the data of each material group.

For the dredged materials, the results showed significant differences ($p < 0.05$) between initial DBD and DBD after the first drying cycle, DBD after the first drying cycle and after swelling and between DBD after swelling and DBD after the second drying cycle. Regarding the aged marsh sediments, the changes in DBD were found to be not significant. Correlation analysis on the relationship between material characteristics and DBD showed that initial DBD of the dredged materials were most closely related to initial water content ($r=-0.897$; $p < 0.01$) sand ($r=0.863$; $p < 0.01$) and clay content ($r=0.837$; $p < 0.01$) of the samples. For the MS samples, no significant relationship between DBD and material properties was found.

Figure 6.4 shows the volume changes (% initial volume) of the materials determined in the course of the first drying cycle, swelling after resaturation and the second drying.

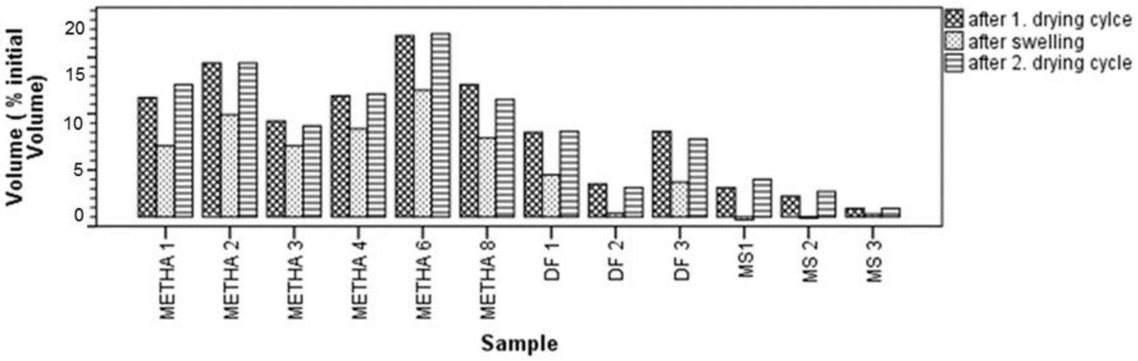

Figure 6.4 Volume shrinkage (% initial volume) of the specimens after the first and the second drying cycle and the intermediate swelling step, as compared to the initial state (DF=Dewatering field, MS=Fine-grained aged marsh sediment).

During the first drying cycle, total shrinkage of the METHA specimens amounted 10.2 - 19.3 Vol. % (compare Figure 6.4) referred to their initial volume (all further shrinkage and swelling amounts are related to the initial volume). Total shrinkage of the DF samples 1 and 3 was found not to differ significantly from the shrinkage of the METHA materials. Sample DF 2 showed a significantly ($p < 0.05$) lower shrinkage of 3.5 Vol. %. Compared to the METHA materials, the fine-grained aged marsh sediments are characterized by significant ($p < 0.05$) lower shrinkage of about 0.9 Vol. % (MS 3) up to 3.1 Vol. % (MS 1) as well.

Saturation of the specimens resulted in a re-swelling of the samples. The swelling was determined with 2.6-5.7 Vol. % for the METHA samples, 3.1-5.4 Vol. % for the DF samples and 0.7-3.4 Vol. % for the MS samples.

Despite comparable water losses during both drying cycles, the shrinkage of the processed dredged materials in the second drying cycle was much lower than in the first drying cycle. Shrinkage determined in the second drying cycle was 2.1-6.5 Vol. % (METHA samples), 2.7-4.6 Vol. % (DF samples) and 0.6-4.3 Vol. % (MS samples).

In Figure 6.5 and Figure 6.6, shrinkage curves of the materials METHA 2, METHA 3, METHA 6, DF 1, DF 2 and MS 2 are presented exemplarily for the three material groups. Soil shrinkage curves are used to relate the volume or rather the ratio of solid to void (void ratio)

of the drying soil with its water content (see Figure 2.3). The latter is expressed as moisture ratio (=volumetric water content in relation to solid volume).
As shown in the graphs, the starting points of each line which represents the compaction of the materials with an effort of 346 kNm m^{-3} is located near the 1:1-line, where water saturated conditions are indicated.

Shrinkage of the processed dredged materials during the first drying cycle was characterized by pronounced proportional shrinkage, i.e., a decrease in void ratio proportional to a decrease in moisture ratio, followed by residual shrinkage, i.e. the phase in which the decrease in the volume of voids is less than the corresponding decrease in volumetric moisture.

Shrinkage of the fine-grained aged marsh sediments was characterized by the absence of initial (proportional) shrinkage. In the second drying cycle, the shrinkage curve determined on the processed dredged material could be subdivided into distinct structural and proportional shrinkage ranges, followed by a range of residual shrinkage. The range of moisture ratio during which proportional shrinkage occurred, however, was much narrower than in the first drying cycle.

The drying decreased the saturated void ratio of the dredged materials and narrowed the range of void ratio determined in the second drying cycle from an average of 0.39 to 0.13 cm^3 cm^{-3} (METHA samples) and from 0.23 to 0.11 cm^3 cm^{-3} (DF samples 1 and 2). Dewatering field sample DF 2, which was characterized by a much lower water content (44 % DW) than the other processed dredged materials at the beginning of the experiment, exhibited a shrinkage behavior similar to that of the fine-grained aged marsh sediments. On these materials, no significant decrease in the saturated void ratio was observed.

The reversible proportion of shrinkage calculated from the void ratio at the end of the first drying cycle and after saturation/the beginning of the second drying cycle of the METHA samples ranged from 2.2 % (METHA 3) to 7 % (METHA 6) and did not differ significantly from that of the DF samples DF 1 (4.6 %) and DF 3 (4.0 %). On the MS samples, the reversible proportion of shrinkage was determined with 0.56-4.37 %. Regarding the METHA materials, the percentage share of reversible shrinkage in relation to total shrinkage was determined with an average of 34 %. The reversible proportion of the shrinkage of the DF materials accounted for 49 % (DF 1) and 51 % (DF 3) of total swelling. On sample DF 2, 86 % of the total shrinkage was found to be reversible. For the marsh sediments, the entire shrinkage was determined as reversible.

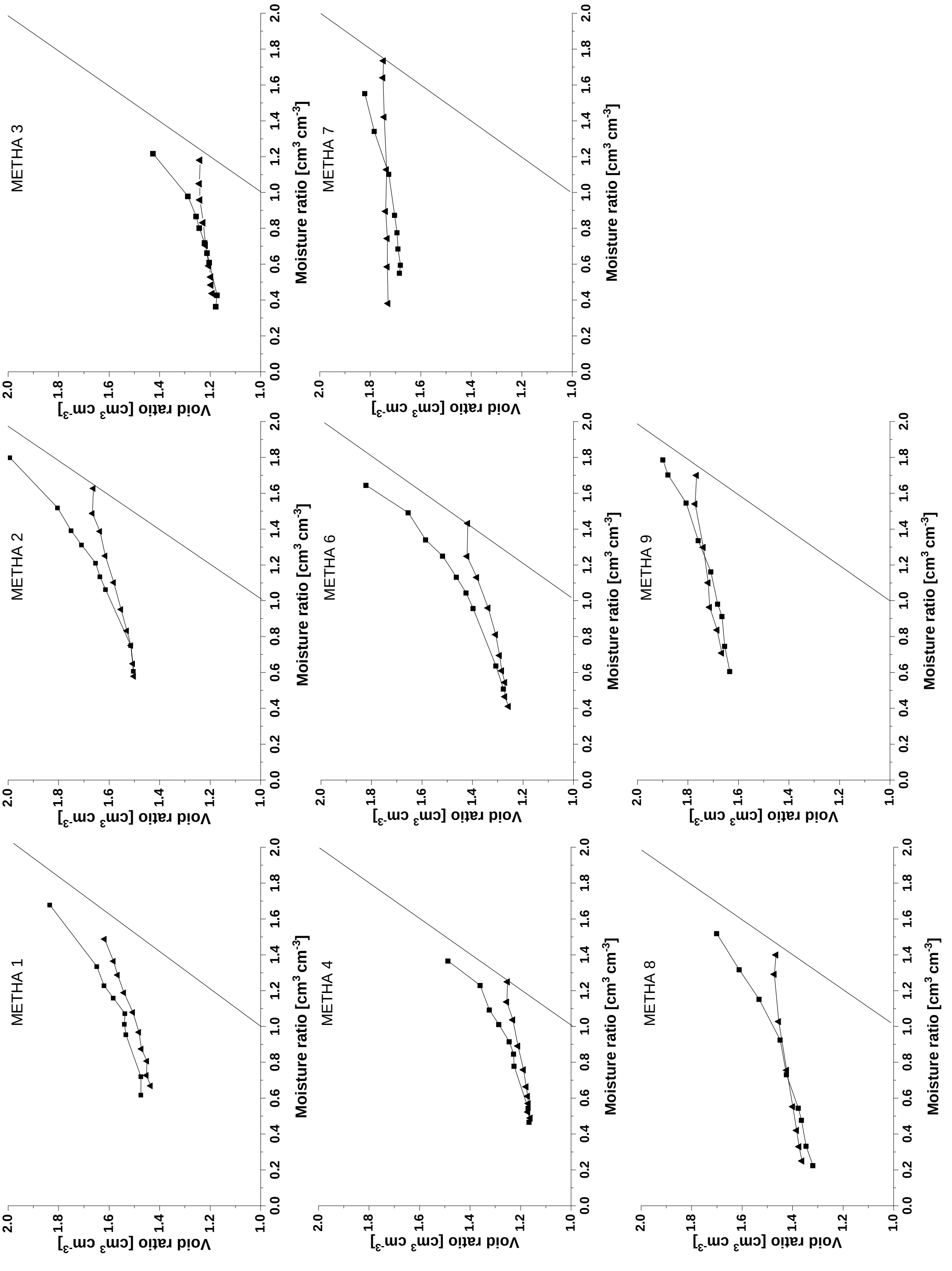

Figure 6.5 Shrinkage curves (square signature: shrinkage first drying cycle; triangle signature: shrinkage second drying cycle, line: saturation line) of the METHA materials.

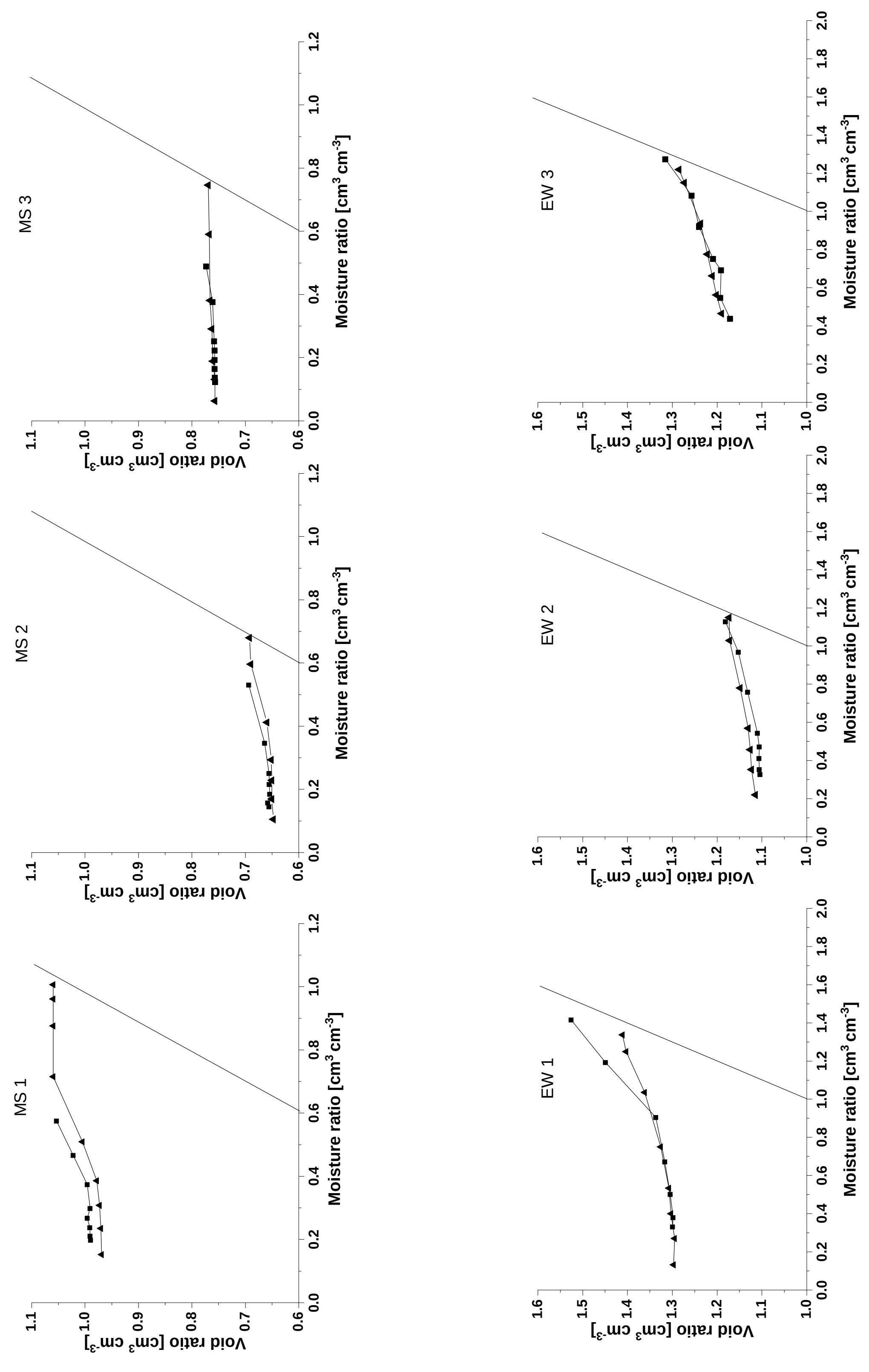

Figure 6.6 Shrinkage curves (square signature: shrinkage first drying cycle; triangle signature: shrinkage second drying cycle, line: saturation line) of the fine-grained aged marsh sediments (MS) and the dewatering field materials (DF).

The swelling of the processed dredged materials calculated from the proportion of reversible shrinkage was in the range of 3.2 % (METHA 3) to 6.8 % (METHA 3), 4.8 % (DF 1) to 5.5 % (DF 3) and 0.57-3.5 % (MS samples). The swelling of the dredged materials was found to be closely correlated with clay content (METHA: r=0.942, $p < 0.01$; DF: r=1.00, $p < 0.01$), sand content (METHA: r=-0.979, $p < 0.05$), TOC content (METHA: 0.848, $p < 0.05$) and initial water content (r=0.929, $p < 0.01$). By means of stepwise multiple regression analysis, the clay content was found to be the parameter with the strongest effect on the swelling behavior of the processed dredged materials (METHA: ß=0.927, $p < 0.01$), (DF samples ß=1.00, $p < 0.01$). Regarding the fine-grained aged marsh sediments, strong but not significant correlations between swelling and TOC content (r= 0.992, $p > 0.05$) and clay content (r=0.768, $p > 0.05$) were found.

The irreversible proportion of shrinkage, calculated from the void ratios at the beginning of the first drying cycle and after swelling/at the beginning of the second drying cycle, was in the range of 7.4 % (METHA 1) and 14.8 % (METHA 6). The proportion of irreversible shrinkage of the dewatering field samples DF 1 and 3 was determined with 4.7 % and 3.8 %. For sample DF 2, irreversible shrinkage was determined with 0.46 %.

Correlation analyses on the relationship between total shrinkage, reversible and irreversible proportion of shrinkage and material properties revealed that total shrinkage of the METHA materials was closest related to clay content (r=0.845; $p < 0.05$) and sand content (r=-0.814; $p < 0.05$).

Regarding the dewatering field samples, no significant correlations between soil properties and shrink-swell behavior were found. For the MS samples, the shrinkage during the first drying cycle showed significant correlation with TOC content (r=0.999, $p < 0.05$). The relationship between initial water contents of the samples and total shrinkage during the first drying cycle was quite strong, but not significant (METHA: r=0.712, $p > 0.05$; DF: r=0.985, $p > 0.05$; MS: r=0.990, $p > 0.05$). However, regarding the METHA materials the relationship between initial water content and the proportion of reversible shrinkage was found to be strong and highly significant (r=0.918, p =0.01). Clay content (r=0.895, $p < 0.05$) and initial dry density (r=-0.882, $p < 0.05$) were found to be significantly correlated with the reversible shrinkage of these materials as well. Regarding the MS samples, the coefficient of correlation for the relationship between reversible shrinkage and initial water content was found to be high (r=0.984), but not verifiable statistically ($p > 0.05$). The only significant relationship of the reversible shrinkage of these materials could be determined with organic carbon content (r=1.00, $p < 0.05$).

Between the proportion of irreversible shrinkage and material properties, no statistically significant relationship was found.

6.1.4 Comparison of the results of the different shrink experiments

To examine the transferability of the results of the small-scale experiments on the shrink behavior of the METHA material in the large-scale experiment, regression analyses were carried out. The correlation coefficient was found to be high ($r=0.953$, $p < 0.01$) for the relationship between $COLE_{rod\_u}$ of the materials and volumetric shrinkage during the first drying cycle. As shown in Figure 6.7, $COLE_{rod\_u}$ was about 6 % lower than the volumetric shrinkage determined on the specimens in the large-scale shrinkage experiment.

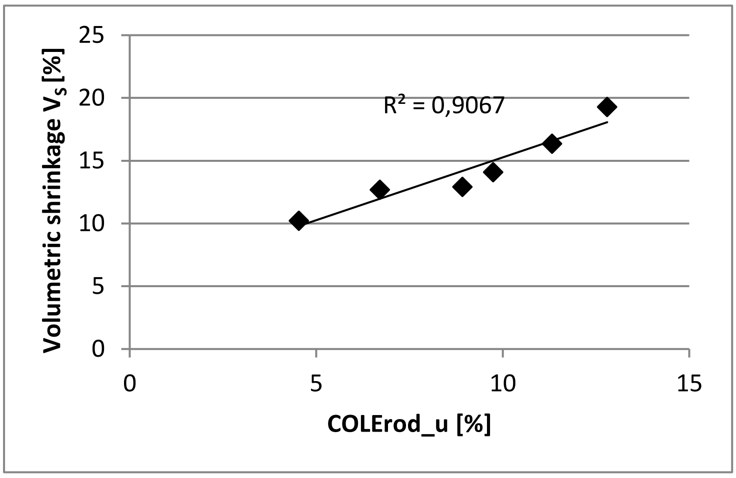

Figure 6.7 Relationship between Volumetric shrinkage V_S and $COLEr_{od\_u}$.

This is probably due to the partial desiccation of the samples for the $COLE_{rod}$ determination. Conferred on the process of shrinkage this indicates that in the average 6 % of the shrinkage occurred during the desiccation at 33 kPA.

The relationship between volumetric shrinkage and the degree of shrinkage was found to be less close and not significant ($r=0.751$, $p > 0.05$). This can be attributed to water contents at the beginning of the shrink experiments as well. For the determination of shrinkage limit and degree of shrinkage, the water contents of the samples were adjusted to a water content which is 1.1 times higher than liquid limit. Therefore, water contents for the determination were much higher with up to 114 % DW than the water contents of the samples at the beginning of the large-scale experiments (47-72 % DW).

6.2 Discussion

6.2.1 Small-scale shrinkage experiments

The results of the physical characterization of the aged marsh sediments and the different processed dredged materials revealed considerable differences between the groups of materials. In the small-scale shrink experiments as well as in the large-scale shrink-swell experiment, the METHA samples showed the highest shrinkage capacities, while the fine-grained aged marsh sediments exhibited the lowest.

Beside the correlation of the shrinkage limit (w_S) and volumetric shrinkage rate (V_S) with grain-size fractions, strong correlations of these parameters with liquid limit and plastic limit were determined for some of the investigated material groups. In other studies on the relationship between soil properties and shrinkage indices, no satisfactory correlation between shrinkage limit, liquid limit or plasticity index could be found (Sridharan and Prakash, 1996; Izdebska-Mucha and Wójcik, 2013).

Correlation analyses on the relationship between $COLE_{rod\_u}$ of the materials and soil properties showed that this parameter was closest correlated with clay content. This is consistent with several other investigations on the relationship between COLE and soil properties (Schafer and Singer 1976b; Gray and Allbrook 2002; Vaught et al. 2006; Peng and Horn 2013; Lucian 2016).

Peng and Horn (2007) reported that organic matter increases the shrinkage capacity and that shrinkage of the organic-rich soils investigated in their study was significantly higher than that of inorganic Gleysols. In another study, Peng and Horn (2013) reviewed data of 270 soils and examined that the coefficient of linear extensibility (COLE) had, beside the relation to wet bulk density and clay content, a positive relation with soil organic carbon (SOC) content. An effect of TOC on the shrinkage behavior of the materials in the small-scale shrinking experiments could be verified statistically for the volumetric shrinkage of the METHA materials and $COLE_{rod\_u}$ of the aged marsh sediments. Onweremadu and Igwe (2007) also reported significant, but with r values of about 0.59 and 0.64 not very close, relationships of COLE, measured on soil clods of different parent material soils from Central Southeastern Nigeria, with liquid limit and plastic limit. Correlation coefficients between these parameters and $COLE_{rod\_u}$ of the dredged materials and the aged sediments investigated in our study were found to be much higher. Furthermore, a strong and highly significant relationship between shrinkage limit and $COLE_{rod\_u}$ of the METHA materials was determined.

Results of the correlation analyses and the Mann-Whitney U test indicate that the differences between the shrink indices of the METHA samples and the DC samples in the small-scale shrink experiments are due to differences in their grain-size composition. The METHA materials showed significantly higher shrinkage limits than the DC samples because of their significantly lower sand contents. As the clay content of the METHA and OD samples was found not to be significantly different, but the shrinkage behavior of these materials differed significantly, the disparate behavior of these two types of processed dredged material may be traced back to the ripening stage of the materials. The divergent shrinkage behavior of the METHA samples compared to the MS in the small-scale experiments could not be related to the soil properties of the samples. By means of the Mann-Whitney U test only the parameter TIC was shown to differ significantly between the METHA samples and the aged marsh sediments. However, no significant correlation between TIC and volumetric shrinkage rate or $COLE_{rod\_u}$ of these samples could be found by means of correlation analysis. Therefore, the disparate shrinkage behavior may also be related to the ripening stage of the materials.

Particularly in relation with heavy clays the process of repeated wetting and drying has been referred to as 'ripening' (Bronswijk 1990). Ripening of sediments is an early stage in the soil formation process, characterized by oxidation and desiccation of the material, leading to characteristic structural development and thus changing physical properties (Pons and Zonneveld 1965; Rijniersce 1983; Vermeulen et al. 2003). Structure development is caused by shrinkage and swelling. During shrinkage, mineral particles are tied together by capillary forces which increase the number of points of contact and result in a higher bulk density (Horn, 2004). Since the shrinkage is not completely reversible, it can be assumed that the particles in the aged marsh sediments have a denser bearing than in the dredged material and therefore exhibit less shrinkage when dewatering is repeated. This assumption is underpinned by the fact that the aged marsh sediments exhibited higher specific densities than the processed dredged materials.

The results of the $COLE_{rod\_r}$ determination of the ripened processed dredged materials revealed that laboratory ripening leads to a significant decrease in the samples' capacity to irreversible shrinkage. While $COLE_{rod\_u}$ of the majority of the unripened materials can be classified as high (COLE 0.06-0.09) or very high (COLE > 0.09), $COLE_{rod\_r}$ of the ripened materials can be assigned to the class of moderate (COLE 0.03-0.06) or even low (COLE < 0.03) shrinkage (Parker et al. 1977). The effect of drying on COLE of paddy soils was investigated by Deng et al. (2014). In their investigation, COLE of pre-dried samples was found to be considerably lower than COLE of the samples without pre-drying.

In investigations on the effect of wetting/drying (WD) cycles on COLE it was shown that intense WD cycles lead to a considerable decrease of COLE in organic rich soils, but to an increase of COLE in a Calcic Gleysol. A frequency dependency of intense WD cycles could not be found in these investigations (Peng et al, 2007).

$COLE_{rod}$ of the METHA materials that had been able to ripe under natural conditions (DC and OC samples), were significantly lower than of the unripened METHA materials, but significantly higher than of the laboratory ripened METHA materials. This implies that the samples were dried to a larger extent in the laboratory than the DC and OC samples have been in the field. $COLE_{rod}$ of the DC material was found to be significantly higher than of the OD material. The latter material was sampled about 20-30 cm under surface of the storage place and therefore had been desiccated to a larger extend than the DC samples which were taken from the lower part of a dike cover layer.

Overall the small-scale investigations on the shrinkage behavior reveal that the determination of COLE is a useful and, above all, convenient method to determine the ripening status of dredged material.

6.2.2 Large-scale shrink and swell experiment

The results of the large-scale shrink-swell experiment revealed that the shrinkage behavior of the processed dredged materials in the first drying cycle was significantly different from that of the fine-grained aged marsh sediments.

Compared to the marsh sediments, the METHA materials and two of the three investigated dewatering field materials showed significantly higher volumetric shrinkage. Total shrinkage of the METHA materials was found to be correlated with clay content and inversely with sand content. The relationship between initial water content and total shrinkage was found to be quite strong, but not significant. However, between reversible shrinkage and initial water content a strong positive relationship was determined.

Wysocka et al. (2006) and Widomski et al. (2015) showed in their investigations on the relationship between compaction water content and shrinkage potential of one natural clay soil and two loam soils, and two technical clay materials respectively that shrinkage potential of these soils increased with water content during compaction. Birle et al. (2008) showed in their investigations on the effects of initial water content and dry density on shrinkage behavior of Lias clay that the rate of volume change during drying to water contents near shrinkage limit of this material increased with increasing compaction water content, while the rate of volume change during the following residual drying appeared to be unaffected by the compaction water content. Contrary to the results presented in this study, the influence of the dry density after installation on the shrinkage of the Lias clay was found to be negligible.

In contrast to the marsh sediments, where swelling of the samples after saturation with water resulted in sample volumes equal or slightly higher than at the beginning of the experiment, the shrinkage of the processed dredged material was found to be partly irreversible. The mean reversible proportion accounted for 38 % of total shrinkage and was found to be correlated with clay content and initial water content of the samples. For the irreversible proportion of shrinkage, no statistically significant correlations with material properties were determined. However, as for the reversible proportion of shrinkage, positive relationships both between the clay content and irreversible shrinkage and initial water content and irreversible shrinkage were found.

Correlation analysis revealed that regarding the aged marsh sediments the TOC content and the clay content were the parameter with significant influence on their swelling behavior. These two parameters were also found to correlate significantly with the swelling behavior of the METHA materials. Swelling is a consequence of water adsorption on mineral surfaces and cations adsorbed on them as well. Since the clay fraction offer the largest surface area in the soil and contain most of the exchangeable cations, swelling is more pronounced in soils rich in clay. TOC may also contribute to the water adsorption capacity and therefore exert an influence on the swelling of soils (Scheffer and Schachtschabel, 2016).

The water content of the processed METHA materials indeed was significantly higher than of the marsh sediments, but referred to the initial water contents, the decrease in water content during the first drying cycle was comparable for both materials. The increase in bulk density, as response of the soil matrix to desiccation, however, was significantly smaller for the aged marsh sediments than for the METHA materials. This implies that the matrix of the aged fine-grained marsh sediments is more rigid than that of the processed dredged material, which had not been exposed to desiccation before. Desiccation, i.e. pre-shrinkage results in a more rigid structure of soils, so the soils gain more stability against mechanical and hydraulic (capillary) stresses (Peng et al. 2009, Horn et al. 2014).

By means of soil shrinkage curves, the differences in the shrinkage behavior of the processed dredged materials and the marsh sediments and changes in the shrinkage behavior of the processed dredged materials due to the ripening could be examined also. In contrast to the processed dredged materials, where initial (proportional) shrinkage and residual shrinkage were determined during the first drying cycle, the fine-grained aged marsh sediments exhibited only residual and zero shrinkage in the investigated moisture range. The shrinkage curve of some METHA samples (i.e. METHA 2 and METHA 6) could be subdivided into distinct structural and proportional shrinkage ranges. This behavior was similar to that of a Gleysol and a Stagnosol investigated by Horn (2014). According to Horn (2014) such separation in distinct shrinkage ranges can be caused by the overlapping of various processes such as the shrinkage of the entire soil body, the formation of coarser macropores and the simultaneous shrinkage of soil aggregates.

In the second drying cycle, the range of proportional shrinkage of the processed dredged material narrowed markedly, while a pronounced structural and residual shrinkage was determined. The shrinkage curve determined on the aged marsh sediments in the second drying cycle was found to be parallel to that of the first cycle over a wide range of moisture ratio and, like those of the processed dredged materials characterized by a pronounced structural shrinkage behavior. From these results it can be deduced that the shrinkage behavior of the processed dredged material becomes more similar to that of the aged marsh sediment due to repeated drying or ripening respectively.

The drying in the first cycle decreased the saturated void ratio of the dredged materials and narrowed the range of void ratio during the second drying. A decrease in saturated void ratio, as it was determined on the processed dredged materials after the first drying cycle, was also observed by Peng et al. (2007) on a Eutric Histosol and a Histic Gleysol after an intense WD cycle and by Bronswijk (1990) after ripening of clay soils. As a consequence of the narrowed range of void ratios in the second drying cycle, the shrinkage in the second drying cycle decreased in comparison to the shrinkage determined in the first drying cycle. Several authors showed that the impact of the first WD cycle on soil structure is greatest and decreases with subsequent cycles (Basma et al. 1996; Tripathy et al. 2002).

From the results of the large-scale shrinkage experiments it can be inferred that shrinkage of the processed dredged materials in the second drying cycle depends mostly on the drying intensity of the first drying cycle. On the METHA samples, on which slightly lower water contents than after the first drying cycle were yielded in the second drying cycle, a further shrinkage was observed. This is consistent with findings of Peng et al. (2007), who showed in their investigations on the shrinkage behavior of different organic and inorganic soils that shrinkage of these soils during repeated wet and dry cycles depend mostly on the maximum intensity of the previous WD cycles. They concluded that repeated drying that causes stresses smaller than the pre-stress will result in re-shrinkage, while new and initial (i.e. proportional) shrinkage will occur when the capillary stress becomes higher than the pre-shrinkage stress (Peng et al. 2007).

The results indicate that further processing of processed dredged material by enhanced drying can ameliorate the shrink behavior of this particular material. The determination of $COLE_{rod}$ on un-ripened and ripened dredged materials showed, that ripening, i.e. repeated drying, leads to a decrease of shrinkage capacity of 20-80 %.

The results of the large-scale shrink-swell experiment showed that contrary to the marsh sediments, only a minor proportion of the shrinkage of the processed dredged materials in the first drying cycle was reversible by swelling. The degree of shrinkage in the second drying cycle was found to depend mostly on the maximum drying intensity of the first drying cycle. Dewatering of the processed dredged material to an extent equal to the first drying cycle resulted in re-shrinkage but not in further shrinkage, while drying to a larger extend than in the first drying cycle lead to an increase in total shrinkage i.e. to further shrinkage. Referred to the shrinkage stages, this shows that in the large-scale shrink well experiments, the stage of zero shrinkage, in which no further shrinkage occurs on further dewatering, has not been reached.

It is assumed that one intense drying cycle would be sufficient to alter the shrinkage behavior of the processed dredged material and to make it more comparable to that of fine-grained aged marsh sediments, which only showed residual and zero shrinkage, but no initial (proportional) shrinkage in the investigated moisture range. Based on the evaluation of volumetric water contents determined on the test field layers constructed from METHA material Gröngröft et al., 2016), minimum water contents of about 13 - 18 % DW are to be expected for future dike cover layers in Hamburg, constructed similarly to the layer in the test field. Based on these results and the results from the shrinkage experiments, it is recommended to air dry the processed dredged materials to water contents of less than 12 % DW as further processing step before use as construction material of dike cover layers.

7 Leaching behavior of contaminants

When assessing the suitability of treated dredged material for dike construction, it must be ascertained whether the pollutants present in the material can pose a risk to the environment in general and to specific pathways. Depending on the intended use, both the path of propagation of contaminants into the vegetation and into the groundwater are to be considered.

Due to the concentrations in the solid, the METHA material is classified in class "Z2" according to LAGA assessment criteria (Gebert and Gröngröft, 2010). Although the monitoring conducted at the test fields showed that the leachates from the METHA material exceed the test values permitted by the regulations for groundwater and soil protection in the long term only with regard to sulphate, nitrate and electrical conductivity (Gröngröft et al., 2016), there was a further demand for investigation with regard to the question of which pollutant emissions can possibly occur from fresh METHA material after installation in dikes, in the mid-term through ripening and in the long-term through processes such as acidification or mineralization of the organic substance, which lead to a change in the materials' chemical properties.

To answer these questions, two different investigation approaches were applied. In the first approach, the leaching of pollutants from fresh and ripened materials was examined by means of standardized methods (BBodSchV, 1999; LAGA, 2004). The ripened materials investigated in this approach originated from the large scale shrink-swell experiments. This means that the material has undergone two drying cycles and one re-wetting cycle. In the second approach, worst-case studies were conducted. In these studies, potentially pollutant mobilizing processes are simulated in the laboratory to determine the maximum pollutant emission potential of the materials in a time-lapse effect (Eschenbach et al. 1998, 2001) and to assess in which time periods processes may take place that can enhance the contaminants mobility.

7.1 Results

7.1.1 Leaching from fresh and ripened material

The aim of the investigation of the leaching behavior was to determine the potential leaching of contaminants from fresh or rather unripened material and ripened, i.e. chemically essentially unchanged METHA material.

The following elution methods were applied (details see chapter 3.2.5):
- Ammonium nitrate extraction
- Batch extractions
- Percolation column tests
- Water impoundment column method.

7.1.1.1 Trace metals and As

The results of **the ammonium nitrate (AN)-extraction**, which is recommended to determine the plant available proportion of trace elements (BBodSchV, 1999), are compiled in Table 7.1.

Compared to the other groups of dredged material, the METHA material showed the highest amounts of readily soluble trace metals. For this material a decrease in readily soluble trace metal contents (mg/kg DW) was determined in the order:

Zn (1.9) > Cu (0.83) > Ni (0.16) > As (0.038) > Pb (0.034) > Cd (0.031)

In consideration of the percentage share of the leached amounts in relation to the total trace metal contents (% total content), the following order was determined:

Cd (0.86) > Cu (0.54) > Ni (0.39) > Zn (0.31) > As (0.10) > Pb (0.04)

The highest extraction yields were determined on the METHA samples (compare Table 7.1). However, the percentage share of the AN-extractable trace metal contents in relation to the total contents was very small with values between <0.01 % (Pb) and 0.38 % (Cu). For the other MS samples most of the AN-extractable trace metals contents were below the limits of quantification (LOQ). Sample MS 4 showed remarkable high contents of readily available trace metals. For this sample a leaching of about 39 % (Cd), 7.2 % (Ni), 3.3 % (Zn) and 1.8 % (Pb) of the total trace metal contents was determined. The high AN-extractable trace metal amounts of this sample are most probably due to its low pH. In contrast to the other MS samples with pH values in the range of 7.1-7.5, a pH of 3.8 was determined on sample MS 4. The relationship between pH and AN-extractable trace metal amounts could be verified by means of multiple regression analyses. Significant relationships between plant available trace metal contents and the specific soil properties could be determined for Cd and Ni. As expected, the parameters clay (ß=0.526; $p < 0.01$) and pH (ß=-0.484; $p < 0.05$) were the strongest predictors for Cd, i.e. the higher the clay content and the lower the pH, the higher the Cd content soluble in ammonium nitrate. For Ni, the analysis showed a significant relationship of the AN-extractable amount to pH (ß=0.729; $p < 0.01$) and clay (ß=0.457; $p < 0.05$). Contrary to expectations, there is a positive correlation between pH and ammonium nitrate soluble Ni- content. For Ni and Zn, no significant relation between the total contents (aqua regia extraction) and the AN-extractable content was found. For the other trace elements, this relationship was found to be significant but not very strong with r-values in the range of 0.64 (As) – 0.70 (Cu).

Table 7.1 Results of the AN-extraction. DW=Dry weight, METHA=METHA material, DF=dewatering field material, OD=open depot material, DC=dike construction material, MS=marsh sediments, LOQ=Limit of Quantification, SD=Standard deviation.

	AN extractable content [mg/kg DW]					
Sample	**As**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
METHA 1	0.02	0.02	1.26	0.22	0.06	1.74
METHA 2	0.03	0.03	0.74	0.23	0.08	1.98
METHA 3	0.02	0.02	0.65	0.17	0.03	1.59
METHA 4	0.04	0.03	0.57	0.12	0.02	1.78
METHA 5	0.04	0.03	0.91	0.12	0.02	1.93
METHA 6	0.04	0.03	0.80	0.14	0.01	1.85
METHA 7	0.06	0.04	1.15	0.18	0.01	1.95
METHA 8	0.06	0.04	0.66	0.11	< LOQ	2.24
METHA 9	0.03	0.04	0.72	0.15	0.07	2.40
Mean	0.04	0.03	0.83	0.16	0.04	1.94
SD	0.01	0.01	0.24	0.04	0.03	0.25
DF 1	0.05	0.02	0.60	0.04	0.01	1.04
DF 2	0.06	0.01	0.69	0.04	< LOQ	0.83
DF 3	0.04	0.01	0.81	< LOQ	< LOQ	0.36
Mean	0.05	0.01	0.70	0.04	0.01	0.74
SD	0.01	0.01	0.11	0.001	-	0.35
OD 1	0.003	0.01	0.73	0.08	< LOQ	0.89
OD 2	0.03	0.02	0.47	0.10	< LOQ	0.89
OD 3	0.05	0.02	0.41	0.13	< LOQ	1.33
Mean	0.03	0.02	0.54	0.10	-	1.04
SD	0.02	0.01	0.17	0.03	-	0.25
DC 1	0.04	0.02	0.72	0.12	< LOQ	1.35
DC 3	0.08	0.04	0.66	0.23	< LOQ	2.77
DC 6	0.02	0.02	0.59	0.09	< LOQ	1.20
DC 7	0.01	0.02	0.63	0.08	< LOQ	1.22
DC 8	0.004	0.01	0.56	0.06	< LOQ	1.07
DC 9	< LOQ	0.01	0.50	0.05	< LOQ	0.99
Mean	0.03	0.02	0.61	0.11	-	1.43
SD	0.03	0.01	0.08	0.07	-	0.67
MS 1	< LOQ	< LOQ	0.27	< LOQ	< LOQ	0.10
MS 2	0.01	< LOQ	0.27	< LOQ	< LOQ	< LOQ
MS 3	0.01	< LOQ	0.26	< LOQ	< LOQ	< LOQ
MS 4	0.01	0.21	0.46	4.15	0.44	4.41
Mean	0.01	0.21	0.32	4.15	-	2.26
SD	0.002	-	0.10	-	-	3.05

For the investigation of the leaching behavior of inorganic substances and organic substances according to DIN 19529 and DIN 12745-4, batch extractions were performed. The results of the batch-extractions are presented in the following.

The **2:1 batch extraction** according to DIN 19529 was conducted to investigate the elution behavior of inorganic and organic substances with a liquid to solid ratio (L/S ratio) of 2l : 1kg dry mass. Due to problems in the applicability of the formula for calculating the eluate volume to METHA materials (the high water contents resulted in negative water addition quantities), the method was modified and a ratio of 2 l water:1 kg solid wet mass was set. Due to their different initial moisture levels, the L/S ratios for the samples were different (see Table 7.2). The results of the **2:1 batch extraction** are summarized in Table 7.2.

The leached trace metals amounts (mg/kg DW) decreased in the order:

Zn (3.06) > Ni (0.17) > Cu (0.14) > As (0.035) > Cd (0.01) > Pb (<LOQ)

In consideration of the percentage share of the leached amounts in relation to the total trace metal contents (% total content), the following order was determined:

Zn (0.47) > Ni (0.38) > Cd (0.26) > As (0.11) > Cu (0.09) > Pb (<LOQ)

The multiple regression analyses conducted with the results of the 2:1 batch extraction revealed no statistically significant correlations between leached As, Cd, Ni and Zn contents and the soil properties (clay content, TOC content, pH). The influence of the pH of the samples on the trace metal leaching tends to be greatest, since this parameter had the highest standardized regression coefficients. For Cu, a significant ($p < 0.05$) relationship between the pH and the eluted contents could be determined. However, with $r=0.682$, this relationship is not to be considered as very strong.

Table 7.2 Results of the 2:1 batch extraction: Trace metals. METHA=METHA material, LOQ=Limit of Quantification.

Sample	**L/S**	**As**		**Cd**		**Cu**		**Ni**		**Pb**		**Zn**	
	[l/kg]	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**
METHA 1	6	3.0	0.016	1.0	0.009	33.0	0.201	27.0	0.162	< LOQ	< LOQ	690.0	4.202
METHA 2	7	3.0	0.023	4.0	0.032	46.0	0.332	40.0	0.289	< LOQ	< LOQ	960.0	6.985
METHA 3	5	4.0	0.014	1.0	0.005	32.0	0.131	21.0	0.094	< LOQ	< LOQ	345.0	1.483
METHA 4	6	6.0	0.026	0.2	0.001	37.0	0.163	16.0	0.070	< LOQ	< LOQ	282.0	1.237
METHA 5	10	12.0	0.109	0.1	0.001	10.0	0.096	12.0	0.118	< LOQ	< LOQ	98.0	0.583
METHA 6	6	7.0	0.041	1.0	0.006	23.0	0.134	8.0	0.048	< LOQ	< LOQ	263.0	1.534
METHA 7	6	4.0	0.023	4.0	0.027	10.0	0.065	77.0	0.501	< LOQ	< LOQ	1273.0	8.225
METHA 8	8	4.0	0.034	1.0	0.007	9.0	0.067	20.0	0.154	< LOQ	< LOQ	295.0	2.277
METHA 9	6	4.0	0.027	1.0	0.003	7.0	0.045	14.0	0.092	< LOQ	< LOQ	150.0	0.972

Table 7.3 Results of the 10:1 batch-extraction: Trace metals. METHA=METHA material, DF=Dewatering field material, LOQ=Limit of Quantification.

	As		**Cd**		**Cu**		**Ni**		**Pb**		**Zn**	
Sample	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[mg/l]**	**[mg/kg DW]**
METHA 2u	4.5	0.005	0.45	0.005	14.6	0.15	4.5	0.05	< LOQ	-	0.05	0.55
METHA 3u	< LOQ	-	0.26	0.003	3.1	0.03	< LOQ	-	< LOQ	-	< LOQ	-
METHA 5u	< LOQ	-	0.97	0.010	55.3	0.56	4.9	0.05	< LOQ	-	0.09	0.86
METHA 8u	< LOQ	-	0.61	0.006	24.7	0.25	2.7	0.04	< LOQ	-	0.06	0.57
DF 1u	< LOQ	-	0.47	0.005	38.3	0.39	< LOQ		< LOQ	-	0.06	0.57

Since it had been shown, that the 2:1 batch-extraction was not practicable for the determination of the leaching behavior of pollutants from the dredged material, because the L/S ratios of these materials were already too high, the **10:1 batch-extraction** according to DIN 12457-4 was performed instead for the further investigations.

The 10:1 batch-extraction according to DIN 12457-4 was conducted with four samples of fresh i.e. unripened technically processed dredged material from the METHA plant (METHA 2, METHA 3, METHA 5, METHA 8) and one sample of naturally processed dredged material from the dewatering fields (DF1).

The results from the 10:1 batch-extraction are compiled in Table 7.3. As was eluted only from one sample (METHA 2u) in a concentration above the LOQ (4 µg/l). The eluted concentration of 4.5 µg/l corresponds to an As release of 0.046 mg/kg DW or 0.1% of the total contents respectively. The release of Cd in the batch-extraction on average amounted for 0.14 % of the total contents. The Cu contents of the eluates were determined with values between 3.1 µg/l (METHA 3u) and 55.3 µg/l (METHA 5u) corresponding to 0.024 % and 0.29 % of the total Cu contents. The average Ni release from the materials accounted for 0.08 % of the total contents. The Zn contents of the eluates were determined with values between 0.05-0.06 mg/l. In the eluate from sample METHA 3u, the Zn concentration was below the LOQ (0.04 mg/l). The Zn leaching in the 10:1 batch extraction on average accounted for 0.09 % of the total Zn contents.

Regarding the eluted trace metal concentrations (mg/kg DW) the following order was determined:

Zn (11.97) > Cu (0.28) > Cd (0.19) > Ni (0.05) > As (0.05) > Pb (<LOQ)

The ranking based on the eluted amounts in relation to the total trace metal contents of the materials (% of total content) the order was:

Cu (0.18) > Cd (0.18) > As (0.11) > Ni (0.10) > Zn (0.09)

The **percolation column test according to DIN 19528** was used to examine the leaching of contaminant from the processed dredged material over a wider L/S range. To investigate whether ripening may influence the leaching of contaminants, comparative percolation column tests were conducted with unripened materials and ripened materials. The ripened materials originated from the large scale shrink and swell experiments.

In the following, the results with regard to the different elution behavior of the unripened and ripened processed dredged materials and the different elution behavior of the trace metals examined are presented. Subsequently, the trace metal contents eluted in the percolation column test are presented, on the basis of which the release of pollutants from the materials is assessed in chapter 7.2.3.1.

The Figures 7.1-7.5 show the cumulative leaching (Σ mg/kg) of the trace metals As, Cd, Cu, Ni and Zn determined in the percolation column test during elution within a L/S range of 0 - 20. For the determination of the cumulated leached trace metal amounts, values below the LOQ were equated with the LOQ.

Due to a defect of one of the two columns in the percolation test conducted with sample METHA 5 ripened only data up to L/S 4 are available for column 1 for this sample. For METHA 8, the test with one of the two columns operated in parallel had to be terminated prematurely as well.

Overall, the results of the parallel determinations (column1 and column2) were well consistent for all samples. For some materials and trace metals investigated, the parallel determinations corresponded so well that the curves are identical.

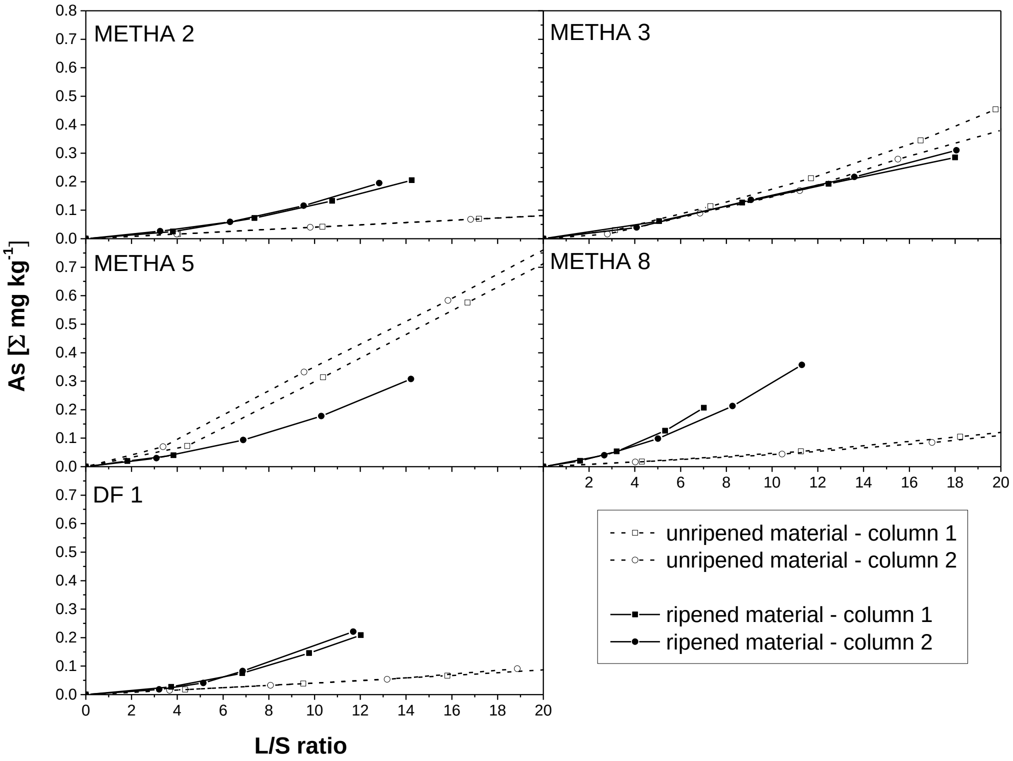

Figure 7.1 Cumulative As leaching in the percolation column tests.

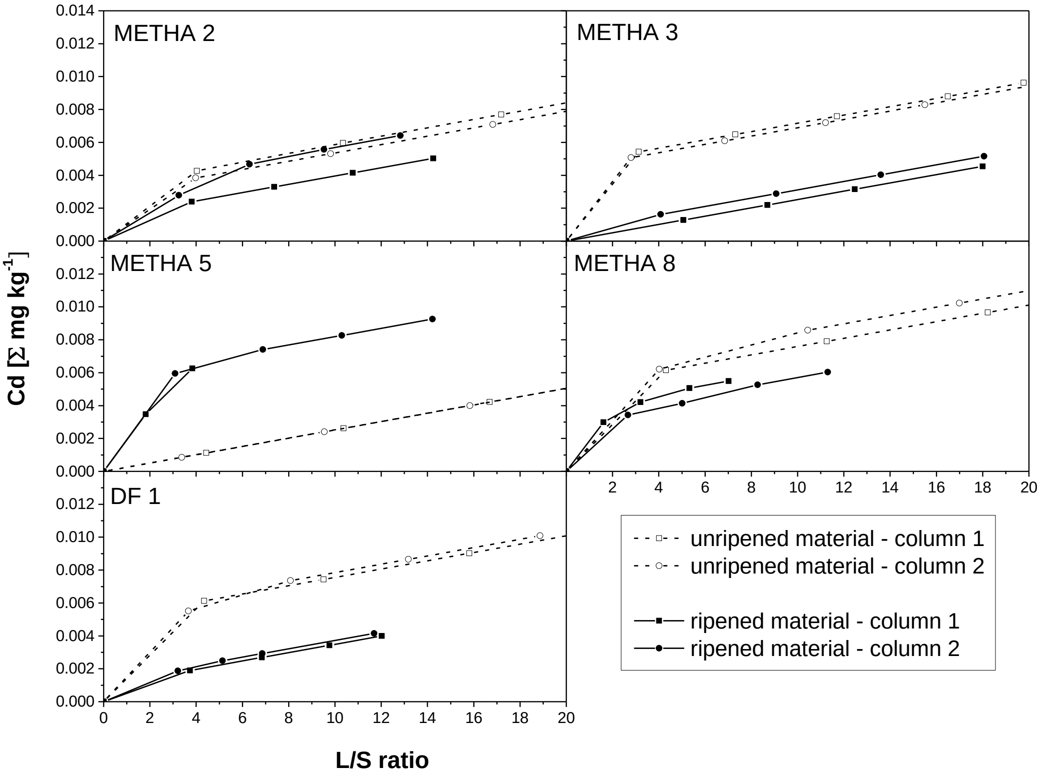

Figure 7.2 Cumulative Cd leaching in the percolation column tests.

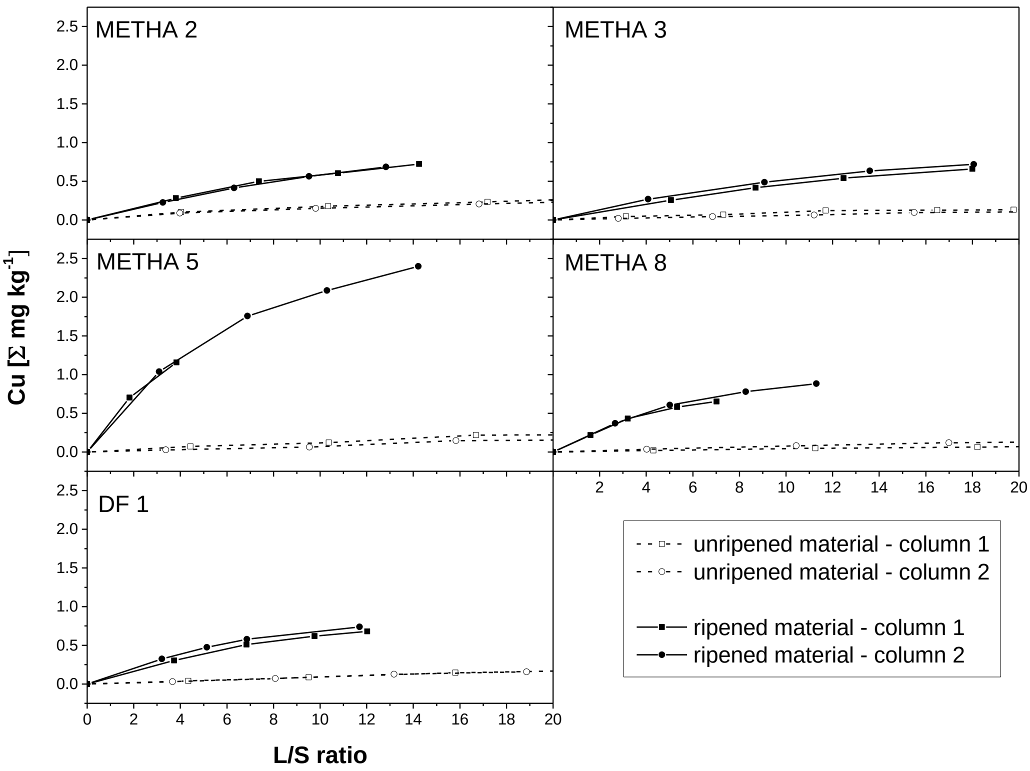

Figure 7.3 Cumulative Cu leaching in the percolation column tests.

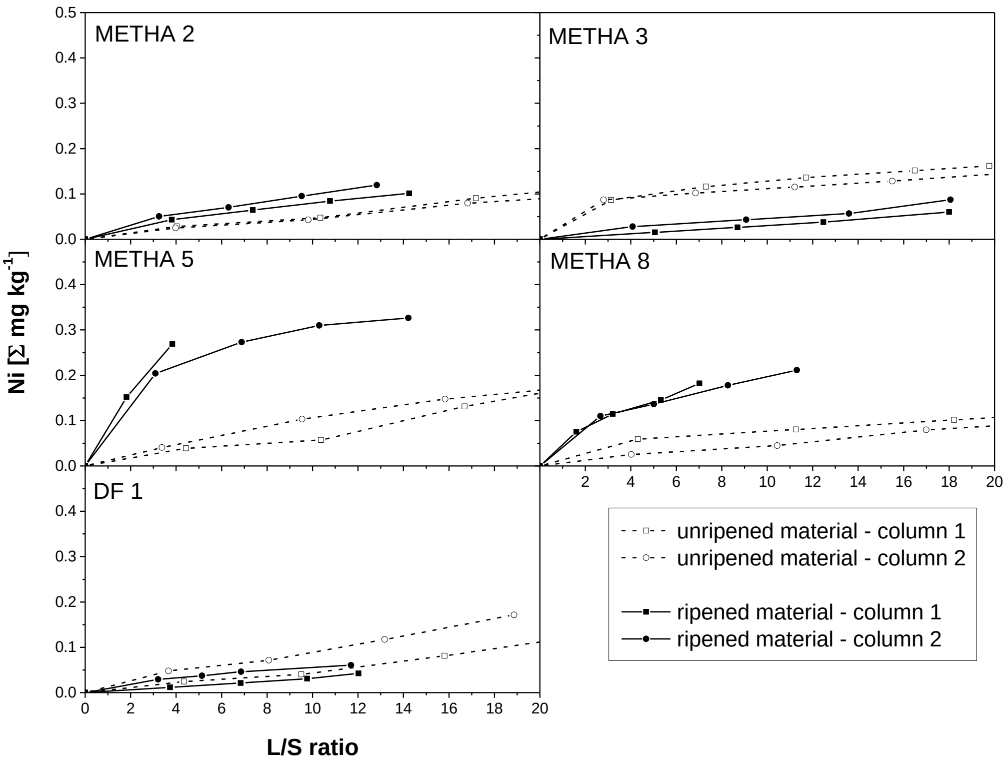

Figure 7.4 Cumulative Ni leaching in the percolation column tests.

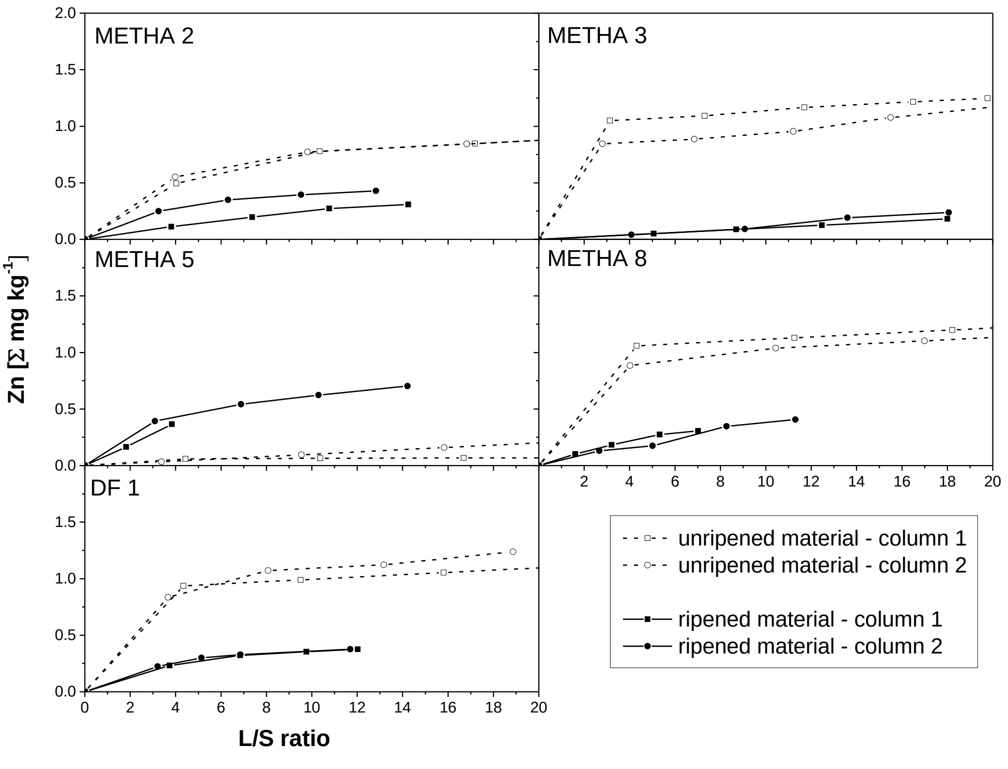

Figure 7.5 Cumulative Zn leaching in the percolation column tests.

As shown in Figure 7.1, the cumulative amount of eluted As increased almost linearly with increasing L/S ratios. With the exception of sample METHA 8, As leaching from the ripened material differed from that of the unripened material. However, the effect of ripening on the leaching of As was inconsistent as for two samples (METHA 2r, DF 1r) an increase in the leaching was observed, while for the samples METHA 3r and METHA 5r lower amounts of As were leached from the ripened material than from the unripened material.

The release behavior of Cd (Figure 7.2) differs in part from that of As. At higher L/S ratios, a linear course of the eluted Cd concentration was observed, but in many cases a strong initial leaching (up to an L/S ratio of about 5) occurred. As for As, the effect of ripening on the leaching of Cd was inconsistent. In three cases, the leaching decreased after ripening, in one case it was almost equal (METHA 2r) and in another case (METHA 5r) the leaching from the ripened material was significantly increased compared to the unripened material.

The amount of Cu leached from the samples METHA, 2, METHA 3, METHA 8 and DF 1 decreased with increasing L/S ratio, in particular with the ripened materials (see Figure 7.3). The leaching from the unripened material was constantly on a low level. In contrast to the other trace metals, Cu leaching was markedly increased after ripening with all samples.

The leaching behavior of Ni was similar to that of Cu. Especially for the ripened materials, high leaching rates were determined at the beginning of the percolation column test (see Figure 7.4). The comparison of the leaching from the ripened material and the unripened material revealed an inconsistent effect of ripening. On for two samples, a significant increase in Ni leaching was observed. For one sample, a slight increase was determined, while for another sample the leaching was found to be almost the same. One sample showed a significant decrease in Ni leaching after ripening.

The leaching behavior of Zn (Figure 7.5) was similar to that of Cd. At the beginning of the percolation column tests a high initial mobility of Zn especially with the unripened materials could be observed. For four samples, a decrease in Zn leaching was observed after ripening. Sample METHA 5 showed an opposite behavior.

The results of the percolation column tests reveal differences in leaching behavior both for the different trace metals investigated and for the different materials examined. Ripening led to an increased leaching of Cu with all samples investigated. The increase of the Cu-leaching due to ripening was found to be statistically significant (t test: $p < 0.05$). As and Ni also showed increased release in three of the five samples examined as a result of ripening. However, contrary to Ni, the cumulated eluted As-amount increases almost linearly with increasing L/S. Due to the inconsistent effect of ripening on the leaching of these two metals, no statistically significant effect of ripening could be found for Ni and As. Cd and Zn behave very similarly. With these two trace metals, a decrease in the leaching of all materials except METHA 5 was observed after ripening. For Zn, the decrease in leaching after ripening could be statistically verified (t-test: $p < 0.05$). Regarding Cd the effect of ripening could not be statistically verified.

In summary, the data from the percolation column test only revealed significant effects of ripening on release behavior for Cu (increase) and Zn (decrease). In the case of cadmium, the data show at least a distinct trend towards a release reducing effect of ripening.

The overall behavior of METHA 5 sample is very different from that of the other dredged materials examined. METHA 5 is the only material where a decrease in arsenic elution was observed after ripening. Furthermore, it is the only material with which ripening does not lead to a decrease but to an increase in the release of Cd and Zn. The comparison of the leaching from the other materials shows, that METHA 2 and METHA 8 behave similar. With these materials a decrease in the leaching of Zn as well as an increase in the leaching of As, Cu and Ni was observed due to ripening. With METHA 3 no increase in As leaching and a decrease in the Ni was determined after ripening. Material DF 1 also showed a slightly different behavior than METHA 3. With this sample, no clear decline in the Ni leaching was found due to ripening.

The material properties of METHA 5 do not differ noticeably from those of the other samples with regard to the determined soil parameters and total pollutant contents. METHA 5 lies rather in the middle range of the spectrum of TOC contents, as well as pollutant loads. Although it has the second highest clay and silt content, MEHTA 3 and METHA 8 have similar particle size distributions and these samples do not show any noticeable behavior in the percolation column test.

The regression analyses on the relationship between trace metal leaching in the percolation column tests and the soil properties revealed only for Cu and clay content a significant correlation. For all other trace metals, the highest standardized regression coefficients were also determined for the parameter clay content. However, these correlations were not statistically significant ($p > 0.05$). Between the trace metal contents leached from the ripened material and the specific soil properties no statistically significant correlations could be determined either. The differences in the effect of ripening on the trace metal leaching from the individual samples could therefore not be explained by their inherent soil properties. This is due to the relatively small set of samples analyzed, the small number of parallels investigated (2 parallels each for the ripened and unripened materials) and due to the fact that the materials examined do not differ markedly from each other with regard to their properties (grain-size distribution, TOC, TIC, pH, total pollutant contents etc.).

For the assessment of the leaching behavior, the concentration of trace metals (As, Cd, Cu, Ni, Pb, Zn) and EPA-PAH in the eluates was determined and the percentage share of the extracted amounts in relation to the total pollutant contents was calculated. In this calculation, it had to be taken into account that in many cases the measurement results were below the LOQ. For the summation of the leached pollutant amounts values below the LOQ were set equal to the LOQ.

According to DIN 19528 and BBodSchV, a L/S ratio of 2 is to be used for the assessment of the eluate contents. The data (cumulated leached amounts) were fitted with a second-degree polynomial function and the eluted loads at defined L/S ratios (L/S=2 and L/S=10) were calculated using the determined function. The results from the curve fitting are compiled in Table 7.4.

Table 7.4 Results of percolation column test determined from the curve fitting functions.

Parameter	Sample	r^2 curve fitting	Cumulative leaching L/S=2 [Σ mg/kg]	Cumulative leaching L/S=10 [Σ mg/kg]	Mean eluate concentration at L/S=2 [µg/l]
As	METHA 2u	1	0.008	0.040	< LOQ
	METHA 3u	0.994	0.030	0.175	15.1
	METHA 5u	0.999	0.079	0.401	39.4
	METHA 8u	0.997	0.007	0.044	< LOQ
	DF 1u	0.997	0.008	0.041	< LOQ
	METHA 2r	0.996	0.013	0.121	6.5
	METHA 3r	0.998	0.025	0.146	12.6
	METHA 5r	0.999	0.017	0.170	8.5
	METHA 8r	0.993	0.034	0.298	17.1
	DF 1r	0.997	0.009	0.155	4.6
Cd	METHA 2u	0.981	0.001	0.006	0.7
	METHA 3u	0.969	0.003	0.006	1.7
	METHA 5u	1.000	0.001	0.003	0.3
	METHA 8u	0.975	0.002	0.008	1.0
	DF 1u	0.980	0.002	0.008	1.1
	METHA 2r	0.964	0.002	0.005	0.7
	METHA 3r	0.990	0.001	0.003	0.3
	METHA 5r	0.977	0.003	0.009	1.6
	METHA 8r	0.979	0.002	0.006	1.2
	DF 1r	0.996	0.001	0.004	0.5
Cu	METHA 2u	0.987	0.037	0.159	18.3
	METHA 3u	0.955	0.013	0.069	6.5
	METHA 5u	0.972	0.015	0.071	7.5
	METHA 8u	0.906	0.014	0.061	6.9
	DF 1u	0.997	0.020	0.092	9.9
	METHA 2r	0.999	0.150	0.589	75.1
	METHA 3r	0.996	0.120	0.492	60.1
	METHA 5r	0.997	0.643	2.518	321.4
	METHA 8r	0.997	0.264	0.841	132.1
	DF 1r	0.995	0.197	0.663	98.6
Ni	METHA 2u	0.988	0.010	0.049	5.0
	METHA 3u	0.926	0.061	0.102	30.3
	METHA 5u	0.978	0.044	0.077	21.9
	METHA 8u	0.958	0.015	0.063	7.2
	DF 1u	0.914	0.016	0.074	8.0
	METHA 2r	0.983	0.025	0.092	12.4
	METHA 3r	0.950	0.007	0.039	3.7
	METHA 5r	0.971	0.124	0.353	62.1
	METHA 8r	0.991	0.070	0.202	35.0
	DF 1r	0.894	0.012	0.044	6.2

Continuation Table 7.4

Parameter	Sample	r^2 curve fitting	Cumulative leaching L/S=2 [Σ mg/kg]	Cumulative leaching L/S=10 [Σ mg/kg]	Mean eluate concentration at L/S=2 [µg/l]
Zn	METHA 2u	0.979	0.196	0.757	98.1
	METHA 3u	0.753	0.603	0.886	301.5
	METHA 5u	0.600	0.017	0.080	43198
	METHA 8u	0.772	0.427	1.093	213.4
	DF 1u	0.846	0.413	1.129	206.5
	METHA 2r	0.924	0.116	0.559	57.8
	METHA 3r	0.975	0.020	0.110	10
	METHA 5r	0.989	0.205	0.667	102.7
	METHA 8r	0.988	0.104	0.382	51.9
	DF 1r	0.997	0.134	0.377	66.7

The As concentration determined from the curve fitting for L/S=2 varied in a wide range with values between < LOQ and 39.4 µg/l (comp. Table 7.4). Compared to the total As content of the samples a leaching of 1.6 % from the unripened material was calculated for a L/S of 10. Leaching from the ripened material up to this L/S was determined with a maximum of 0.7 % of the total As content. These proportions are much higher, than the mobile/easy mobilizable pool of 0.02 % from the total content, determined in the sequential extraction.

The **Cd** concentration in the eluates at L/S=2 (determined from the curve fitting) ranged between 0.3 and 1.7 µg/l. Compared to the total Cd content, this corresponds to a leached proportion of 0.3 % up to L/S=10. The calculated maximum percentage proportion determined for the ripened materials was 0.25 % for sample METHA 5r. These results correspond well with the results from the sequential extraction. Here, the amount of Cd associated with the mobile/easy mobilizable fractions was determined on average with 0.19 % from the total trace metal content.

The calculated cumulative **Cu**-concentrations at L/S=2 for the ripened material ranged between 75 - 321 µg/l and were significantly higher than the eluate concentrations calculated for the unripened materials (7 - 18 µg/l). The maximum cumulative Cu leaching from the unripened materials (0.159 mg/kg) calculated for L/S=10 accounted for 0.1 % of the total Cu content and was determined for sample METHA 2u. The calculated maximum eluted Cu content of the ripened material up to this L/S ratio corresponded to 1.2 % of the total Cu content and was determined on sample METHA 5r.

The calculated concentrations of Ni leached up to L/S=2, varied between 4 and 62 µg/l. The calculated maximum cumulated Ni content leached from the unripened material up to L/S=10 was 0.10 mg/kg and was determined for sample METHA 3u, in relation to the total Ni content this corresponds to 0.4 %. Regarding the ripened material, the maximum leached Ni amount was calculated with 0.35 mg/kg (METHA 5r) corresponding to 0.66 % of the total content.

The highest leaching from the unripened material (up to L/S=10) was determined for sample DF 1 with 1.1 mg/kg DW, corresponding to 0.17 % of the total content. This value corresponds quite well to the mobile/ easy mobilizable fraction, determined in the sequential extraction with an average of 0.18 % of the total Zn content. The maximum cumulated Zn content of 0.66 mg/kg DW in the elution of the ripened material was calculated for sample METHA 5r. In relation to the total Zn content this accounts for 0.09 %.

Regarding the unripened materials the mean eluted trace metal contents (mg/kg DW) calculated until L/S=2 decreased in the order:

Zn (0.301) > Ni (0.029) > As (0.026) > Cu (0.02) > Cd (0.002)

For the percentage share of the eluted trace metal contents (% of total content) in relation to the total contents, the order was determined with:

As (0.095) > Ni (0.078) > Zn (0.057) > Cd (0.053) > Cu (0.013)

Regarding the ripened materials the order of mean eluted trace metal contents (mg/kg DW) calculated until L/S=2 was different with:

Cu (0.275) > Zn (0.116) > Ni (0.048) > As (0.019) > Cd (0.018)

For the percentage share of the eluted trace metal contents (% of total content) in relation to the total contents, the order was also different with:

Cu (0.172) > Ni (0.096) > As (0.059) > Cd (0.047) > Zn (0.017)

The **water impoundment column method** according to Gerth (2007) was applied to enable the examination of the leaching of contaminants from undisturbed samples of ripened material originating from the large-scale shrink experiments. This method was also used to elute the unripened material for comparative purposes. However, these were elutions of disturbed soil samples, as the unripened material was installed and compacted in layers in the columns. The results of the water impoundment column method are shown in Table 7.5. Due to the large deviation of the pollutant contents determined in the eluates of the three parallel columns, the results are given as a range of values.

With the unripened material, As was determined in concentrations of 4.0 µg/l to 7.6 µg/l in the eluates (compare Table 7.5). In the eluates obtained from the ripened material up to a L/S ratio of 0.2-1.2:1, the As- concentrations were below the LOQ of 4 µg/l.

Pb was neither in the eluates from the unripened, nor from the ripened samples determined in concentrations above the LOQ.

The cadmium content in the eluates of the unripened material ranged from 0.5-1.2 µg/l, in the eluate of the ripened material a nearly equal concentration range (0.5-1.3 µg/l) was determined.

The copper content of the eluates of the unripened material was between 2.4 µg/l and 4.9 µg/l. The eluates obtained from the ripened material had copper contents of 4.7 - 15.9 µg/l.

Nickel was determined in the eluates with contents of 20.1 - 29.2 µg/l (unripened material) and of 12.9 - 16.2 µg/l (ripened material).

The zinc content in the eluates of the unripened material ranged from 145 to 303 µg/l. In the eluates from the ripened material zinc was determined in concentrations from 71 µg/l up to 146 µg/l.

Table 7.5 Range of trace metal concentrations determined in the eluates from the water impoundment column method (Results of three parallels). L/S=Liquid to solid ratio, u=unripened, r=ripened, LOQ=Limit of quantification, n.d.=not determined.

		Sample	
		METHA 5	
		u	**r**
L/S	[l/kg]	3-4	0.2-1.2
As	[µg/l]	4.0-7.6	< LOQ
Pb		< LOQ	< LOQ
Cd		0.5 - 1.2	0.5 - 1.3
Cu		2.6 - 4.9	4.7 - 15.9
Ni		20.1 - 29.2	12.9 - 16.2
Zn		145 - 303	71 - 146

The differences of the pollutant contents determined in the eluates of the three parallel columns are probably due to difficulties in operating the water impoundment columns. Due to the very low permeability of the layerwise compacted unripened dredged material and the undisturbed ripened samples, the duration of impoundment and the eluate discharge varied a lot between the individual columns, resulting in different contact times of water and sample. The eluate quantities obtained from the parallel columns differed significantly from each other either, so that the L/S ratios achieved in the tests differed markedly between the columns and between the test runs with the ripened and the unripened dredged materials. From this, it was concluded that the water impoundment column method is not suitable for the investigation of materials with very low hydraulic conductivities such as the ripened dredged material. Therefore, the results are of very limited informative value and will not be discussed further in the following.

7.1.1.2 EPA-PAH

The results of the EPA-PAH determination in the eluates from **the 2:1 batch-extraction** according to DIN 19529 are compiled in Table 7.6.

Table 7.6 Results of the 2:1 batch-extraction: EPA-PAH.

	METHA 3		**METHA 4**		**METHA 5**	
L/S	**5**		**6**		**10**	
	[µg/l]	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**	**[µg/l]**	**[mg/kg DW]**
Naphthalene	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Acenaphthylene	< LOQ	< LOQ	< LOQ	< LOQ	0.001	0.008
Acenaphthene	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Fluorene	0.001	0.004	< LOQ	< LOQ	0.003	0.01
Phentanthrene	0.001	0.01	0.001	0.005	0.004	0.037
Anthracene	0.001	0.004	0.001	0.003	0.001	0.01
Fluoranthene	0.004	0.018	0.005	0.029	0.006	0.056
Pyrene	0.006	0.026	0.007	0.038	0.008	0.079
Benzo[a]anthracene	0.001	0.006	0.001	0.007	0.002	0.021
Chrysene	0.001	0.005	0.001	0.004	0.002	0.018
Benzo[b]fluoranthene	0.002	0.008	0.001	0.004	0.002	0.018
Benzo[k]fluoranthene	0.002	0.012	0.001	0.005	0.002	0.021
Benzo[a]pyrene	0.002	0.007	< LOQ	< LOQ	0.002	0.018
Indeno[1,2,3-cd]pyrene	0.001	0.007	< LOQ	< LOQ	0.002	0.017
Dibenzo[a,h]anthracene	0.001	0.006	< LOQ	< LOQ	0.001	0.015
Benzo[ghi]perylene	0.001	0.007	< LOQ	< LOQ	0.001	0.014
Σ EPA PAH without NAP	0.03	0.12	0.02	0.1	0.04	0.34

The PAH contents determined in the eluates ranged from 0.02 up to 0.04 µg/l corresponding to 0.1-0.34 mg/kg DW. In relation to the total PAH contents of the materials a release of 3.7 % (METHA 3), 2.1 % (METHA 4) and 4.2 % (METHA 5) was determined.

The statistical evaluation of the results of the batch test showed no significant correlations between the total PAH contents and the PAH release, nor between the PAH release and soil properties ($p < 0.05$).

The results of the EPA-PAH determination in the eluates from **the 10:1 batch test** are shown in Table 7.7. In addition to the EPA-PAH, the EPA-PAH values without NAP are also listed in the table, as they are to be used for evaluation based on the threshold values of the soil protection ordinance (BBodSchV).

Table 7.7 Results of the 10:1 batch extraction: EPA-PAH.

Sample	EPA-PAH [µg/l]	 [mg/kg DW]	Σ EPA-PAH without NAP [µg/l]
METHA 2u	0.24	0.008	0.14
METHA 3u	0.18	0.007	0.18
METHA 5u	0.26	0.011	0.25
METHA 8u	0.34	0.014	0.37
DF 1u	0.33	0.013	0.33

As shown in Table 7.7, the EPA-PAH contents determined in the eluates of the unripened materials ranged from 0.18 µg/l (METHA 3u) to 0.34 µg/l (METHA 8u) corresponding to a EPA-PAH leaching of 0.008-0.014 mg/kg DW. In relation to the total PAH contents of the dredged materials, on average 0.13 % were released from the dredged materials in the 10:1 batch-test. The highest percentage release was determined for sample METHA 3u with 0.21 %.

The results from the **percolation column extraction** are compiled in Table 7.8. The highest PAH content in the eluates from the unripened material was determined with 0.12 µg/l for sample METHA 2u. The maximum PAH content of the eluates of the ripened materials was determined with 0.35 µg/l for sample METHA 5r.

Table 7.8 Results percolation column tests: EPA-PAH. u=unripened, r=ripened.

Sample	L/S [l/kg]	Σ EPA-PAH [µg/l]	Σ EPA-PAH without NAP [µg/l]
METHA 2u	4	0.12	0.11
METHA 3u	3	0.05	0.05
METHA 5u	4	0.08	0.08
METHA 8u	4	0.05	0.04
DF 1u	4	0.08	0.07
METHA 2r	4	0.05	0.04
METHA 3r	5	0.04	0.04
METHA 5r	2	0.35	0.21
METHA 8r	2	0.25	0.18
DF 1r	2	0.07	0.06

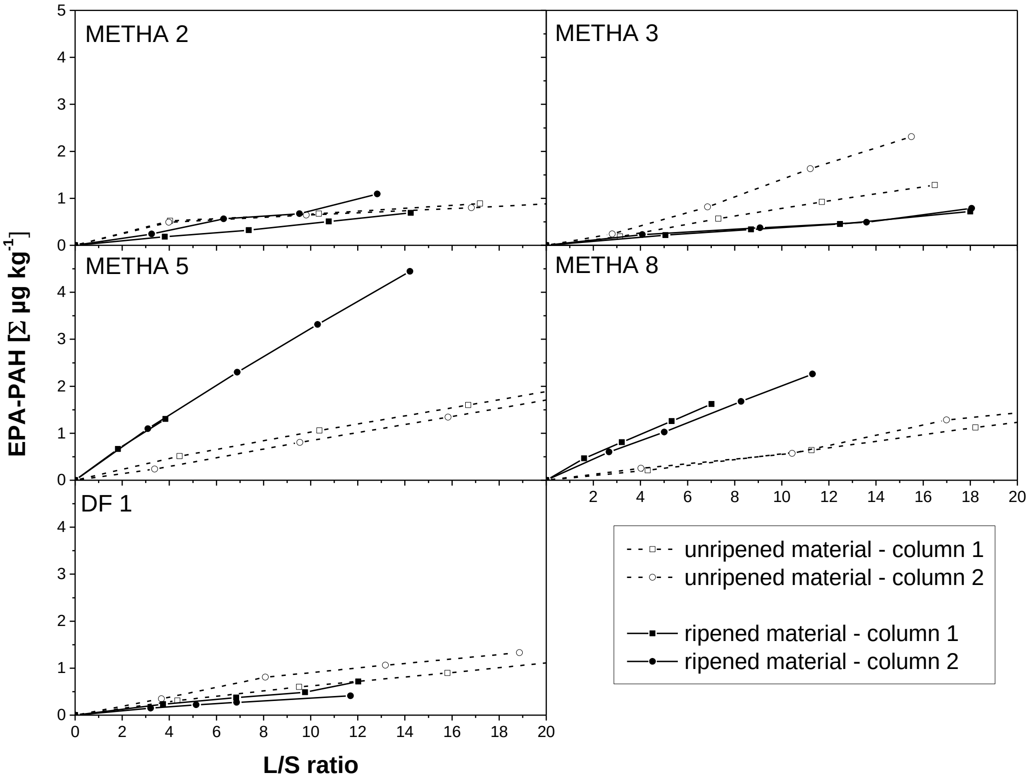

Figure 7.6 Cumulative EPA-PAH leaching in the percolation column tests.

The **EPA-PAH** leaching from the samples was relatively constant over the course of the percolation experiment but as shown in Figure 7.6, leaching from the different samples varied at different levels. The parallel columns were usually found to have a high degree of similarity, as shown by the almost congruent curves for example with METHA 3 (ripened material) or METHA 2 (unripened material). However, in some cases the leaching from the parallels examined differed markedly (sample METHA 3 unripened).

Ripening led to an increased leaching from two materials (METHA 5 and METHA 8). With two other materials leaching remained more or less constant (METHA 2 and DF 1), while a decrease in leaching was determined for METHA 3. The highest cumulative EPA-PAH elution from the unripened material was determined with 1.48 µg/kg for sample METHA 5u. The leached amount from the ripened material of this sample (4.45 µg/kg) also exceeded the leaching from the other samples. In relation to the total PAH content of this sample, 0.02 % were released from the unripened material. The leaching from the ripened material accounted for 0.05 % of the total EPA-PAH content.

The results of the multiple regression analysis showed no significant correlations ($p > 0.05$) between PAH leaching in the column extraction and the soil properties but the results indicate that the clay content is the most important predictor for PAH leaching from the unripened dredged materials (ß=0.784). For the ripened materials, the highest standardized regression coefficient was determined for the parameter TOC with ß=0.584. No statistically significant relationship ($p < 0.05$) could be determined between the results from the percolation test with the unripened and ripened material and the total PAH contents. The correlation coefficients were low to very low with r=0.592 and r=0.216.

The statistical evaluation of the results from the percolation column extraction with unripened and ripened material revealed that the leaching behavior of EPA-PAH overall was not significantly altered by ripening. The EPA-PAH contents released from the ripened material did not differ significantly from the EPA-PAH contents released from the unripened material (t test: $p > 0.05$). However, the release of EPA-PAH from two (METHA 5, METHA 8) of the five investigated samples increased markedly due to ripening. Because of the small number of parallels (n=2) investigated, the increase in leaching caused by ripening could not be statistically verified.

7.1.2 Potential maximum leaching

For the investigations on the potential maximum leaching of pollutants from the dredged materials, two different approaches were applied. The first step was to determine the trace metal and EPA-PAH contents of differently available or mobilizable fractions by means of sequential extractions. The further investigations followed a so-called worst-case approach. These investigations were carried out to assess the potential maximum release of contaminants from the processed dredged materials under most unfavorable conditions.

7.1.2.1 Sequential extractions

To differentiate between operationally defined binding forms of As, Cd, Pb and Zn in the recently produced (unripened) processed dredged material, sequential extractions were carried out. In order to investigate if naturally occurring processes such as ripening and mineralization of the organic substance cause a change in the speciation and therefore the mobility and hazardous potential of these metals, sequential extractions were also conducted with ripened and incubated materials. The ripened materials originated from the large-scale shrink experiments, the incubated samples were obtained from the incubation experiments conducted to examine the effect of the mineralization of OS on the pollutant leaching.

In the following, the results of the sequential extractions are presented.

The percentage of the trace metals amounts (mean of 3 parallels) determined in the individual fractions of the sequential extraction in relation to the total extracted amounts are compiled in Table 7.9. In Figure 7.7 and Figure 7.8 the percentage share (mean of three parallels) of the fractions from the sequential extraction of the trace metals in relation to the sum of the total extracted amounts are presented.

Table 7.9 Percentage of the trace metals amounts (mean of 3 replicates) determined in the fractions of the sequential extraction in relation to the total extracted amounts.

	Sample	Ammonium nitrate- fraction (F1) [%]	Acetic acid-fraction (F2) [%]	Hydroxylamine hydrochloride-fraction (F3) [%]	Ammonium acetate-fraction (F4) [%]	Aqua regia-fraction (F5) [%]
As	METHA 2u	0.23	2.55	71.21	8.24	17.76
	METHA 3u	0.18	3.24	73.23	9.05	14.3
	METHA 5u	0.15	2.69	68.94	9.7	18.51
	METHA 8u	0.2	2.91	71.21	9.63	16.05
	DF 1u	0.1	1.73	75.69	7.81	14.68
	METHA 2r	0.1	1.01	73.98	7.85	17.06
	METHA 3r	0.15	1.08	76.25	6.46	16.07
	METHA 5r	0.2	1.64	78.55	5.97	13.64
	METHA 8r	0.02	1.01	78.85	4.13	15.99
	DF 1r	0.07	1.04	78.94	3.52	16.43
	METHA 2i	0.06	2	54.79	15.28	27.87
	METHA 3i	0.05	1.95	68.79	10.27	18.94
	METHA 5i	0.11	2.02	38.41	22.64	36.82
	METHA 8i	0.07	3.54	49.18	19.16	28.06
	DF 1i	0	2.43	68.03	11.41	18.17
Cd	METHA 2u	1.26	13.14	81.78	3.42	0.41
	METHA 3u	1.35	28.03	65.68	4.62	0.32
	METHA 5u	0.93	13.36	84.05	1.35	0.31
	METHA 8u	1	16.32	80.37	2	0.31
	DF 1u	0.89	27.63	69.29	1.57	0.62
	METHA 2r	0.28	11.48	85.65	2.44	0.15
	METHA 3r	0.27	21.78	75.7	2.04	0.22
	METHA 5r	0.51	11.97	84.97	2.48	0.07
	METHA 8r	0.79	18.88	77.82	2.14	0.37
	DF 1r	0.28	18.22	79.05	2.08	0.37
	METHA 2i	0.73	14.31	77.61	6.98	0.36
	METHA 3i	1.38	30.24	64.13	3.98	0.28
	METHA 5i	0.17	12.3	79.66	7.61	0.27
	METHA 8i	0.44	18.24	71.8	9.23	0.29
	DF 1i	1.32	29.94	64.51	3.86	0.37

Continuation Table 7.9

	Sample	Ammonium nitrate- fraction (F1) [%]	Acetic acid-fraction (F2) [%]	Hydroxylamine hydrochloride-fraction (F3) [%]	Ammonium acetate-fraction (F4) [%]	Aqua regia-fraction (F5) [%]
Pb	METHA 2u	0.08	0.01	77.4	14.58	7.96
	METHA 3u	0.12	0.04	77.75	12.38	9.71
	METHA 5u	0.11	0.13	65.96	21.7	12.1
	METHA 8u	0.1	0.09	49.86	20.58	29.37
	DF 1u	0.1	0.29	67.86	15.52	16.23
	METHA 2r	0.01	0.05	76.02	13.82	10.11
	METHA 3r	0.01	0.06	84.61	7.03	8.29
	METHA 5r	0.03	0	70.58	18.62	10.78
	METHA 8r	0	0.01	70.09	15.93	13.97
	DF 1r	0.01	0	75.72	10.57	13.75
	METHA 2i	0	0	53.76	31.14	15.26
	METHA 3i	0.01	0.08	79.65	11.32	8.96
	METHA 5i	0.04	0	40.49	39.09	20.49
	METHA 8i	0.05	0	58.51	29.58	12.5
	DF 1i	0.04	0	79.02	12	9.94
Zn	METHA 2u	0.69	14.1	68.49	8.94	7.78
	METHA 3u	0.42	31.53	54.51	7.42	6.12
	METHA 5u	0.29	12.51	70.84	9.36	7
	METHA 8u	0.34	18.5	67.56	8.01	5.6
	DF 1u	0.2	29.65	56.38	6.91	6.86
	METHA 2r	0.12	13.9	71.25	7.97	6.76
	METHA 3r	0.13	25.17	62.51	6.56	5.63
	METHA 5r	0.2	11.6	73.72	8.64	5.85
	METHA 8r	0.28	20.94	64.52	7.68	6.57
	DF 1r	0.15	19	63.58	8.42	8.86
	METHA 2i	0.23	8.78	73.35	10.07	7.57
	METHA 3i	0.26	23.78	60.87	8.18	6.91
	METHA 5i	0.16	6.78	72.41	11.96	8.69
	METHA 8i	0.21	16.84	66.3	9.5	7.16
	DF 1i	0.23	27.55	57.37	7.34	7.51

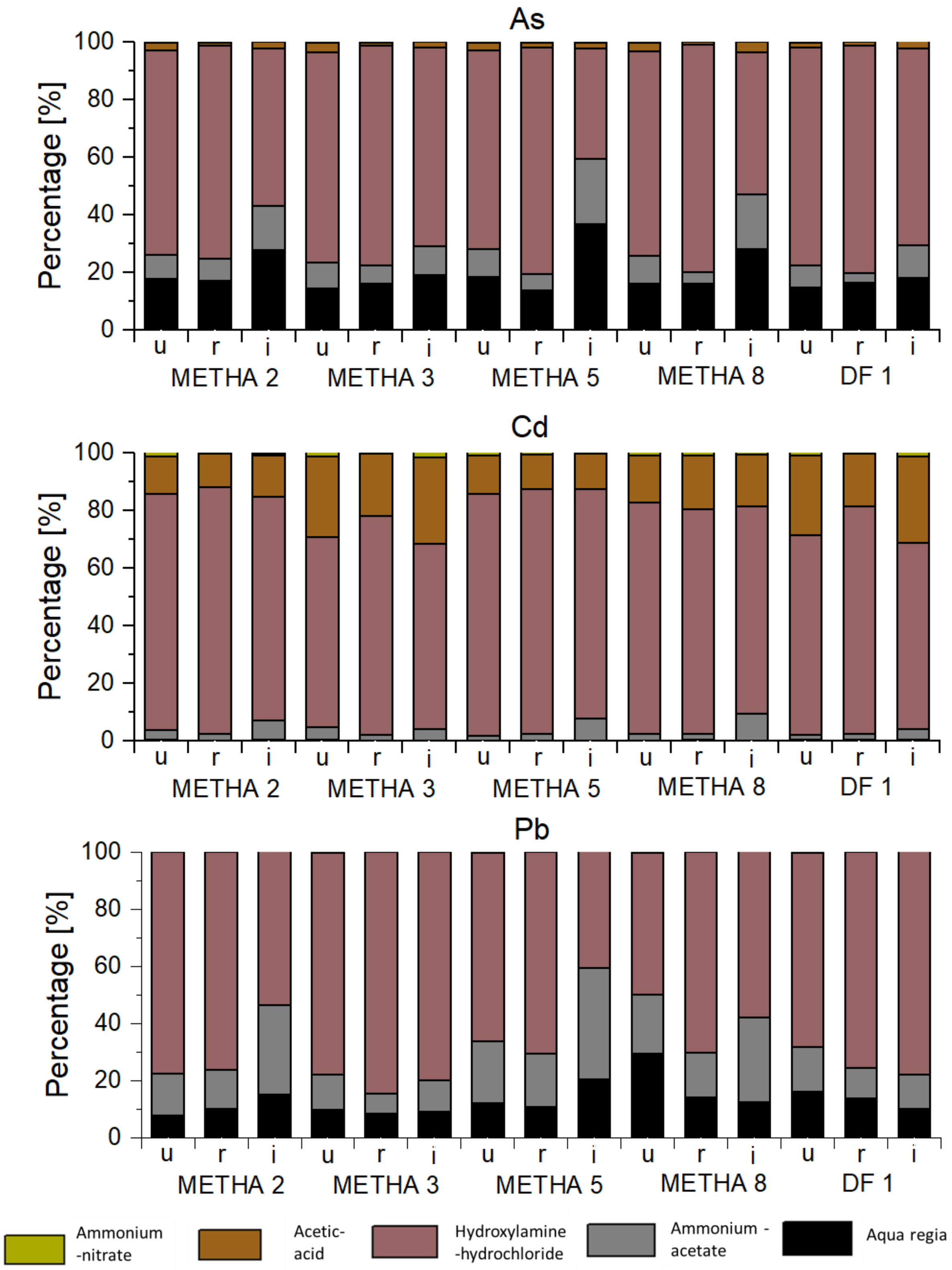

Figure 7.7 Percentage of As, Cd and Pb determined in the fractions of the sequential extractions. u=unripened, r=ripened, i=incubated.

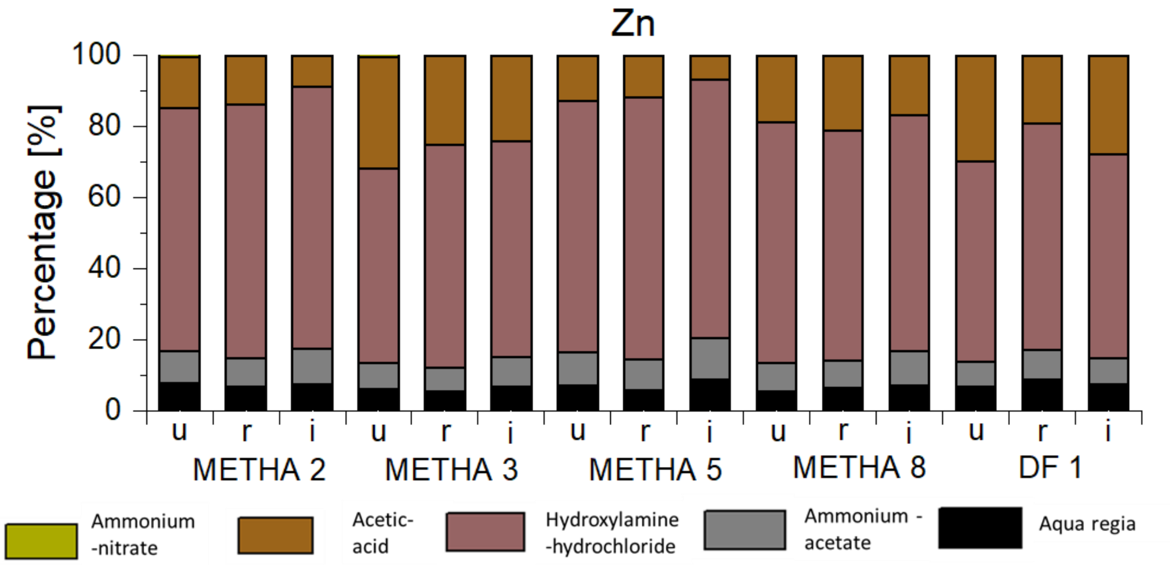

Figure 7.8 Percentage of Zn determined in the fractions of the sequential extractions. u=unripened, r=ripened, i=incubated.

With an average **As** content of 21.3 mg/kg DW, the moderately mobilizable fraction (F3) was found to be largest fraction in all samples and treatment variations. The percentage share of this fraction in relation to the total extracted As content determined as sum of the contents of all fractions was determined with an average of 72 % (compare Figure 7.7). The second largest fraction was the residual fraction (F5) with an average proportion of 16 %. The smallest fraction was the mobile fraction (F1) with a maximum As content of 0.08 mg/kg DW corresponding to a percentage of < 1 %.

Ripening showed a significant influence on the As distribution on the different fractions in all samples. The proportions of the mobile fraction (F1) of the samples METHA 2 and METHA 8 were significantly (t-test: $p < 0.05$) smaller after ripening. Furthermore, ripening led to a decrease in the As proportions of the mobile/easily mobilizable fraction (F2) of the samples METHA 2, METHA 3, METHA 5 and METHA 8. On the other hand, the proportions of the moderately mobilizable fraction (F3) were slightly increased after ripening.

The incubation may have led to a redistribution of As in the samples to a stronger binding form. The proportion of the mobile fraction (F1) decreased in comparison to the proportion of this fraction determined on the unripened materials in four of the five samples examined. The only exception was sample METHA 5i, where no significant change in the proportion of fraction F1 was observed (t-test: $p < 0.05$). The As content of two samples (METHA 3, METHA 5) determined in the mobile/easily mobilizable fraction (F2) was lower after incubation, while the proportion of this fraction increased in sample METHA 8.

With **Cd** contents between 1.44 mg/kg DW (METHA 3i) and 3.93 mg/kg DW (METHA 2r), the moderately mobilizable fraction (F3) was found to be the largest, followed by the mobile/easily mobilizable fraction (F2). The average proportions of these fractions were determined with 76 % (F3) and 20 % (F2) (compare Table 7.9). In the hardly mobilizable (F4) and mobile fraction (F1) lower Cd proportions of 3 % (F4) and 1 % (F1) where determined. The residual fraction F5, from which a release is unlikely under natural conditions, was found to be very small with an average Cd content of 0.01 mg/kg DW.

Ripening led to a significant (t-test: $p < 0.05$) decrease in the proportions of the AN-extractable fraction (F1) for all samples. With three samples (METHA 3, METHA 5, DF 1) also ripening also led to a decrease in the proportion of the mobile/easily mobilizable fraction (F2). However, a significant increase of the percentage shares of the moderately mobilizable fraction (F3) could only be observed for the samples METHA 3r and DF 1r.

Incubation led to a decrease in the percentage share of fraction F1 for three of five investigated materials (METHA 2, METHA 5, METHA 8). On sample DF 1 an increase of the proportion of this fraction was determined after incubation. The incubation did not have a significant effect on the Cd content of fraction F2 (mobile/easily mobilizable fraction). Since the proportions of the moderately mobilizable fraction (F3) were significantly reduced in three samples and the proportions of the hardly mobilizable fraction (F4) were significantly increased in all samples, there is evidence, that incubation led to a redistribution of Cd towards a stronger binding form.

The highest **Pb** concentrations were determined in the moderately mobilizable fraction (F3). In this fraction, the proportionate Pb content was determined with 68 % on average. Therefore, Pb was found to be mainly bound to oxides and hydroxides in all samples and treatment variations. In addition, the hardly mobilizable fraction (F4) also have a large proportion in the samples METHA 2, METHA 3 and METHA 8 (mean proportion: 16 %). With maximum Pb contents of 0.04 mg/kg DW (F1) and 0.08 mg/kg DW (F2), which corresponds to less than 1 % of the sum of the total extracted proportions the mobile or mobile/easily mobilizable fractions were very small. For one sample (METHA 8r) the results showed a significant ($p < 0.05$) decrease in the proportion of fraction F1.

In comparison to the other investigated elements, the effect of ripening and incubation on the distribution of trace metal contents on the different fractions was found to be least for Pb. Ripening led to a significant (t-test: $p < 0.05$) decrease in the proportion of fraction F1 only for one sample (METHA 8).

Incubation led to a decrease in the proportion of fraction F3 for sample METHA 2.

Regarding **Zn**, the moderately mobilizable fraction (F3) was dominating with Zn concentrations in the range of 205.63 mg/kg DW (METHA 3r) up to 462.99 mg/kg DW (METHA 2g) corresponding to an average percentage share of about 64 % (see Figure 7.8). The second highest Zn contents were determined in fraction F2 (21 % on average). The Zn contents of the more strongly bound fractions F4 and F5 were found to be nearly on a similar level (F4: 8 %, F5: 7%), whereas the contents of the mobile fraction (F1) were very low with an average of 1.42 mg/kg DW (< 1%).

Ripening had an effect on the proportions of the fractions F2 (decrease) and F3 (increase) of the samples METHA 3 and DF 1. Furthermore, the percentage share of fraction F1 was smaller after ripening with the samples METHA 2 (by a factor of 6), METHA 3 (factor 3) and METHA 5 (factor 2). Whether the decrease in the Zn content of this fraction is due to a redistribution into more strongly bound forms could not be statistically verified.

Incubation led to a significant (t-test: $p < 0.05$) decrease in the Zn-proportions of the mobile fraction (F1) with all samples except DF 1. For two samples (METHA 3, METHA 5) also a decrease in the proportion of the mobile/easily mobilizable fraction (F2) was determined due to incubation.

The order, the trace metals associated with different fractions in the unripened processed dredged materials followed, is summarized in Table 7.10.

Table 7.10 Ranking order of the fractions of the sequential extraction determined for the unripened material.

Element	**Ranking of fractions**
As	F1 < F2 << F4 < F5 << F3
Pb	F1 < F2 << F5 < F4 << F3
Cd	F5 < F1 < F4 << F2 << F3
Zn	F1 < F5 < F4 < F2 << F3

For the elements As and Pb, the proportions determined in the more mobile fractions (F1, F2) are very small. With regard Cd and Zn, fraction F2 is ranked second in the ranking (compare Table 7.10). Fraction F1 (mobile/ readily available fraction) is ranked fourth or fifth with significantly lower proportions. The proportions determined in the moderately mobile fraction (F3) are by far the highest for all elements and samples (As: 72 %, Pb: 68 %, Cd: 76 %, Zn: 64 %). Major proportions of As (97.2 %) and Pb (99.8 %) were bound in the moderate to heavily and non-mobilizable fractions (F5, F4, F3). For Cd and Zn, the sum of the proportions of these fractions were 79.2 % and 78.3 %. The percentage share of fraction F2 (mobile/easily mobilizable) of these trace metals was determined with 19.8 % and 21.3 % respectively.

Both, ripening and incubation did not cause a change in the ranking order of the fractions. As with the unripened materials, the trace metal and As proportions associated with the moderately mobilizable fraction (F3) were the highest in the two treatment variations (As: 98.7 %, Pb: 99.9 %, Cd: 80.6 %, Zn: 81.7 %).

In the case of As and Pb, significant changes in the percentage share of all fractions except the residual fraction (F5) were determined after ripening. Furthermore, ripening caused significant changes in the Cd proportions in all fractions except fraction F4. For Zn an effect of ripening on the proportions of the fractions F1, F2 and F3 was observed. The percentage share of fraction F3 (moderately mobilizable) of all elements increased due to ripening by an average of 3.6 % points (Zn) to 7.4 % points (Pb). The proportions of the mobile and moderately mobilizable fractions decreased (As: -1.2 %, Pb: -0.18 %, Cd: -4 %, Zn: -3.4 %). From these results it can be drawn, that an increase of the release of the trace metals Cd, Pb, Zn and As is not to be expected as a result of ripening.

The incubation led to a decrease in the proportion of fraction F3 (moderately mobilizable) by an average of 4.7 % points (Cd) to 16 % points (As) for all elements except Zn. In the case of Zn, the proportion of F3 in the incubated materials was about 2.5 % points larger than in the unripened materials. For all trace metals, an increase in the percentage share of the stronger bound fraction (F4) was determined after incubation. The share of this fraction was increased on average by 1.3 % points (Zn) to 7 % points (Pb). In the case of As, Pb and Zn, incubation also led to a decrease in the average proportions of mobile (F1) and mobile/easily mobilizable (F2) by 0.36 % points (As), 0.16 % points (Pb) and 4.73 % points (Zn). In the case of Cd, the proportion of fraction F2 increased by an average of 1.03 % points due to incubation. Overall, the influence of incubation was least for Pb. Significant changes in the percentage shares of the fractions were observed only in the mobile fraction (F1) and the hardly mobilizable fraction (F4). According to the results of the sequential extraction after incubation, no increased release of the examined trace metals by a degradation of the organic substance is to be expected, except for Cd.

Correlation analyses did not reveal significant correlations between soil properties (clay content, TOC content, pH) and the trace metal contents of the first two fractions. The As, Cd and Zn contents of fraction F3 (moderately mobilizable) correlated significantly with the TOC content of the dredged material samples ($r=0.916$, $p < 0.05$; $r=0.942$, $p < 0.05$; $r=0.925$, $p < 0.05$). For Cd and Zn, a relationship between the clay content and the contents of fraction F3 was also determined ($r=0.896$, $p < 0.05$; $r=0.970$, $p < 0.01$). Fraction F3 is known to extract trace metals associated with Fe- and Mn-oxides and hydroxides, however, the contents of Fe- and Mn- oxides or hydroxides of the samples have not been determined. The correlations may also be due to a correlation of the oxide and hydroxide contents with the clay fraction and the organic matter.

In the case of Zn, a strong significant relationship between the contents of F4 (hardly mobilizable fraction) and the clay content ($r=0.985$, $p < 0.01$). The Pb content determined in the F4-fraction was significantly correlated with the clay content ($r=0.895$, $p < 0.05$) and TOC content ($r=0.931$, $p < 0.05$). For As, a close and highly significant relationship ($r=0.985$, $p < 0.01$) between the release in fraction F4 and the TOC content of the dredged material samples could be determined. The correlation of the trace metal contents of this fraction with the content of organic matter is to be expected, as within this fraction, besides trace metals bound in sulfides, trace metals bound to the organic substance are recorded. Since the content of organic matter correlates with the clay content, a significant correlation was also determined for the relationship between the trace metal content of fraction F4 and clay content.

Correlation analyses with the trace metals released from the ripened and the incubate materials and the soil properties overall in similar relationships.

To determine if and to what extent EPA-PAH are present in the dredged material samples in water-soluble/mobile form and whether accelerated mineralization (incubation at 30°C for about 11 weeks) of the organic substance may cause a change in the amounts of potentially mobile EPA-PAH, a two-step sequential extraction scheme was applied. The extraction scheme consisted of a batch test with demineralized water (L/S=10), followed by a Soxhlet extraction with n-hexane as solvent. The results from the two-step sequential extraction of EPA-PAH determined on unripened or rather unincubated materials and incubated materials are presented in Figure 7.9.

In the sequential extraction, on average less than 1% of the EPA-PAH were extracted with water as solvent. More than 99 % of the EPA-PAH contained in the dredged materials were determined in the n-hexane fraction after Soxhlet extraction. The differences in the distribution of the EPA-PAH contents on the two fractions determined on the unincubated and incubated samples were very small. With the exception of METHA 3, no significant differences were found between the unripened materials and the incubated materials. Compared to sample METHA 3u, significantly higher amounts of PAH were extracted from sample METHA 3i in the batch-extraction with water. As with the trace metals, there are difficulties in interpreting the results of sequential extraction, as the sum of the individual fractions in part differs considerably to the total contents of EPA-PAH content determined by means of Soxhlet extraction. With three of the five samples examined, only about half as much PAH was extracted in the sum of the two fractions as the total content was determined. For sample METHA 3, the content extracted in sum of the two fractions of the sequential extraction with 10.6 mg/kg DW was higher than the total content which was determined with 7.8 mg/kg DW.

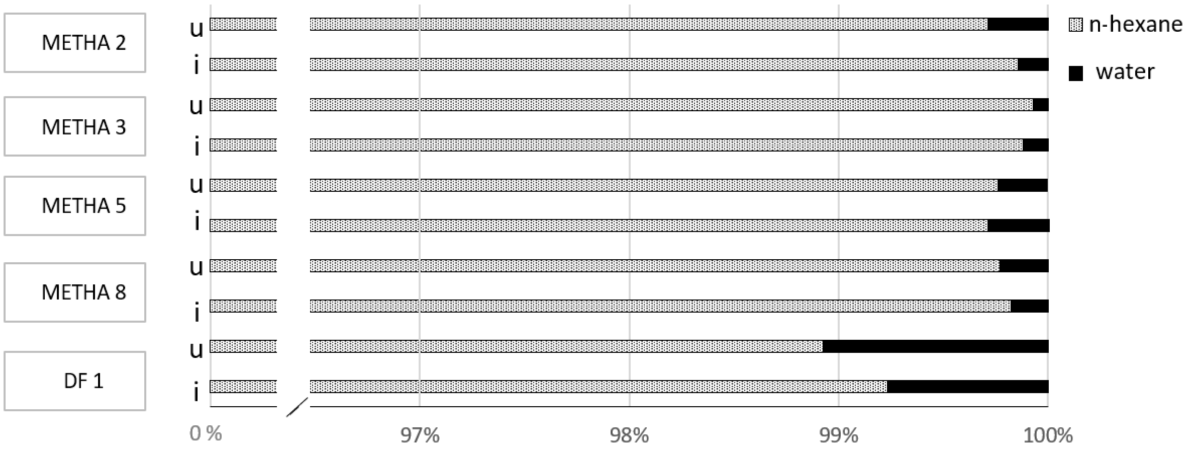

Figure 7.9 Percentage EPA-PAH proportions (mean of three replicates) determined in the fractions of the two-step sequential extraction in relation to total extracted amount [%]. u=unripened, i=incubated.

7.1.2.2 Worst-case scenarios

In the following, the results from the investigations on the potential maximum pollutant emission examined by means of worst-case scenario approaches are presented.

The following pollutant-releasing processes/ scenarios were investigated:

(i) Acidification
(ii) Mineralization of soil organic matter
(iii) Destabilization of soil organic matter
(iv) Destabilization of soil aggregates

Worst-case scenario Acidification

First step in the investigations on the effect of acidification on the leaching behavior of trace metals from the processed dredged material was the determination of the materials' acid neutralization capacity (ANC) by means of a titration test. Over a period of 124 days, the pH value of the continuously stirred samples was determined daily and gradually adjusted to the respective target pH value by adding 0.1 M HCl (target pH values: 6, 5, 4). The ANC was calculated from the amount of protons added.

In Table 7.11, the ANC of the samples at the target pH values are listed. In addition to the ANC, the pH of the samples determined before acid addition (initial pH) and at the end of the experiment (end pH) are given in the table.

Table 7.11 ANC of the samples at defined target pH values.

	Initial pH [-]	ANC [mmol kg^{-1}]			End pH [-]
Sample		**pH 6**	**pH 5**	**pH 4**	
METHA 2	6.82	1528	1755	1920	3.99
METHA 3	6.13	1095	1300	1382	4.03
METHA 5	6.55	1926	2206	2472	4.03
METHA 8	6.82	1407	1577	1667	3.98
DF 1	6.69	825	984	1069	4.03

The ANC of the dredged material samples differed markedly from one another. Sample DF 1 showed the lowest ANC. Here 1069 mmolH$^+$ kg^{-1} had to be added to reach the target pH of 4. In the case of the sample METHA 5 the target pH was reached after addition of 2472 mmol H$^+$ kg^{-1}. Since sample DF 1 showed the lowest TIC content (0.88 %, compare Table A1 in the Appendix) and sample METHA 5 the highest TIC content (1.19 %), the ANC of the samples in the investigated pH range is correlated with the TIC content of the samples.

Upon completion of the titration test, the samples were found to be still buffering as shown in pH measurements 2 weeks after the last acid addition (results not shown). Overall, the ANC of the tested dredged materials can be rated as very high.

The next step in the investigations on the effect of acidification on the leaching behavior of contaminants from the processed dredged material was the determination of the trace metal leaching in batch extractions with a pH of 5. Based on the results of the ANC, a 10:1 batch extraction was conducted with a proton addition of about 984 mmolH$^+$ kg^{-1} (DF1) – 2206 mmolH$^+$ kg^{-1} (METHA 5) to set a target pH of 5. In the first experimental approach (approach 1), the samples were immediately filtrated after shaking. In a further experimental approach (approach 2) the samples were left to rest for 2 weeks after shaking. The results of the determination of As, Cd, Ni Pb and Zn in the eluates from these extractions are compiled in Table 7.12.

Table 7.12 Results from the 10:1 batch extraction after acidification (means of three replicates). LOQ=Limit of Quantification.

	Sample	**pH**	**As [µg/l]**	**Cd [µg/l]**	**Ni [µg/l]**	**Pb [µg/l]**	**Zn [mg/l]**
approach 1	METHA 2	5.5	< LOQ	245	539	< LOQ	15.1
	METHA 3	5.8	< LOQ	107	169	< LOQ	7.1
	METHA 5	5.5	< LOQ	288	529	< LOQ	18.6
	METHA 8	5.5	< LOQ	250	350	< LOQ	14.0
	DF 1	5.8	< LOQ	82	102	< LOQ	5.1
approach 2	METHA 2	6.1	< LOQ	172	304	< LOQ	6.7
	METHA 3	6.3	< LOQ	73	140	< LOQ	3.1
	METHA 5	6.0	< LOQ	209	341	< LOQ	8.5
	METHA 8	6.1	< LOQ	211	296	< LOQ	8.0
	DF 1	6.5	< LOQ	16	56	< LOQ	1.7

The pH of the samples in the first batch test (approach 1) was determined with values between 5.5 and 5.8 (compare Table 7.12). The high buffering capacity of the samples led to the fact that the aspired target pH of 5 was not reached by the acid addition. Compared to the total trace metal content of the samples about 50 % of the Cd, 18 % of the Zn and 9 % of the Ni content could be released by lowering the pH to a value of about 5 (approach 1). After a rest period of 2 weeks (approach 2), the pH of the eluates was determined with values between 6.0 (METHA 5) and 6.5 (DF 1) due to continuous buffering and the trace metal concentrations of the eluates decreased significantly ($p < 0.05$) compared to the first approach. On average, the Cd concentrations in the eluates were 37 % points lower compared to the first approach. For Ni, the concentrations in the eluates of the second approach were found to be about 34 % points lower compared to the first approach. Regarding the Zn contents, a decrease of about 55 % was determined comparing the leaching in the first and second approach. In the second approach, smaller proportions of the investigated trace metals were leached with about 34% (Cd), 8% (Zn) and 5% (Ni) of the total content.

For comparison purposes both the leaching Cd, Ni and Zn in the two test approaches (approach 1=immediately filtrated after shaking, approach 2=left to rest for two weeks after shaking) and in the 10:1 batch-extraction conducted with the unripened material (unacidified) are presented in Figure 7.10.

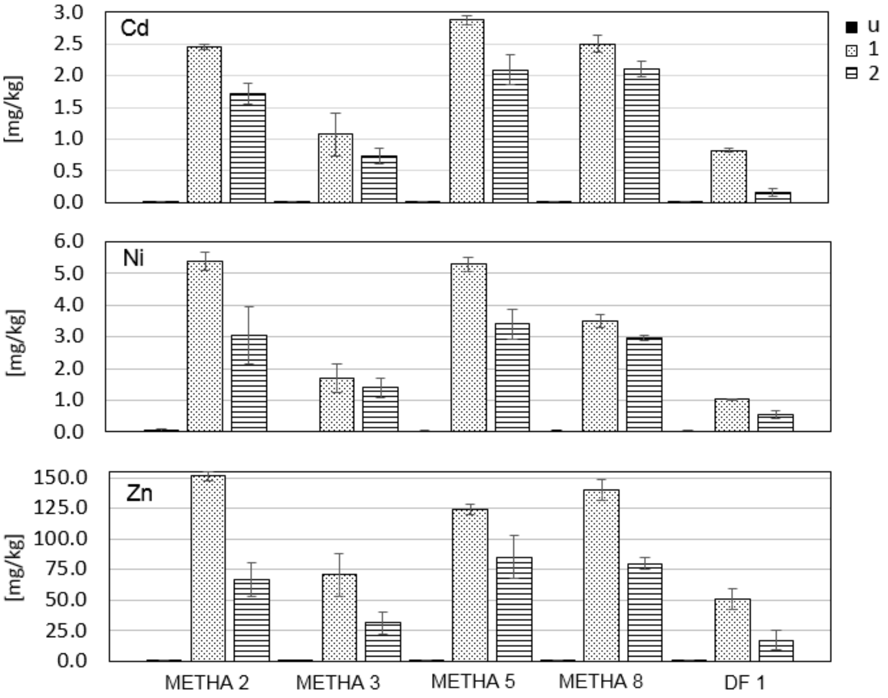

Figure 7.10 Leaching of Cd, Ni and Zn in the batch-extractions (mean of three replicates). 1=approach 1, 2= approach 2, u=unripened material (unacidified).

In percolation columns tests with strongly acidified water (pH 2.9), the change in pH and the leaching of trace metals were investigated over a period of two weeks. Finally, the L/S ratio was about 90, which means, that high amount of liquid and H^+ respectively, has percolated the samples. The pH of the leachates remained at high levels over the test period with values between 6.8 and 7.7 (results not shown).

Table 7.13 shows the trace metal contents determined in the eluates from the percolation columns test with acidified water (pH 2.9) on the first day of sampling (L/S=5).

Table 7.13 Results of the percolation column test with acidified water (mean of two replicates). LOQ=Limit of Quantification.

Sample	**L/S [l/kg]**	**As [µg/l]**	**Cd [µg/l]**	**Cu [µg/l]**	**Ni [µg/l]**	**Pb [µg/l]**	**Zn [mg/l]**
METHA 2	5	< LOQ	0.62	1.59	5.77	< LOQ	0.07

The trace metal concentrations determined in the eluates were overall low. In the case of As and Pb, the eluate content was below the LOQ of 4 µg/l (As) and 8 µg/l (Pb). The Cd concentration was determined with 0.62 µg/l (see Table 7.13). This corresponds to a release of 0.07 %

of the total Cd content. Cu was determined with a content of 1.59 µg/l in the eluate, which corresponds to a release of 0.01 % of the total content. The Ni content of 5.77 µg/l leached in the percolation test with acidified water amounted for 0.07 % of the total content. The Zn concentration in the eluate was 0.07 mg/l and corresponded to a release of 0.05 % of the total Zn content. After the first initial release, no trace metal contents above the respective LOQ (Cd: 0.25 µg/l, Cu: 1.25 µg/l, Ni: 3 µg/l, Zn: 0.05 mg/l) were detected in the eluates in the further course of the test (up to L/S 90).

To compare the results of the trace metal leaching in the percolation column test with acidified water with the leaching in the test with non-acidified water. The leaching (mg/kg DW) determined in both tests are compiled in Table 7.14.

Table 7.14 Comparison of the leaching determined in percolation column tests with and without acidified water as eluent.

	L/S	**As**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
	[l/kg]	**[mg/ kg DW]**	**[mg/ kg DW]**	**[mg/ kg DW]**	**[mg/ kg DW]**	**[mg/ kg DW]**	**[mg/ kg DW]**
not acidified	4	< LOQ	0,004	0,093	0,03	< LOQ	0,523
acidified	5	< LOQ	0,002	0,009	0,023	< LOQ	0,25

The comparison shows that percolation with acidified water did not lead to an increased release of arsenic or trace metals from the sample investigated (METHA 2).

The results of the pH determination of the different layers of the column material after completion are compiled in Table 7.15. The initial pH of the material (METHA 2) in column 1 was 7.9. For column 2, the initial pH was determined with 7.6 (compare Table 7.15). In column 1, the percolation with acidified water (pH 2.9) only led to a significant decrease of the pH in the lower 3 cm (3.9, 0-1.5 cm and 6.9, 1.5-3 cm). In column 2, an effect of acidification was observed up to a height of 6 cm. The pH of the material was determined with 4.1 (0-1.5 cm), 4.3 (1.5-3 cm), 5.8 (3-4.5 cm) and 6 (4.5-6 cm).

Table 7.15 pH, Cd and Ni content of the column material sampled from different column heights.

Column height	pH [-]		Cd [mg/kg DW]		Ni [mg/kg DW]	
	column 1	column 2	column 1	column 2	column 1	column 2
29.5-30 cm	7.9	7.6	3.8	4	34.1	36.6
22-23.5 cm	7.9	7.6	4.3	4.5	41.2	41.4
15-17.5 cm	7.8	7.6	4.8	4.5	42.8	43.1
9-10.5 cm	7.8	7.6	4.8	4.6	43.1	45.3
4.5-6 cm	7.8	6	4.8	6.7	45.7	60.4
3-4.5 cm	7.8	5.8	5.4	6.4	51.8	51.5
1.5-3 cm	6.9	4.3	8.5	2.6	64.6	39
0-1.5 cm	3.9	4.1	1.3	0.9	31	26.7

The determination of the trace metal contents of the material of different layers showed a remarkable relocation of Cd, Cu, Ni, Zn and Pb from the bottom layer (0-1.5 cm) into the overlying layer (1.5-3 cm) of column 1. In column 2, where the acidification effect was noticeable up to a height of 6 cm (from the bottom), Cd, Cu and Zn were relocated from the bottom layer (0-3 cm) to the overlying layers (3-4.5 cm and 4.5-6 cm). Pb was relocated from the bottom layer to a column height of about 4.5 cm, As to a height of about 3 cm.

The results show that the lowering of the pH value leads to a mobilization of trace metal amounts from the processed dredged material sample (METHA 2), but also that these amounts are mainly re-sorbed to the soil matrix in areas where acidification is less advanced due to buffering or where acidification has not yet taken place. The leaching of trace metals accordingly amounted to only 0.01 to 0.07 % of the total element contents.

Worst-case scenario Mineralization of the organic substance

To investigate the potential impact of the release of adsorbed or organically bound pollutants (trace metals and EPA-PAH) by **mineralization of organic matter**, the changes in the available pollutant fractions after accelerated mineralization of the organic substance (incubation at 30°C for about 11 weeks) were determined in sequential extractions and the pollutant leaching from incubated materials was examined by means of batch-extractions.

The percentage degradation rates of the organic substance in the 11-week incubation test calculated on the basis of dry weights and TOC contents of the samples at the beginning of incubation are compiled in Table 7.16.

Table 7.16 Percentage degradation rates of organic carbon in the incubation experiment (mean of two replicates).

Sample	Degradation calculated based on CO_2-release [% DW]	Degradation calculated based on CO_2-release [% TOC]	Degradation calculated based on C-determination [% TOC]
METHA 2i	0.41	11.2	5.2
METHA 3i	0.31	12.2	5.4
METHA 5i	0.45	12.7	7.9
METHA 8i	0.39	9.8	10.9
DF 1i	0.31	12.8	5.2

After an incubation period of about 80 days, the loss of C (in relation to % DW) calculated from the CO_2 release of the samples ranged from 0.31 % DW (METHA 3 and DF 1) to 0.45 % DW (METHA 5). The degradation rates calculated from the CO_2-release in the incubation test conducted for the quantification of microbial carbon degradation ranged from 9.8 % TOC to 12.7 % TOC. The degradation rates determined on the basis of the determination of the total carbon content of the material from the experimental approach for material production deviate in some cases significantly from this with values between 5.2 % TOC and 10.9 % TOC. The deviations are probably due to different test conditions for the incubation approaches. Due to the larger amount of material in the incubation vessels during the experimental preparation for material extraction, the material clumping occurred during the course of the experiment, so that the decomposition conditions (O_2-availability) were probably less favorable than in the experimental preparation, which was used exclusively for determining the degradation rates. Overall, the determined decomposition rates are expected to be at a level for Hamburg dredged material (cf. Gröngröft and Eschenbach, 2015).

The results of the batch tests conducted to investigate the contaminant release potential after accelerated degradation of the organic substance are shown in Table 7.17.

Table 7.17 Trace metal and EPA-PAH contents (mean of three replicates) in the eluates of the 10:1 batch-extraction conducted with incubated materials. i=incubated, LOQ=limit of quantification.

Sample	As	Cd	Cu	Ni	Pb	Zn	Σ EPA PAH	Σ EPA-PAH without NAP
	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[mg/l]	[µg/l]	[µg/l]
METHA 2i	10.9	0.98	58.6	8.5	< LOQ	0.08	0.17	0.14
METHA 3i	6.6	0.67	59.5	< LOQ	< LOQ	0.05	0.30	0.29
METHA 5i	14.3	0.69	53.9	9	< LOQ	0.07	0.27	0.24
METHA 8i	14	1	61.7	9.5	< LOQ	0.08	0.26	0.22
DF 1i	7.4	1.07	38.1	6.7	< LOQ	0.07	0.56	0.53

The As release from the incubated materials corresponded to 0.2 % - 0.56 % of the total As content of the samples. The average percentage Cd release from the incubated material was determined with 0.24 %. The Cu contents of the eluates ranged from 38.1 µg/l (DF 1) up to 61.7 µg/l, corresponding to an average release of 0.35 % of the total content. Ni was eluted from the incubated materials with an average of 0.18 % of the total content. Pb could not be determined in any of the eluates in a concentration above the LOQ (8 µg/l). Zn contents of 0.05 mg/l (METHA 3) to 0.08 mg/l (METHA 8) were determined. In relation to the total Zn content of the samples on average 0.12 % were released from dredged materials after incubation. In the eluates of the incubated samples, EPA-PAH contents of 0.17 µg/l (METHA 2) to 0.56 µg/l (DF 1) were determined. Based on the total EPA-PAH contents of the samples, about 0.19 % were eluted in the 10:1 batch-extraction from the incubated materials on average.

To evaluate the results of the investigations on the influence of the degradation of the organic substance on the release of trace metals and As, the trace metal amounts released from the unripened material and the incubated material in the 10:1 batch-extraction are compared in Figure 7.11.

In comparison with the results from the batch tests with the unincubated materials, the release rate increased from 0.12 % to 0.33 % (factor 2.75) of the total content for As, from 0.15 % to 0.24 % (factor 1.60) for Cd and from 0.18 % to 0.35 % (factor 1.94) for Cu. The statistical evaluation (Wilcoxon signed-rank tests) showed that the release of As, Ni and Zn was significantly increased after incubation ($p < 0.05$). In the case of Cd and Cu, the observed increase could not be statistically verified ($p < 0.05$). With regard to the incubated material, the clay content appears to have a stronger influence on the elution behavior of Ni, Zn and Pb in the batch-test, whereas with As, Cd and Cu the TOC content can be regarded as a stronger predictor. However, the values could not be statistically verified ($p < 0.05$).

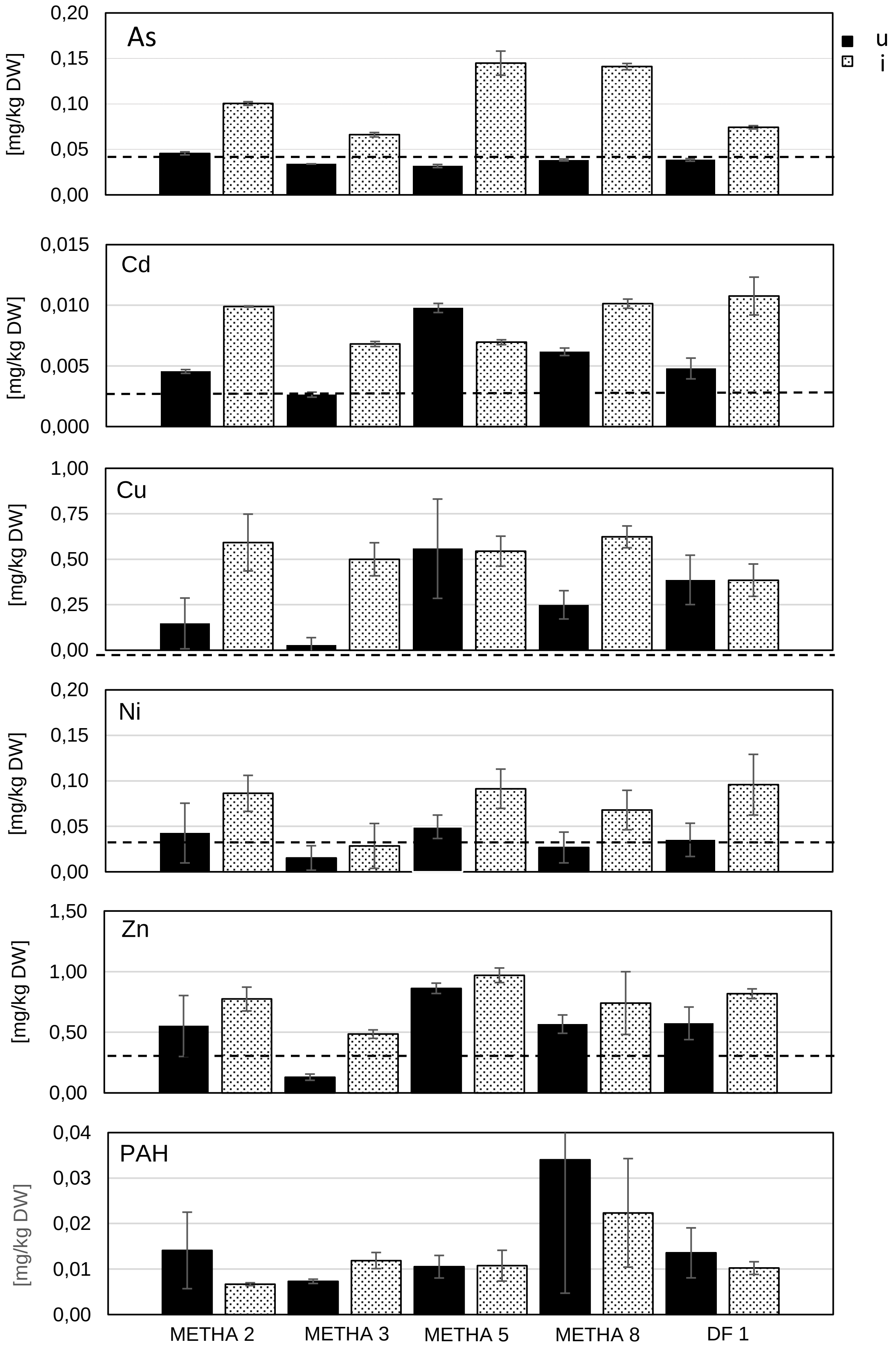

Figure 7.11 Comparison of trace metal and PAH contents leached from the unripened material (u) and the incubated material (i) in the 10:1 batch-extractions. Line: limit of quantification.

Worst-case scenario Destabilization of the spatial structure of organic substance

The influence of the **destabilization of the organic substance** on the contaminant release from the dredged material was investigated by the use of competing complexing agents. The extraction was conducted in accordance with Eschenbach et al. (1998) with a 0.05 M Na_2-EDTA solution and a L/S ratio of 6:1. The results of the determination of trace metal and EPA-PAH contents in the EDTA extracts are summarized in Table 7.18.

Table 7.18 Trace metal and EPA-PAH contents (mean of three replicates) determined in the EDTA extracts.

Sample	As [µg/l]	Cd [µg/l]	Pb [µg/l]	Zn [mg/l]	Σ EPA PAH [µg/l]	Σ EPA-PAH without NAP [µg/l]
METHA 2	84.6	377	4421	22.4	1.556	1.505
METHA 3	63.7	227	3532	15.8	2.538	2.478
METHA 5	59.7	315	2976	21.3	1.476	1.424
METHA 8	55.6	378	7161	24.4	2.703	2.661
DF1	149.8	274	3396	20.4	3.079	3.020

In order to classify the results, the **trace metal** amounts released by EDTA extraction were compared with the releases determined in the 10:1 batch-extraction with the unripened materials. By means of Wilcoxon signed-rank test it was shown that the extraction with 0.05 M EDTA solution led to a significant ($p < 0.05$) increase in the release of trace metals and As from both the METHA samples and the dewatering field sample. On average, the release of Cd and Zn was 390 and 200 times higher than in the 10:1 batch-extraction with water as solvent. In relation to the total trace metal and As contents, the proportions released by EDTA treatment amounted for 2 % (As), 20 % (Zn), 30 % (Pb) and 55 % (Cd) on average.

Comparison of **EPA-PAH** releases in the batch-extraction with and without EDTA treatment showed that the addition of the complexing agent (0.05 M EDTA) also for PAH results in a significant increase of all samples ($p < 0.05$). Based on the total PAH contents of the samples, an average from 0.22 % (METHA 5) up to 2.45 % (METHA 3) were released due to the EDTA treatment.

Correlation analyses of the relationship between trace metal release after EDTA treatment and soil properties showed a strong correlation between the released Cd proportions and the parameters TOC content ($r=0.937$, $p < 0.05$) and clay content ($r=0.884$, $p < 0.05$) and between the released Zn proportions and TOC content ($r=0.913$, $p < 0.05$).

The examination of the relationship between the trace metal proportions determined in the individual fractions of the sequential extraction and the contents released after EDTA treatment showed, as expected, a strong highly significant relationship to the sum of the contents of the first four fractions for Cd ($r = 0.995$, $p < 0.01$) and Zn ($r = 0.956$, $p < 0.01$). According to the operationally defined assignment of the fractions to the binding forms of the trace metals in the soil, the fourth fraction consists of trace metal fractions which are bound to the organic substance and thus also to clay-organic complexes. These complexes are destabilized by the EDTA treatment. In addition, this highly invasive treatment also mobilized trace metal components associated with the first three fractions.

Worst-case scenario Destabilization of soil aggregates

To examine the importance of the effect of the **destabilization of aggregates** on the leaching behavior of contaminants, investigations were carried out in which the aggregate structure of the samples was mechanically destroyed by ultrasonic treatment. Subsequently, the release of trace metals and EPA-PAH was determined in batch extractions (L/S=10). The results are shown in Table 7.19.

Table 7.19 Trace metal and EPA-PAH contents (mean of three replicates) determined in the eluates after ultrasound treatment.

Sample	As [µg/l]	Cd [µg/l]	Cu [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [mg/l]	Σ EPA PAH [µg/l]	Σ EPA-PAH without NAP [µg/l]
METHA 2	< LOQ	1.66	16.5	19.0	< LOQ	0.25	0.219	0.217
METHA 3	< LOQ	0.42	5.1	3.3	< LOQ	0.04	0.436	0.433
METHA 5	< LOQ	1.31	28.2	13.5	< LOQ	0.17	0.287	0.281
METHA 8	< LOQ	0.94	17.3	6.7	< LOQ	0.12	0.378	0.372
DF1	< LOQ	0.52	12.2	3.4	< LOQ	0.06	0.239	0.234

The comparison of trace metal release with and without ultrasound treatment by means of Wilcoxon signed-rank tests revealed that statistically significant higher amounts of Cd were leached after ultrasonic treatment. Ni and Zn were also released from all samples in significantly higher quantities ($p < 0.05$) after ultrasonic treatment. Cu revealed a mixed picture. For two samples (METHA 2 and METHA 3) higher Cu amounts were found in the eluates after ultrasonic treatment, for three samples the opposite was true. Based on the total content of the samples the trace metal release after ultrasonic treatment ranged between 0.1 % (Cu) up to 0.3 % (Cd).

For the EPA-PAH, the comparison of the release in the batch-extraction with and without ultrasonic treatment indicated that the mechanical destabilization has no influence. Although the averaged EPA-PAH release from sample METHA 3 was slightly higher after ultrasonic treatment, the results of the other samples showed a reverse picture. Overall, no significant effect of ultrasound treatment on the release of EPA-PAH from the samples could be determined ($p > 0.05$). Simple Regression analyses on the correlation between soil properties and trace metal release after ultrasonic treatment showed significant correlations between released amounts of Cd and Zn and clay content ($r=0.912$, $p < 0.05$; $r=0.889$, $p < 0.05$).

The correlation analyses on the relationship between soil properties and EPA-PAH release after ultrasonic treatment did not reveal any significant correlations.

7.2 Discussion

In the first two sections of the discussion on the leaching behavior of contaminants from processed dredged material from the Hamburg harbor, the results from the various leaching experiments are discussed with regard to literature available on the topic of contaminant leaching from sediments and dredged material and with regard to processes influencing the release of contaminants.

In the third section, the results are evaluated on the basis of legislative standards that are to be used to prove the harmlessness of the utilization of processed dredged material in dike construction. Furthermore, the results of these leaching experiments were compared to the results from the 11-year leachate monitoring (Gröngröft et al., 2016) conducted at the test field where a part of the dike cover layer consists of METHA material and the transferability of the laboratory results on in-situ conditions in dikes was evaluated in this section.

7.2.1 Leaching from fresh and ripened materials

7.2.1.1 Trace metals and As

Compared to the other groups of dredged material (DF, OD, DC) the fresh METHA material showed the highest proportion of readily soluble trace metals in the AN-extraction. In relation to the total contents, the highest leached proportions were determined for Cd followed by Cu > Ni > Zn > As and Pb. In their investigations on the mobility of trace metals in dredged material from the area of Bremen, Lager et al. (2005) also determined a comparatively high Cu and Cd leaching in the ammonium nitrate extraction. They attributed the increased solubility of Cu, which generally is considered to be less mobile in soils, to the formation of tetra-amino-complexes with Cu ($[Cu(NH_3)_4]^{2+}$.

One sample of the fine-grained aged marsh sediments revealed readily available trace metal proportions that were many orders of magnitudes higher than those of the dredged materials. As unspecifically adsorbed trace metal amounts are released during AN-Extraction and sorption and desorption processes in soils and sediments are strongly driven by pH, the high mobile trace metal content of this sample is most probably due to its acidic pH of 3.8. The dependency of AN-extractable proportions and pH was also affirmed by the results of the statistical examinations conducted with the data. The importance of pH on metal solubility is well recognized but difficult to segregate from the influence of other soil characteristics that are often auto-correlated (Sauvé, 2000). By means of multiple regression analyses, a significant relationship between AN-extractable trace metal content and specific soil properties (clay, TOC, pH) could be determined for Cd and Ni. As expected, the parameters clay and pH were significantly correlated with extractable amounts of Cd, i.e. the higher the clay content and the lower the pH, the higher the AN-extractable Cd content. However, all of these soil properties were shown to be auto-correlated as well. For Ni, the multiple regression analysis showed a significant relationship between plant available content and the parameters pH and clay content, whereby the influence of pH, unlike for Cd, was shown to be more important than that of clay content with a standardized correlation coefficient. However, contrary to expectations, there was a positive correlation between pH and ammonium nitrate-soluble trace metal content.

Overall, the trace metal amounts leached from the unripened material in the **batch** extraction according to DIN 19529 were low with < 1 % of the total contents. Trace metal shares leached in the 10:1 batch extraction were in the same range. Therefore, the results of the batch extractions are in a good agreement with the results obtained by means of sequential extractions. The sequential extractions revealed that for Cd, Zn and Pb as well as for As, the proportions associated with the mobile/easily mobilizable fraction are below or equal 1 % of the total content of the dredged materials.

In relation to the total trace metal contents, the highest trace metal proportions leached in the batch extraction according to DIN 19529 were determined for Zn followed by Ni > Cd > As > Cu > Pb. In the 10:1 batch extraction, the order was Cd > Zn >Ni >Cu > As. The comparatively high mobility of Cd and Zn is well known from the literature (Beesley et al., 2010; Vamerali et al., 2009). Compared to As and Pb, higher proportions of these metals are, as shown in the sequential extraction, associated with the mobile/easily mobilizable fraction and therefore considered to be unspecifically adsorbed. This kind of binding is considered to be relatively weak. Pb and Cu are generally less mobile in soils (Tack et al., 1999). In contrast to Cd, Ni and Zn, these two trace metals have a greater tendency to form hydroxocomplexes. These complexes are preferably sorbed, thus also the tendency to a stronger specific adsorption, for example on oxides, increases for these metals (Savric, 2001).

The results from the **percolation column** tests conducted with the unripened i.e. unripened material revealed marked differences in the leaching behavior of the different trace metals investigated. For Cd, Ni and Zn a strong initial leaching (up to L/S o about 3-4) followed by a decrease in the leached amounts was observed whereas the leaching rate of As and Cu from the majority of samples appears to be constant over the course of the percolation column tests. The phenomenon of a strong initial release of Cd and Zn was also reported by Beesley et al (2011), who investigated the leaching behavior of As, Cd and Zn from a multi-element contaminated soil sourced from a canal embankment in Kidsgrove, UK, on which dredged sediments had been dumped without any treatment at an unknown period of time. The authors ascribed the strong initial leaching of Cd and Zn to the relatively high water-soluble/readily exchangeable fractions of these trace metals. Compared to the results of Beesley et al. (2010), where water soluble percentage shares of up to 8 % and 7 % of the total contents of Cd and Zn were determined, a much lower mobility of these trace metals were found in our investigation (on average 0.19 % Cd and 0.18 % Zn). However, the results are not directly comparable because the trace element contents of the samples investigated by Beesley et al. (2010) where much higher and a different sequential extraction scheme was applied to determine mobile trace metal contents. However, compared to As for which, according to the results from the sequential extraction, very low amounts of about 0.03 % were found to be associated with the mobile or easily mobilizable fractions the solubility of Cd and Zn in the samples was high which correspond well to the higher initial release of these trace metals in the percolation column tests. The comparison of the results from the percolation column test and the determination of the mobile/easy mobilizable fractions by means of the sequential extraction showed that the amount of Cd and Zn leached until L/S 10 corresponded well with the first two fractions of the sequential extraction. The increase in the leaching of these elements may therefore be attributed to the depletion of the more mobile fractions.

Caille et al. (2003) also observed a strong initial leaching of Cd, Cu and Zn and a subsequent decrease in the leaching of Cd and Zn and attributed this behavior to re-adsorption and co-precipitation of these trace metals onto more soluble solid phases such as carbonates, ferric hydroxides and clay minerals.

The results of the percolation column tests reveal the sensitivity of As to changing redox conditions. In the course of the column leaching experiments, reducing conditions occur. As is known to be immobilized by iron oxides (Hartley et al., 2009). Due to the reduction of iron oxides under reducing conditions, shares of As can be mobilized. Furthermore, a reduction of As(V) to the more mobile As (III) can occur under reducing conditions, leading to an increase in As solubility (Wenzel et al., 2002). According to Xie et al. (2009) moderately reducing conditions are favorable for As release from sediments.

For most of the trace metals investigated, the effect of **ripening** on the trace metal leaching in the percolation column tests was inconsistent. Consequently, the statistical evaluation of the data from the percolation column tests showed that the leaching behavior of As and the trace metals Cd, Ni and Pb was not significantly altered by ripening i.e. repeated wetting and drying. Zn was released in significantly lower proportions from the dredged material samples after ripening. This is in contradiction to the findings of the sequential extractions according to which a shift of Zn fractions towards less strong binding forms was observed as a result of ripening.

Cu was the only trace metal that showed a significantly increased leaching after ripening. According to the results of Calmano et al. (1994), Cu proportions of the oxidizable fraction in anoxic sediments from area of the Port of Hamburg are significantly higher than the proportions of the trace metals Cd, Pb and Zn in this fraction. After oxidation, higher proportions of the moderately reducible fraction were observed (Calmano et al., 1994). Cappuyns et al. (2004) also determined an increased mobility of Cu after aeration and sediment ripening. They concluded that oxidation leads to a release of Cu co-precipitated with Fe-sulfides and discrete Cu-sulfides. The increased release of Cu from the ripened material may therefore be explained by an increased release through oxidation of sulfide compounds and subsequent reduction of the recently formed moderately reducible proportions due to reduced conditions during the percolation column test. Additionally, the comparatively high release of Cu may be explained by the high affinity of Cu for the formation of dissolved organic complexes reported in the literature (Sauvé, 2000; Cappuyns et al., 2003; Amery et al., 2007; Rinklebe and Shaheen, 2014). Drying as it was performed twice during the laboratory ripening of the dredged materials may cause an increase in the concentrations of dissolved organic carbon in the soil solution after rewetting. Fründ et al. (1994) stated that by drying, the organic substances fixed in the clay-humus-complexes may become progressively released. These compounds as well as microbially formed and potentially water-soluble organic compounds, whose further degradation was slowed down under dry conditions (Savric, 2001) may be accumulated during drying and released under re-wetting. According to Sauvé (2000) the majority of dissolved Cu is found in metal organic complexes. More than 98 % of dissolved Cu was found to be bound to dissolved organic matter in nonacidic soil solutions (Sauvé, 1997). Contrary to trace metals with a lower affinity to DOM, which are re-adsorbed or precipitated to solid sediment constituents, Cu may be leached in larger amounts than the other trace metals after ripening due to the discharge of proportions bound in complexes with dissolved organic matter. However, as the partitioning of Cu in the dredged materials has not been investigated in the sequential extractions and the evolution of DOM release was not determined during the column leaching experiment, the behavior of Cu cannot be explained conclusively on the basis of the experiments carried out. Another explanation for the comparatively high Cu leaching after ripening may be its affinity for strong complexation by calcium ions that was determined by Caille et al. (2003) by means of speciation calculations. The dissolution of $CaCO_3$ due to the production of protons during the oxidation of sulphides may have led to an increase of Ca in soil solution resulting in a discharge of Cu bound to these Ca ions. Besides the release of Ca, HCO_{3^-} is released during the dissolution of calcium carbonates. HCO_3- may also prevent Cu from re-adsorption onto solid phases because it acts as an inorganic ligand for Cu in soil solution (Scheffer and Schachtschabel, 2010).

7.2.1.2 EPA-PAH

In relation to the total EPA-PAH contents of the dredged materials, on average 0.13 % were released from the dredged materials in the 10:1 batch-test. In the batch extraction according to DIN 19529, a maximum of 0.2 % of the total PAH content was released.

Compared to the results from the percolation column tests, the shares of the total amounts leached in the batch extractions were markedly higher (factor 5-10). According to Peiffer et al. (2003), organic contaminants often have higher eluate contents in batch tests than in the percolation column tests due to the mechanical stress that occurs during the batch extractions. The mechanical stress may cause a destruction of soil aggregates and a hence a release of contaminants. Furthermore, the mechanical stress increases the concentration of dissolved organic carbon, which is known to act as a mobility-enhancing carrier for organic contaminants (Busche and Hirner, 1997). In the percolation column tests, the leached EPA-PAH amounts were overall very low.

The results of the multiple regression analysis showed no significant correlations ($p > 0.05$) between EPA-PAH leaching in the percolation column extraction and the soil properties but indicated that the clay content is the most important predictor for PAH leaching from the unripened dredged materials (ß=0.784). For the ripened materials, the highest standardized regression coefficient was determined for the parameter TOC with ß=0.584. The latter relationship was to be expected because of the high affinity of PAH to organic substance (compare Chapter 2.3). The correlation of the EPA-PAH leaching and the parameter clay content may be due to an autocorrelation of the parameters clay and TOC. However, this relationship may also be an indication that the clay content has an influence on the permeability or the available contact surface between eluent and solid respectively. However, one would expect an inverse relationship, since it can be assumed that an increased clay content would reduce the permeability of the compacted materials installed in the columns. This would result in less contact surface available, which would reduce the release of pollutants.

In relation to the total contents of the samples, the amounts of leached EPA-PAH accounted for 0.02 % on average. From the ripened material an average amount of 0.05 % of the total contents was eluted in the percolation procedure. Compared to the leaching from unripened materials, an increase in the PAH leaching was determined after ripening for two of the five samples investigated. With two other samples, leaching remained more or less constant, while a decrease in leaching was determined for another sample. As reviewed by Busche and Hirner, numerous studies have shown that DOC increases the solubility of hydrophobic organic contaminants and thus may be responsible for the mobilization and relocation of contaminants in soil. DOC acts as a carrier because PAH can be adsorbed at the hydrophobic regions of DOC molecules (Busche and Hirner, 1997).

Following the line of reasoning for the release of Cu and because of the high affinity of PAH to dissolved organic matter, one could theoretically also expect increased leaching of PAH after ripening of the dredged material. However, despite to Cu were the changes in the redox conditions during the laboratory ripening caused an initial release, less PAH were released from the material during ripening, consequently the effect of ripening on the leaching of PAH was despite the expected increase in concentrations of dissolved organic carbon, less strong.

7.2.2 Potential maximum leaching

7.2.2.1 Sequential extractions

Besides the information on actual heavy metal mobility, predictions about the long-term behavior of contaminants are necessary to perform a risk assessment (Cappuyns et al., 2004; Swennen and Devivier, 2006).

Since leaching behavior and potential toxicity of trace metals are generally dependent on the chemical form or speciation in which they are present in soils and sediments, it is important to identify the fractions of trace metals (Baran and Tarnawski, 2015). For the purpose of the assessment of the solid-phase speciation of trace metals in sediments sequential extraction are an appropriate method (Calmano et al., 1986; Tack et al., 1995; Stephens et al., 2001). Furthermore, the physico-chemical conditions and reactions occurring during sequential extractions can, according to Cappuyns et al. (2007), be considered as a worst-case simulation of physico-chemical processes (acidifications, oxidation, etc.) under natural conditions. Therefore, a sequential extraction scheme was applied to differentiate between operationally defined binding forms of As, Cd, Pb and Zn in the processed dredged material and to investigate if naturally occurring processes such as ripening and mineralization of the organic substance cause a change in the speciation and therefore the mobility and hazardous potential of these metals. Regarding the EPA-PAH, a two-step sequential extraction scheme was applied to estimate if and to what extent PAH are present in the dredged material samples in water-soluble/mobile form and whether accelerated mineralization of the organic substance may cause a change in the amounts of potentially mobile PAH.

When evaluating the results of the sequential extraction of trace metals, the problem occurred that the sum of the trace metal contents of the individual fractions deviated in part significantly from the total contents determined by way of aqua regia digestion. For the vast majority of the samples (80 %), lower trace metal contents were determined in the sum of the fractions than in the total content determination. These differences are presumably due to a combination of sample inhomogeneity and material losses, which cannot be ruled out during decanting. Both factors are gaining in importance for sequential extraction against the background of the low sample weight (1 g) that is used. However, as the samples METHA 2 and METHA 8 which are more contaminated show higher sums of the individual fractions than the less contaminated samples, the results of the sequential extraction reflect the original contaminant load. For this reason, it can be assumed that the statements made on the distribution of trace metals to the fractions and the information on the binding forms in which the trace metals are present in the dredged materials derived from the proportion of these fractions are coherent.

For all trace metals examined, the largest proportions were found in the moderately mobilizable fraction, which is associated with iron and manganese oxides and hydroxides. As reviewed by Caille et al. (2003) heavy metals in anoxic sediments are generally found to be associated with phases qualified as ‘residual’ or ‘oxidable’ (Kersten and Förstner, 1986; Giani et al., 1994; Cauwenberg and Maes, 1997; Yu et al., 2001) so that they are considered to be associated with sulfide and organic compounds. This was also confirmed in a study from Sabra et al. (2001) in which it was shown that Cu, Pb and Cd were mainly associated with the sulfides and with the organic matter fraction in anoxic sediments. Calmano et al. (1993) investigated the speciation of Cd, Cu, Pb and Zn in an anoxic sediment from the Hamburg Harbor and showed that 65 % (of total content) Cd, 90 % Cu, 80 % Pb and 40 % Zn were bound to the sulfidic/organic fraction. According to the ranking of the factions in the present study, the proportion of the oxidizable fraction was only in the third place. Regarding Pb, this fraction was found to be the second largest. This shows that the dredged material investigated in our study was already (partly) oxidized by processing and storage at the time the sequential extractions were conducted. Therefore, the comparability of our results with results from studies on trace metal speciation in anoxic sediments is limited.

The results of the sequential extraction of the unripened material showed that compared to the other trace metals investigated, Cd and Zn where less firmly bound since about 20 % of their total contents were determined in the acid extractable mobile/ easily mobilizable fraction. This indicates that they were either adsorbed on solid phases such as clay minerals or Fe/Mn Oxides or associated with carbonates (Tessier et al., 1997, Singh et al., 2000). As the water soluble and exchangeable as well as the carbonate bound fractions are considered as most bioavailable (Rinklebe and Shaheen, 2014), the results also imply that the potential mobility of Cd and Zn in the dredged materials is high and thus may result in a transfer into plants or leaching into the groundwater.

For Pb comparatively high proportions were found to be associated with the oxidizable and residual fractions. As Pb is known to have a high affinity to organic matter (Rinklebe and Shaheen, 2014) and the samples were already partly oxidized before the sequential extraction was conducted, it is likely that the amounts determined in the oxidizable fraction were rather associated with organic matter than with sulfides. Regarding Pb, Cd and Zn our results are in a good agreement with the results from Cappuyns et al (2007). Both, in the present investigation and in their study, Pb was found to be less soluble and mostly recovered in the residual and reducible fractions while Cd and Zn showed the highest solubility and displayed a similar distribution on the different fractions which according to Cappuyns et al. (2006), this is usually the case in soils and sediments. The results are also consistent with the results of Baran and Tarnawski (2015), who investigated the heavy metal mobility in contaminated sediments and determined high proportions of Cd and Zn in the mobile fraction. However, the high variation in the acid-extractable fraction of Cd and Zn for different samples observed by Cappuyns et al. (2007) could not be observed in the present investigation.

As was found to be largely associated with the moderate to heavily and non-mobilizable fractions (F5, F4, F3). However, the proportion of the residual fraction was found to be lower than in a study of Cappuyns et al. (2007) where more than 40 % of the total As content were determined in this fraction.

Ripening of the processed dredged material led to a significant decrease in the proportion of mobile and easily mobilizable fractions and a marked increase in the reducible fraction. This is in a good agreement with the results of Ho et al. (2012) who observed a transfer of As, Zn and Pb from the exchangeable and carbonate bound fraction into the reducible fraction after oxidation of riverbed sediments from the Cam River-mouth (Vietnam). In the case of Cd, a redistribution from the oxidizable fraction in the reducible fraction was determined due to oxidation. In the present investigation, no significant change in the proportion of the oxidizable fraction was observed for Cd. Calmano et al. (1993) investigated how changes in the redox conditions and pH of dredged material from the Hamburg Harbor affect the speciation and mobility of trace metals. Although the results of their study are not directly comparable to the results presented in this study, as they applied a different sequential extraction scheme and did not determine the trace element proportions associated with the residual fraction, the generally observed shifts in the distribution of the trace metals due cycles of oxic and anoxic conditions are considered to be comparable to the results obtained with the ripened material in our study. As a result of oxidation Calmano et al. (1993) observed a decrease in the percentage share of Cd, Cu, Zn and Pb in the sulfidic / organic fraction and an increase in the less stable bound carbonate and exchangeable fractions. Buykx et al. (2000) and Zoumis et al. (2001) also found that during sediment oxidation, the binding forms of Cd and Zn changed from stronger bound oxidizable fractions to less stable bound carbonate fractions. Buykx et al. (2000) also observed in their investigation that the speciation of Ni, Pb was not affected by oxidation of the river sediments.

Overall, the results on the distribution pattern of Cd, Zn and Pb correspond well with results of Singh et al (2000) who investigated the changes in trace metal speciation with time since disposal of dredged canal sediments on land. In their investigation Cd and Zn were largely associated with the acid extractable fraction, while Pb was found to be more strongly bound in the sediments.

The results of the statistical evaluation on the behavior of the trace metals Pb and Zn after incubation showed that the accelerated mineralization of the organic substance leads to a significant reduction in the proportions present in mobile or mobilizable form in the samples. For these two trace metals and As a significant increase in the moderately to not mobilizable proportions was determined after incubation. Regarding Cd, a statistically significant increase in the easily mobilizable fraction was determined. However, it could not be conclusively assessed from which factions the shares that led to the increase in the proportion of this faction originated. However, in the context of the contaminant-releasing process of the mineralization of organic substance investigated here, it seems most likely that the proportions originated from the pool that was initially bound to the organic substance.

In the sequential extraction of EPA-PAH with water and hexane only about 1 % of EPA-PAH contained in the dredged material samples was determined in the water extractable fraction, while 99 % of the total extracted amounts was determined in the hexane fraction. The phenomenon of the "hydrophobic binding" of PAH described in Chapter 2.3 was apparent in the sequential extraction. The observed leaching during extraction with water may be explained by the binding of PAH to colloidal/particulate substances mobilized with water (Pyka, 1994) especially during mechanical shaking in batch-extractions (Peiffer et al., 2003).

The comparison of the distribution of PAH shares of the two fractions determined for the unripened material and the incubated material showed no statistically significant differences. However, it should be noted that for all samples a slight decrease in the hexane extractable proportion was found after incubation. For three samples also a slight decrease in the water extractable fraction was observed after incubation. Possible causes for the decreasing amounts of extracted PAH are both the metabolization of PAH and the formation of non-extractable residues (Eschenbach et al., 2000).

7.2.2.2 Worst-case scenarios

Acidification

Because soil pH is one of the key parameters controlling heavy metal behavior in soils and sediments, the assessment of evolution of pH with time is necessary to make predictions of heavy metal mobility in the long-term (Cappuyns and Swennen, 2010). Changes in soil pH upon addition of protons in their turn are determined by the acid neutralizing capacity of soils and sediments (Cappuyns et al., 2004). The amount of acid added to a soil/water suspension to keep the pH on a predefined level gives an estimate of the acid neutralizing capacity (ANC) of this sample (Cappuyns et al, 2003). In the present study, the ANC of selected dredged materials and fine-grained aged marsh sediments was determined by means of a titration experiment over a period of 124 days. The results revealed that the processed dredged material from the Hamburg Harbor exhibits a very high buffering capacity. This finding is in a good agreement with other studies conducted with processed dredged material from Hamburg (Gröngröft et al., 1994; Dickschas, 2001).

The results of the multiple regression analysis showed that the TIC content was the parameter with the strongest influence on the acid neutralization capacity of the processed dredged material. According to Scheffer and Schachtschabel (2010) the carbonate buffer is the dominant buffer in calcareous soils.

The effect of **acidification** on the leaching behavior of As and selected trace was examined in batch-extractions in two different approaches. In approach 1, pH and trace metal contents of the eluates were measured immediately after 16 hours of shaking. In this approach acidification of the samples to a pH of approximately 5 led to a considerable increase in the leaching of Cd, Ni and Zn compared to the batch-extraction without acid addition. This is in a good agreement with literature on the pH dependent mobilization of trace metals. The limits for the initial mobilization of the individual trace metals differ markedly from one another. While Cd becomes mobile from a pH of < 6.5, the threshold pH value for Zn is 6.0-5.5, 5 for Ni, 4.5 for Cu, 4.5-4 for As and 4 for Pb (Brauer, 2013). In the batch test, the adjusted pH values were lower than the threshold pH values of Cd, Ni and Zn. The threshold pH values of As and Pb are lower than the pH values adjusted in the experiment. Therefore, no leaching of these trace elements took place in the batch-extraction approaches. Calmano et al. (1993) investigated the leaching of Cd, Cu, Zn and Pb from oxic and anoxic sludge from the Hamburg Harbor area by means of batch-experiments with various fixed pH values. For all investigated trace metals and treatments (oxic/anoxic conditions) they observed an increase in mobility at pH values < 4.5. Lager et al. (2005) investigated the mobility of heavy metals in harbor sediments from Bremen. In their pH stat leaching experiments, they determined a very high Zn leaching at pH 4-6. Cd, Cu and Ni where also leached in high amounts due to acidification. As in the batch-extractions conducted in the present study, no effect of acidification was observed for Pb by Lager et al. (2005).

In investigations on the leaching behavior of trace metals by means of potentiometric titrations, Cappuyns et al. (2004) showed that a significant release of Cd, Ni and Zn started at a pH of about 4-5, while Cu and Pb were released exclusively in the pH range of 2-3. They attributed the strong release of Cd and Zn to the partial dissolution of carbonates. Tack et al. (1999) suggested that carbonates are an important sink that controls the solubility of Cd and Zn. Cu and Pb are reported to be less mobile in this pH range because even at a pH of about 4, these two trace metals are still strongly retained by iron-oxides (Kinniburgh et al., 1976), complexed by organic matter (Brümmer, 1986; Livens, 1991) or adsorbed to clay minerals (Cavallaro and McBride, 1984; Yong et al., 1990). According to Cappuyns and Svennen (2010), complexes of Cu and Pb with organic matter are stable until pH 3.

Buffering and the accompanied increase in pH from approximately 5 to a pH of 6 lead to a significant decrease in the trace metal leaching in the second experimental approach of the batch tests conducted in this study. Due to the increase in pH, Zn was determined in the eluates of the batch extraction in statistically significant lower concentrations than in the eluates with a lower pH. The decreased leaching in the second approach can be ascribed to re-adsorption and probably also precipitation processes. Especially Zn is known to be re-adsorbed onto clay minerals and organic substances in the pH range present in the samples after 2 weeks of buffering.

The impact of changing pH conditions on both mobilization and retention, i.e. by re-adsorption of trace metals were studied in more detail by means of percolation column tests with strongly acidified water (pH 2.9). In these experiments it was shown that due to the high buffer capacity of the processed dredged material, the pH of the eluates remained on a high/alkaline level over the whole period investigated (2 weeks, L/S=90). The results of the pH determination of the different layers of the solid matter after completion of the percolation column test revealed that the percolation with acidified water only led to a significant decrease of the pH in the lower 3-6 cm (from the bottom). Above this area no pH change could be detected due to buffering.

The determination of the trace metal contents of the material of different layers revealed that acidification led to a relocation of Cd, Cu, Ni, Zn and Pb from the lower 1-3 cm to the overlying layers (up to 6 cm). Pb was relocated from the lowest layer to a column height of about 4.5 cm, As to a height of about 3 cm. The results hence showed that although the pH decrease leads to a mobilization of the trace metals, these are mainly re-adsorbed to the soil matrix or re-precipitated in areas where acidification is less advanced due to buffering or where no acidification has taken place.

Lager et al. (2005) also performed column leaching extractions with acidified water (pH 4) to investigate the leaching behavior of trace metals from dredged material from Bremen. In their investigations they also observed the phenomenon of the development of different pH values within different heights in the columns. They denoted the narrow zone in which the pH increased sharply from about 4.2 to 7.8 "reaction front". In their investigations they could show, that this front moved throughout the material according to its buffer capacity. The authors stated that along this reaction front, dissolution reactions related to the low pH occur and that further down the flow-path at higher pH values phases can re-precipitate.

In the present study, the discharge of trace metals correspondingly only amounted 0.01 to 0.07 % of the total element contents. The comparison between trace metal amounts leached in the percolation column test with and without acidification showed no statistically significant differences. Percolation with acidified water did not lead to an increased release of As or trace metals from the investigated processed dredged material.

Mineralization of the organic substance

Since both trace metals and organic contaminants such as PAH are known to be retained in soils and sediments by adsorption on or complexation with the organic substance (Gisi, 1997; Du Laing, 2006; Schleuß and Wu, 1996; Kabata-Pendias, 2011) which, under natural conditions, is subjected to continuous turnover processes, it was investigated whether an accelerated mineralization of the organic substance leads to a mobilization of trace metals or PAH.

In previous incubation experiments conducted to investigate the composition and quality of the organic matter of fresh sediments from the Hamburg area it was shown that only 7-20 % and 4-11 % of the organic carbon contained in the fresh sediments were microbially degradable under aerobic and anaerobic conditions. By means of these investigations it was shown that the organic carbon of the dredged material from Hamburg mainly consists of organic substance which cannot be degraded during an incubation period of up to 180 days (Gröngröft and Eschenbach, 2015). In these experiments a TOC mineralization of 10-13 % was determined in incubation experiments. The TOC degradation rates determined in the aerobic incubation experiment conducted in the present study were in line the results of Gröngröft and Eschenbach (2015).

According to the results of the batch tests with the previously incubated materials, the partial mineralization of the organic substance had the greatest effect on the release of As, followed by Cd and Cu. Regarding Zn and Ni, no significant change in the leaching behavior could be observed in this experiment. These results are well comparable with results from Savric (2001), who investigated the influence of various soil properties on the mobilization of contaminants in sandy soils from a sewage irrigation field in Berlin. In her small-scale column leaching tests Savric (2001) did not determine an influence of the mineralization of the soil organic substance on the leaching of Ni and Zn. The author ascribed this to the low affinity of Ni and Zn to soil organic matter.

The increase in Cu leaching after incubation may be due to a destruction of metal-organic complexes. Studies have shown that Cu is mainly organically bound in sediments and that only small proportion of Cu are adsorbed to crystalline iron oxides (Ramos et al., 1994). The bonding between the organic substance and Cu is comparatively strong and is considered insoluble regardless of soil pH. The decomposition of organic matter or changed redox conditions can destroy the complexes and consequently mobilize Cu (Barona et al., 2001; Caplat et al., 2005; Di Palma and Mecozzi, 2007). Herms and Brümmer (1984) stated that in periods of intensive microbial degradation of organic soil substances with a mobilization of trace metals, soluble organic heavy metal complexes can be formed. Mobilization of heavy metals by soluble organic complexing agents takes place in the order Cu > Cd > Zn > Pb.

According to the results of the sequential extraction after incubation, no increased release of the examined trace metals by a degradation of the organic substance is to be expected, except for Cd. In the case of Cd, the contents of the mobile/ easily mobilizable fraction (F2) increased by an average of 1 % points due to incubation. However, this increase is very low. In relation to the total Cd content of the samples, still only very small proportions of about 0.24 % were leached from the materials after incubation and the Cd contents determined in the batch test with incubated materials were all far below the threshold values. The release of Cd may be explained by its affinity for soluble organic complexing agents. In contrast to Cu and Cd, the increase in As leaching after incubation is surprisingly because As is not known to have a high affinity for soil organic matter. However, the mineralization of OM may indirectly influence the mobility of As in soils. Hartley et al. (2010) observed a relationship between phosphorous concentrations and DOM concentrations in their leaching experiments. Due to its chemical similarity and behavior P is known to compete for binding sites with As (Adriano, 2001). Therefore, the increase in DOM in the course of the mineralization of the OM and a concurrent release of P may have led to a higher As leaching after incubation.

The EPA-PAH release from the incubated material was significantly higher ($p < 0.05$) than from the unripened material only for one sample. In all other samples, the release from the incubated material was significantly lower than from the unripened material. Overall, the mineralization of organic matter had only an unexpectedly small effect on the release of PAH from the dredged material samples, which may be partly explained by the fact that the proportions of organic matter mineralized during laboratory incubations were overall small and the remaining surface binding sites were capable to re-adsorb any contaminants released. Another explanation for the small effect of the mineralization of the organic substance on the release of the EPA-PAH may be the fact that PAH degradability and extractability in soils in general decrease with time. This so called 'aging' is well known from experiments with the addition of substances to soils (Hatzinger and Alexander, 1995; Chung and Alexander, 1998; Eschenbach, 1999) However, this phenomenon should not play a distinct role for the behavior of the PAH in the dredged material since the contamination the material has already taken place a long time ago.

Destabilization of the spatial structure of the organic substance

The organic substance is stabilized by metal-organic complexes and the formation of clay-humus complexes. According to Lützow et al. (2006) also crosslinking via polyvalent cations contributes to the stabilization of organic matter. The use of competing complexing agents such as EDTA (ethylenediaminetetraacetic acid) is intended to dissolve the humus-stabilizing metal ions from metal-organic complexes leading to a destabilization of the spatial structure of the organic substance (Eschenbach et al., 1998). The extraction with 0.05 M EDTA solution led to a significant increase in the release of trace metals and As from the dredged materials. The release of Cd and Zn was even 390 and 200 times higher than in the 10:1 batch-extraction with water as solvent. In relation to the percentage share of the total trace metal and As contents extracted in the other experiments, the proportions released by EDTA treatment were comparatively high. In the case of Cd, the release amounted even for more than 50 % of the total content. The Cd proportions released due to EDTA treatment are by far higher than the proportions which are, based on the results of the sequential extraction, associated with the organic substance. This shows that with this strongly invasive treatment also trace metal components associated with other soil constituents are mobilized.

The high amounts of released Cd and Zn in the EDTA extraction may partly be due to an influence of the slightly acidic pH of about 4.6 of the EDTA-solution. In the case of Cd the results may also reveal its high affinity for organic complexing agents which may also be released due to EDTA treatment.

For the PAH, the EDTA treatment also resulted in a significant increased release. For one of the five samples the released amount of PAH even accounted for 2.5 % of the total content. In the sequential extraction, the water-soluble amount of PAH was determined with about 1 %. In the batch extractions with water as solvent even lower percentage shares of PAH were (on average 0,2 % of the total contents) were leached. Therefore, it is obvious that the EDTA treatment led to a mobilization of initially not mobile shares of the PAH. Previous studies have shown, that by changing the spatial structure of the organic substance, a release of non-extractable sequestered residues of organic substances is possible (Eschenbach and Oing, 2013). Studies by Eschenbach et al (1998) and (2001) on ^{14}C labelled PAH residues in soil have shown that the use of EDTA as a competing complexing agent leads to a significant release of previously non-extractable residues. An effect that was neither achieved by the addition of humusdegrading microorganisms nor by mechanical stress treatment of the soil structure by freezing and thawing (Eschenbach et al., 1998). However, as the PAH content of the solid residues was not determined after EDTA extraction it is unclear whether the EPA-PAH amounts released in the EDTA extraction consisted from hexane extractable proportions or at least in part from the pool of non-extractable residues.

Destabilization of soil aggregates

Aggregation and occlusion may prevent the mobilization of certain amounts of contaminants in soils (Eschenbach et al., 2000; Eschenbach et al., 2001). In order to examine the effect of the **destabilization of aggregates** on the leaching behavior of contaminants, investigations were carried out in which the aggregate structure of the samples was mechanically destroyed by ultrasonic treatment. The release of trace metals and PAH from the treated samples was subsequently determined in 10:1 batch extractions. The trace metal release from the samples treated with ultrasound was overall low with less than 1 % of the total content. These results may indicate that only very small amounts of the trace metals in the samples are entrapped inside soil aggregates. The low leaching is, however, presumably also due to the fact that released amounts of trace metals become rapidly re-adsorbed especially since it can be assumed that the mechanical destruction of the aggregates will considerably increase the number of binding sites accessible for adsorption. However, Wilcoxon signed-rank tests revealed that statistically significant higher amounts of Cd, Ni and Zn were leached after ultrasonic treatment. Cu revealed a mixed picture.

The comparison of PAH release in the 10:1 batch-extraction with that determined after ultrasonic treatment indicated that the mechanical destabilization of the aggregates has no influence on the release of PAH from the dredged material. Although the averaged PAH release from sample METHA 3 was slightly higher after ultrasonic treatment, the results of the other samples showed a reverse picture. Regarding the PAH, no statistically significant effect of ultrasound treatment on the leaching could be determined ($p > 0.05$).

From the results it can be deduced that the mechanical destruction of the aggregates did not lead to a destruction of the organic substance and a resulting increase in the DOC concentration. If this had been the case, higher releases would have been observed, as in the experiments to degrade the organic substance and to chemically destabilize the organic substance.

7.2.3 Assessment of the leaching behavior of contaminants

The aim of the investigations on the leaching of selected trace metals and EPA-PAH with elution methods defined in the regulations (BBodSchV, 1999; LAGA, 2004) was to examine the potential leaching of harmful substances from fresh and ripened, i.e. chemically essentially unchanged processed dredged material from the area of the Port of Hamburg. For the assessment, the results from the conducted batch-extractions and percolation column tests were compared to different legislative standards. Furthermore, the results of these leaching experiments were compared to the results from the 11-year leachate monitoring conducted at the test field where a part of the dike cover layer consists of METHA material and the transferability of the laboratory results on in-situ conditions in dikes was evaluated.

The aim of the worst-case scenario investigations was to enable a prognosis of potentially mobilizable proportions of contaminants and to assess in which time periods processes may take place that enhance the contaminants mobility. The results from the worst-case scenarios investigated are also compared to legislative standards. In addition, the results obtained in these investigations were evaluated taking into account the probability of occurrence of the scenarios under field conditions.

7.2.3.1 Leaching from fresh and ripened material

According to the BBodSchV (1999) the **ammonium nitrate extraction** is to be applied for the assessment of the transfer of Cd and Pb into agricultural crops. The threshold and action values specified in the BBodSchV refer to a soil depth of 0-30 cm. As it is planned that the thickness of the covering of the dredged material with fine-grained aged sediments in the dikes will be at least 30 cm, these threshold and action values are not directly valid for the assessment of the dredged material intended for use in dike construction. As there are no other threshold values for the assessment, these values are used to assess the readily available trace metal contents in a makeshift manner. Both, the action value for Cd (0.1 mg/kg DW) and the threshold value for Pb (0.1 mg/kg DW) were found not to be exceeded by the trace metal concentrations determined in the AN-extracts of the dredged material samples. However, the trace metal contents in the AN- extract of one marsh sediment sample (MS 4) were significantly higher than these values with 0.21 mg/kg DW (Cd) and 0.44 mg/kg DW (Pb). The high AN-extractable trace metal content in this sample is due to the combination of moderate level of contamination and a very low pH (pH 3.8).

The evaluation of the results of the leaching experiments (batch-extraction and percolation column tests) was primarily conducted on the basis of the threshold values for the soil - groundwater path, specified in the BBodSchV (1999). Furthermore, the assignment values of LAGA (2004), the thresholds of the Groundwater Ordinance (GrwV, 2010), the environmental quality standards (UQN) and maximum permissible concentrations (ZHK-UQN) of the Surface Waters Ordinance (OGewV, 2016) and the threshold values from the latest draft of the Substitute Building Materials and Soil Protection Umbrella Ordinance (MantelV, 2017) were used for the assessment.

The threshold values applied for assessment are compiled in Table 7.20.

Table 7.20 Reference values for the assessment of leachate concentrations: Threshold values for the soil-groundwater path (BBodSchV, 1999), assignment criteria according to LAGA (2004), threshold values of the Groundwater Ordinance (GrwV, 2010), environmental quality standards of the Surface Water Ordinance (OGewV, 2016) Threshold values according to the draft of the Mantelverordnung (MantelV, 2017).

Parameter	**Unit**	**BBodSchV**	**LAGA TR**			**GrwV**	**OGewV**		**Draft MantelV**	
		Threshold value soil-groundwater path	**Assignment criteria Z1.1**	**Assignment criteria Z1.2**	**Assignment criteria Z2**	**Threshold value**	**JD-UQN**	**ZHK-UQN**	**Threshold value Soil-groundwater location of samplingTOC ≥ 0,5 %**	**Threshold value Soil-groundwater location of assessment**
		1999	2004	2004	2004	2010	2016	2016	2017	2017
As	µg/l	10	14	20	60	10			25	10
Cd	µg/l	5	1.5	3	6	0.5	0.08-0.25*	0.45-1.5*	7.5	3
Cu	µg/l	50	20	60	100				80	50
Pb	µg/l	25	40	80	200	10	1.3	14	85	10
Zn	µg/l	500	150	200	600				600	600
Ni	µg/l	50	15	20	70		8.6	34	60	20
Σ EPA-PAH (without Naphthalin)	µg/l	0.2								0.2

* depending on water hardness

Simplistically and conservatively it was assumed for the following assessment that during the transport of mobilized contaminants from dredged material installed in dikes (source term) to the saturated zone no mineralization or retention processes take place, i.e. the concentration of the source term corresponds to that at the place of assessment (compare section 2.1). This assessment approach was chosen particularly because in dikes the position of the place of assessment, that under normal conditions can be equated with the groundwater level of the surrounding area, changes with the water level of the adjacent river and may even be located in the upper layer of the dike cover in the case of high tides. In this unfavorable case, the transition zone from unsaturated to saturated conditions (place of assessment) is located within the source of pollutants (the dredged material) so that the pollutant load of the leachate cannot be reduced by the passage through the unsaturated zone.

The As, trace metal and EPA-PAH concentrations determined in the leaching tests can be evaluated as follows:

As: The comparison of the results from the 2:1 batch-extraction according to DIN 19529 conducted with the unripened METHA materials, listed in Table 7.2, with the threshold values compiled in Table 7.20 revealed some exceedances for one of the samples examined. With an eluate content of 12 µg/l, the test value of the BBodSchV, the draft of the MantelV and the threshold value of the GrwV for As of 10 µg/l was exceeded for sample METHA 5. The test value specified in the draft of the MantelV (25 µg/l), that is to be applied for the assessment of the leachate concentration at the location of sampling, would not be exceeded. Accordingly, an exceedance of the test value at the place of assessment (transition zone of unsaturated to saturated conditions) is not to be expected. The evaluation of the calculated eluate contents at L/S=2 (Table 7.4) in the percolation column tests showed that both the eluate contents of two of the unripened materials and two of the ripened material exceeded the threshold values of the BBodschV and the draft of the MantelV at the location of assessment as well as the threshold value of the GrwV of 10 µg/l. The eluate content of sample METHA 5 (unripened material) was calculated with 39.4 µg/l. Thus, the LAGA Z1.2 value of 20 µg/l and the test value of 25 µg/l of the draft of the MantelV (2017) were exceeded in the case of this sample. From the dredged material installed in the test field, elements bound to iron and manganese oxides, such as arsenic, were released initially under reducing conditions and occasionally during the transition to reducing conditions (Gebert and Gröngröft, 2010). The mean As concentrations in the leachate were determined with values between 1.2-4.0 µg/l (compare Table 8.3) depending on the time since installation and redox conditions prevailing in the dike cover layer partly constructed from METHA material. However, as in the laboratory leaching tests, occasional exceedances of the threshold values for As were determined on the test field leachates between 2004-2015. The maximum As content in the leachates was determined with 36 µg/l which is in the order of magnitude of the arsenic content calculated for METHA 5 (ripened) at L/S 2.

Cd: The Cd concentrations in the eluates of the batch-extraction were all below the test value of the BBodschV for the soil-groundwater path of 5 µg/l. The LAGA assignment value for Z1.2 material (3 µg/l) was exceeded in the case of two samples. The eluate contents of five of the nine samples examined were below the Z1.1 value of 1.5 µg/l. The threshold value of the GrwV was exceeded by the eluate concentrations of nine samples. In seven out of ten cases, the Cd contents calculated for a L/S ratio of 2 in the percolation column test, both for the unripened material and the ripened material exceeded the threshold value of the GrwV of 0.5 µg/l. In two cases the LAGA Z1.1 value and the maximum permissible concentration of

1.5 µg/l according to the environmental quality standard (UQN) of the OGewV were exceeded. The test value of 3 µg/l for the soil-groundwater path specified in the draft of the MantelV as well as the test value of 5 mg/l of the BBodSchV were not exceeded with any sample examined. In the leachate from the test field mean Cd contents in the range of < 0.1-0.35 µg/l were determined. The lowest Cd contents (mean < 0.1 µg/l) were determined in the period from 2013-2015. The highest Cd emissions (mean 0.35 µg/l) were determined in the initial phase of the monitoring (2004-July 2006) i.e. during the phase in which oxidation conditions developed in the dredged material (compare Table 8.3). Compared to the Cd contents in the leachates from the test field, higher amounts of Cd were leached in the laboratory leaching tests (batch extraction and percolation column test).

Pb: Pb was not leached from any of the samples investigated in the batch-extractions in concentrations above the LOQ (8 µg/l). In the percolation column tests, Pb has not been determined in concentrations above this LOQ as well. The results from the test field monitoring revealed that Pb is released only in very small amounts from the METHA material under in-situ cnditions. The mean Pb concentrations of the leachates were determined with 0.62 µg/l (2004-Juli 2006), 0.26 µg/l (August 2006-2009), 1.34 µg/l (2013-2015) and thus were far below the threshold values (compare Table 8.3).

Zn: The Zn contents determined in the eluates of three samples after batch-extraction exceeded the test value of the BBodSchV of 500 µg/l, the Z2 value of the LAGA TR and also the test value for the groundwater of 600 µg/l proposed in the MantelV. The Z1.2 value of 200 µg/l was also exceeded by the eluate contents of four samples. Zn is the only element that was found to be leached in smaller amounts from the ripened material than from the unripened material in the percolation column test. In the case of two of the five unripened materials investigated, the eluate contents calculated for a L/S ratio of 2 exceeded the LAGA Z1.2 value of 200 µg/l. However, the test value of the BBodSchV for the soil-groundwater path (500 µg/l) was not exceeded for any sample examined. The eluate contents calculated for the ripened materials were well below the unripened values applied. The Zn contents determined in the in the leachate monitoring on the test field were determined below test value of the BBodSchV for the soil-groundwater path (500 µg/l). After a maximum content of 300 µg/l in the transition phase from reduced to oxidized conditions (2005), zinc was determined in concentration below 50 µg/l in the leachates from the test field. Therefore, the results of the leachate monitoring are in good agreement with the results from the comparative percolation tests in which decreased Zn leaching occurs after ripening. However, with regard to the absolute concentrations, the laboratory results overestimate the release under in-situ conditions by far.

Ni: The threshold value of the BBodSchV (50 µg/l) and the LAGA Z2 value (70 µg/l) were exceeded for sample METHA 7 in the 2:1 batch extraction. The eluate content of this sample and of sample METHA 2 exceeded the maximum permissible concentration of the OGewV of 34 µg/l. The LAGA Z1.2 value of 20 µg/l was exceeded by the eluate contents of the samples METHA 1 and METHA 3. In the percolation column tests, the calculated eluate contents of four (two unripened materials and two ripened materials) samples exceeded the LAGA Z1.2 value (20 µg/l). The ZHK-UQN of the OGewV of 34 µg/l for Ni was exceeded for two ripened materials

(METHA 5 and METHA 8). The calculated eluate concentration of the ripened sample METHA 5 at L/S 2 also exceeded the test value of the BBodSchV of 50 µg/l and the test value of 60 µg/l applicable at the location of sampling (MantelV, 2017). The mean Ni concentration determined on the leachate from the test field in the period of 2004-July 2006, with 41.5 µg/l (Table 8.3) were slightly below the threshold value of the BBodSchV (50 µg/l). In the following, a steady decrease in the Ni contents of the leachate was observed (August 2006-2009: 9.7 µg/l; 2013-2015: 3.8 µg/l). Compared to these results, a higher Ni leaching was determined in the laboratory leaching tests.

Cu: The test value for the soil-groundwater path (BBodSchV) was not exceeded with any eluate content in the batch-extractions. The Cu contents of the eluates of five of the nine samples examined were below the LAGA Z1.1 value of 20 µg/l as well. The calculated eluate contents in the percolation column test at L/S 2 were all below the test value of the BBodSchV and the draft of the MantelV of 50 µg/l and also below the LAGA Z1.1 value. Cu is the only trace metal for which an increased leaching was determined after ripening. All eluate contents calculated for the ripened materials at L/S of 2 exceeded the test value of BBodSchV and the draft of the MantelV. The test value of the MantelV that is to be applied for location of sampling (80 µg/l) was also exceeded for three of the five investigated ripened samples. The LAGA Z2 value of 100 µg/l was exceeded in two cases. The results of the percolation column tests with the ripened material also showed that the Cu release was inversely exponential, i.e. decreased with increasing L/S ratio. Therefore, a potentially critical release took place only initially. With the exception of one sample, no Cu concentrations above the test value (BBodSchV 50 µg/l) were determined at the end of the percolation column tests. Nevertheless, the elution behavior of Cu has to be classified as critical on the basis of the laboratory results. Also, on the basis of the results of the leachate monitoring at the test field, the release behavior of copper has to be classified as critical. Although the concentrations of copper in the leachates from the test field were determined with mean values of 6.8 µg/l (2004-July 2006), 20 µg/l (August 2006-2009) and 38.4 µg/l (2013-2015) and therefore below the threshold value of the BBodSchV (50 µg/l), occasionally much higher Cu contents in the leachates were determined (last on May 2016 with 96 µg/l). Furthermore, the data from the monitoring show an increasing trend (compare Table 8.3) which is in line with the results of the comparative studies of the percolation tests, after which increased copper release occurs as a result of ripening.

EPA-PAH: According to the results from the determination of PAH in the eluates from the batch-extraction, the test value of 0.2 µg/l (Σ EPA-PAH without naphthalene) of the BBodSchV and the draft of the MantelV was not exceeded. The results of the EPA-PAH determination in the eluates of the percolation column tests showed one exceedance for samples METHA 5 (ripened material). On this sample an eluate content of 0.209 µg/l was determined. As the standard deviation of the four parallels investigated was determined with 0.014 µg/l, the exceedance of the test value has not been statistically verified. The results obtained in the percolation column test are well in line with the results of leachate analysis from the test field. Here, the analyses revealed no relevant emissions of EPA-PAH either (compare section 2.2 and Gröngröft et al., 2016).

To test the transferability of the results of the laboratory leaching tests to field conditions, it was calculated in which periods of time the L/S ratios set during the tests can theoretically occur in the test field. Taking into account the area of the test field with METHA material in the subsoil (127.8 m^2), the average thickness of the dredged material layer (0.7 m) and its average bulk density (0.95 g cm^{-3}), the mass of the METHA material was calculated at 670 kg m^{-3}. The seepage quantity, determined in four years without flooding (March 2008-January 2012), was determined at 514 l m^{-2}. This corresponds to an annual quantity of 128.5 l m^{-2} a^{-1} and thus approximately to the average climatic water balance in the period 2004-2015, which was determined with 124 l m^{-2} a^{-1} (Gröngröft et al., 2016). In the period September 2012-December 2015 with nine flood events, the seepage quantity was determined at 1016 l m^{-2}, corresponding to 254 l m^{-2} a^{-1}. Based on the calculated seepage in the four years without flooding, a L/S ratio of 2, as used for the evaluation of the percolation column tests, would be achieved after a period of about 11 years. Under these conditions, a L/S ratio of 10 would only be achieved after 52 years. Based on the leachate quantity from almost four years with nine flooding events, a L/S ratio of 2 would be achieved after 5.5 years. A L/S ratio of 10 after about 26 years. From these calculations it can be concluded that under in-situ conditions the release processes are many times slower than in laboratory leaching tests.

When transferring the laboratory results to in-situ conditions occurring after the installation of processed dredged materials in dikes, it must also be borne in mind that in principle the laboratory tests cannot realistically represent the physicochemical conditions prevailing in the dike (redox state, permeability or contact interface of water and dredged material). Furthermore, in some laboratory leaching tests such as the batch-extractions mechanical stress is applied to the soil materials which may cause a destruction of soil aggregates and a hence an increased release of contaminants. Mechanical stress also increases the concentration of dissolved organic carbon, which is known to act as a mobility-enhancing carrier for organic contaminants (Busche and Hirner, 1997). Therefore, as shown by the comparison of the results from the leachate monitoring on the test field with the results from the batch extractions and percolation column tests in the section above, laboratory tests, especially batch-extractions, tend to overestimate the possible contaminant release from dredged material installed in dike cover layers.

7.2.3.2 Potential maximum leaching of contaminants

In the following chapter the results from the investigations on the potential maximum leaching from the dredged material under worst-case conditions are also assessed according to the threshold values specified in the BBodSchv (1999) for the soil-groundwater path. Because the time scale by which release of contaminants occurs will largely determine the severity of the environmental hazard the results are also discussed against the background of the likelihood of occurrence of the applied worst-case conditions under in-situ conditions.

Worst-case scenario Acidification

When evaluating the results from the worst-case scenario acidification on the basis of the action and threshold values of the BBodSchV, the differences between the results obtained from the batch- extraction and the percolation column test become apparent. The Cd, Ni and Zn contents of the eluates from the batch-extraction exceeded the threshold values by far (Cd: by factor 58, Ni: factor 11, Zn: factor 37). The trace metal contents determined in the eluates from the percolation column test with acidified water were all below the test values.

With the results of the determination of the acid neutralization capacity of the dredged material samples compiled in Table 7.11, the acid neutralization potential for sample DF 1, which has the lowest ANC of the samples examined, was determined with 6.850 years (until a pH of 6 is reached), 8.180 years (pH 5) and 8.890 years until a pH of 4 is reached in a 0.7 m thick layer of the dredged material. For sample METHA 5, which exhibited the highest ANC of the dredged material samples examined, the acid neutralization potential was calculated with 16.000 years to pH 6, 18.300 years to pH 5 and 20.500 years until a pH of 4 is reached.

The results of the calculation of the acid neutralization potential underline the high buffer capacity of the dredged material against acid inputs. Furthermore, the results show that such a low pH as it was set in the worst-case approach investigated (pH range 6-4) under field conditions, may develop in thousands of years (approx. 7,000-20,000 years). It should be noted that a) the total acid neutralization potential of the dredged material is even higher than the values from the ANC determination used for the calculation of the above-mentioned periods and b) under the conditions of a dike it can be assumed that flood-induced inputs of bases such as Ca and Mg at least slow down acidification. Therefore, no acidification-related release of trace metals from the METHA material is to be expected within a reasonable time frame.

Worst-case scenario Mineralization of the OS

The assessment of the results of the batch-extraction with the incubated material revealed only for Cu and As breaches of the threshold values of the BBodSchV by factor 1.2-1.4. The Cd, Ni and Zn contents of the eluates were far below the threshold values. The threshold value of 0.2 µg/l for EPA-PAH (without naphthalene) was exceeded by factor 1.1-2.7 with four of the five samples investigated.

For the assessment of the results obtained in the worst-case scenario 'mineralization of the OS' the degradability of the organic substance contained in the dredged material from Hamburg was examined. Data collected on dredged materials used for the construction of the upper seal of the Francop landfill in Hamburg, as well as results from investigations on the gas formation determined for various dredged materials in the dewatering fields, were used in evaluations to determine the gas formation potential of the dredged material from Hamburg.

According to the results of these analyses, the half-life (t½) of the degradable organic substance of the dredged material under anaerobic conditions at an assumed mean soil temperature of 10 °C is 3.57 years (HPA, 2012). Based on a microbially degradable carbon content of 12 % on average, this would theoretically be degraded after about 26 years. Conversely, this means that a degradation of about 10 % of the organic substance as achieved in the worst-case scenario would only be expected after more than 20 years.

In assessing the probability of occurrence of the 'mineralization of the OS' scenario, consideration should also be given to the question of whether the carbon turnover in soil could be accelerated by a change in climatic conditions in the course of climate change, in particular by an increase in temperature. According to the so-called Q10 rule, according to which biological activity doubles with a temperature increase of 10 °C, a degradation of 10 % of the organic substance would thus be possible after about 10 years. Based on the maximum degradable 20 % of the organic matter contained in the dredged material, a complete degradation of this proportion would be expected approximately after 13 years.

However, by mechanisms such as occlusion inside soil aggregates and fixation in clay-organic complexes, a part of the organic substance in the soil is stabilized and hence protected from degradation. Accordingly, not all contaminants associated with the organic substance (sequestered by incorporation in organic complexes or adsorbed to the organic substance) can be released in the long term. Up to 0.8% of the Zn and 0.9 % of EPA-PAH contained in the samples were released due to the mineralization of about 10% of the OS in the batch-extractions after incubation. Even if the maximum degradable 20 % of the organic substance contained in the dredged material samples would be mineralized, only very small amounts of contaminants would be released in relation to their total contents. The degradation of organic matter in the processed dredged material from Hamburg is, as shown above, a very slow process. A temporally concentrated release caused by the degradation of the organic substance, which leads to a high contaminant load in the seepage water, can therefore be excluded.

Worst-case scenario Destabilization of the spatial structure of the OS

Trace metal and PAH concentrations determined in the eluates after EDTA treatment exceeded the threshold values by far (As: factor 5.6-15, Cd: factor 45-76, Pb: factor 119-286, Zn: factor 32-49, PAH factor7-15).

The worst-case scenario 'destabilization of the spatial structure of the OS' was chosen to assess the influence of the destabilization of the structure of organic matter by competing complexing agents. By using 0.05 M Na_2-EDTA solution, the release under extreme conditions not occurring in nature was simulated. EDTA is contained in many detergents and cleaning agents. An entry of this substance into the environment in concentrations such as those used in laboratory experiments does not take place. Although complexing agents, such as root exudates in soils, are also effective under natural conditions, their strength cannot be compared with that of the complexing agent used in the laboratory experiment conducted in the present study. Under natural conditions, an actual impact of competing complexing agents of comparable strength on soil materials or dredged material used in dike construction is not conceivable.

Therefore, the results from this scenario are no suitable for a hazard assessment of potential pollutant emissions under given and also future environmental conditions, but conclusions can be drawn about the binding of pollutants and the stability of the binding from the increased pollutant release. The results confirm the relevance of metal-organic complexes and the occlusion of pollutants inside of soil aggregates for the binding of pollutants in dredged material from the Hamburg harbor.

Worst-case scenario Destabilization of soil aggregates

Under natural conditions, a destabilization of soil aggregates can occur, for example, due to a change in the ion configuration of the clay minerals. In order to be able to analyze the effect of aggregate destruction in extreme conditions, the use of ultrasound was chosen here. When assessing the probability of occurrence of the worst-case scenario 'destabilization of soil aggregates', it should be noted that the ultrasonic treatment practiced here not only causes destabilization but complete destruction of the aggregate structure due to the high energy input and that contaminants adsorbed to soil constituents can also be dissolved by the high mechanical forces (Kazi et al., 2006; Meegoda and Perera, 2001). The results obtained in this investigated scenario account for the maximum possible release rates by destroying the aggregate structure. This means that the ultrasonic dispersion releases significantly more pollutants than can be expected from the dissolution of aggregates by natural processes. Nevertheless, the results show that even under extreme conditions, i.e. complete destruction of the aggregate structure, no drastic release of the investigated trace metals and EPA-PAH occurs. A relevant release of contaminants due to a destabilization of soil aggregates of under natural conditions thus seems very unlikely even after long periods of time.

8 Assessment of equivalency

When assessing the equivalency of processed dredged material and fine-grained aged marsh sediments for use in dike construction, the first question is what the term equivalency means with respect to the comparison of the two materials and on the basis of which parameters an equivalence of materials intended for the use in dike construction can be proven.
Dikes are earthen buildings constructed to prevent the hinterland against floods. To ensure this function, dikes must provide a high degree of stability against erosion by water and the permeation of water. In the case of river dikes, resistance to erosion plays a subordinate role, as these are less affected by wave impact than sea dikes. River dikes must, however, be able to withstand water damming over long periods of time during floods.

For the assessment of equivalency, the following superordinate properties are considered:
(i) Resistance to erosion
(ii) Impermeability

Furthermore, the leaching of contaminants has to be assed for the evaluation of the equivalency.
The properties are assessed separately in the following.

8.1 Resistance to erosion

As erosion resistance in particular the resistance against wave attack and the overflow of water is to be considered. This property depends on the cohesion and thus the stability and size of the soil aggregates, which in turn can be derived from the parameters loss on ignition, water content and liquid limit (Temmler and Filipinski, 1997). Indirectly, the clay content and the installation water content are also of decisive importance.

The limit values for these properties recommended in EAK (2007) as well as the value ranges of these properties determined for the material groups 'marsh sediments', 'METHA material fresh' and 'METHA material further processed' are presented in Table 8.1.

Table 8.1 Properties valuable with regard to the erosion resistance of dike cover materials and value ranges of these properties determined on the different materials. DW=dry weight, further processed=dewatered.

Material property	**Recommended threshold values according EAK (2007)**			**Marsh sediments**	**METHA materials fresh**	**METHA materials further processed**	**Rating**
	well suited	suited	limitedly suited				
Clay [% DW]	20 - 40	15 – 20	10-15	13 – 64	16 – 29		equal
initial moisture content [% DW]	25 - 60	25 – 50	25 – 45	19 – 56	47 – 73	28 - 50	see text
Loss on ignition [%]	≤ 10	≤ 10	≤ 5	0.8 – 6.1[1]	6-10	6-10	equivalency not limited
Liquid limit [%]	35 - 70	30 – 55	25 – 40	31 – 112	63 – 104	62 - 89	equal

1 Calculated from organic carbon content by multiplication with a factor of 1.72

The comparison of the value ranges determined for the individual material groups with the recommended threshold values shows:

- That the clay contents in the METHA material predominantly fall into the class 'well suited' and in some cases into the class 'suited'. The fine-grained marsh sediments exhibit a wider range of clay contents. One of the four investigated marsh sediments is to be assigned to the class ' limitedly suited', one material would not be suited.
- With regard to their water contents, the fresh METHA materials are only in part rated as 'well suited'. After further processing (dewatering) all METHA materials can be assigned to the class 'well suited'. With regard to the HH Directive (1988), the installation moisture content should range between 20 ≤ w ≤ 40 %. This criterion is not met with all marsh sediments, temporarily stored METHA materials (OD and DC material) or further processed METHA materials. Regarding the fresh METHA materials this criterion is not met at all. Since the installation water content inevitably depends on the question of whether and which pre-treatment was conducted and the weather conditions prior to and during installation, it can be concluded that fresh METHA material is not equivalent to marsh sediments, but METHA material after further processing.
- The values determined for the parameter loss on ignition on the METHA materials are increased compared to the marsh sediments due to the higher TOC contents of these materials. Nevertheless, the METHA materials are classified as 'well suited'. Since a certain amount of organic matter have a positive effect for several properties of dike cover layers, the equivalence of METHA material in comparison to the marsh sediments is not limited by the parameter loss on ignition.

- That the Liquid limit w_L determined for the METHA materials are so high that they either fall into the class 'well suited' or even exceed the values given as criterion for this parameter. The marsh sediments, on the other hand, also cover the 'suited' class and in individual cases also exhibited w_L values exceeding the 'well suited' class. In a comparison of both material groups an equivalence is given.

In summary, it can be stated that the indicators of the erosion resistance of METHA material correspond to the requirements for material intended to be used in dike covers on the condition that the installation water content is adjusted i.e. the materials are further processed. Hence, an equivalency of further processed dredged material with fine-grained marsh sediments is given and the material can be rated as suitable for dike construction.

8.2 Impermeability

The requirements for impermeability refer to the ability of the dike cover to reduce the penetration of water in the event of flooding to such an extent that no negative effects on the stability of the dike are to be expected. In contrast to landfill construction, however, no absolute impermeability is required in dike construction, but rather the fulfilment of properties that more or less directly control the impermeability. Indicators for the impermeability are the dry bulk density achieved during construction of the dike cover layers as well as the degree of shrinkage and swelling. As shown in the investigations on the compactibility and the shrinkage behavior, these properties are strongly dependent on the installation water content.

Table 8.2 Properties valuable with regard to the impermeability of dike cover materials and value ranges of these properties determined on the different materials. DW=dry weight, further processed (dewatered) (Oing et al., 2018a).

Material property	**Recommended threshold values according EAK (2007)**			**Marsh sediments**	**METHA materials (fresh)**	**METHA materials (further processed)**	**Rating**
	well suited	suited	limitedly suited				
Bulk density [g cm^{-3}]	1,1 – 1,45	1,15 – 1,50	1,25 – 1,55	1,51 – 1,61[1]	1,1 – 1,3	1,1 – 1,3	see text
Initial water content [% DW]	see section above						
Shrinkage rate [%]	no indication			13 – 39	28 – 45	13 - 37	equal after further processing

[1] 95 % of Proctor density determined

The comparison of the properties of the METHA material (fresh and after further processing) with the properties determined for the marsh sediments and the recommended threshold values shows:

- That significantly higher dry bulk densities can be achieved with the slightly humic and silt rich marsh sediments than with clay-rich marsh sediments and METHA materials. These differences may be slightly reduced by further processing i.e. further dewatering but remain essentially due to the proportions of organic matter and lime present in the materials.
- That the degree of shrinkage of fresh METHA material is exceeding the degree of shrinkage determined on the fine-grained aged marsh sediments. After pre-drying and thus the anticipation of proportions of primary shrinkage, the METHA material has the same value range as the marsh sediments. Therefore, at least further processed METHA material can be rated as equivalent with marsh sediments with regard to the shrinkage behavior.

When dredged material is used for the construction of dike cover layers, the intensity of cracking is decisive for the required impermeability. With regard to the dry bulk density, lower values are achieved with METHA materials than with typical marsh sediments. However, the METHA material meets the requirements of EAK (2007) for dry bulk density. As far as primary shrinkage was anticipated by further processing of the METHA material, swelling and shrinkage processes occur in the material which correspond to those of the marsh sediments.
Installation of further processes i.e. pre-treated METHA material requires the compaction in layers with heavy tracks or sheep's foot rollers in order to be able to close cavities safely. Assuming suitable pre-treatment and construction site technology, the METHA material can be rated as equivalent to traditionally used marsh sediments and suitable for dike construction in terms of impermeability.

8.3 Leaching of contaminants

EAK (2007) has not defined any requirements for the suitability of materials for use in dike covers with regard to pollutant emissions. Against the background that sediments act as sinks for many pollutants, the equivalence of METHA material and marsh sediments in relation to total pollutant contents does not exist in principle and the comparison of the total pollutant contents of the METHA materials and marsh sediments investigated in the present study also shows that the processed dredged material contain considerably higher amount of contaminants than the marsh sediments (compare Chapter 4.2.2). However, depending on the origin of aged marsh sediments (foreland of river dikes) these materials may also contain comparably higher contents of individual pollutants, than the marsh sediments examined in the present study.

For the assessment of the equivalency of marsh sediments and METHA material with regard to a possible pollutant release, both the soil-groundwater and the soil-plant and dispersion path were considered. For the comparative assessment of pollutant emissions from METHA material and marsh sediments with leachate, the results from 11 years of leachate water monitoring on the test fields (compare Chapter 2.2, Gröngröft et al., 2016) were evaluated. For the evaluation of the transfer of pollutants into the grassland vegetation, the trace metals contents of plant material samples collected from the test fields and the Drewer Hauptdeich on different sampling sites with and without METHA material in the cover layer were determined (Oing et al., 2018a).

In Table 8.3 the mean trace metal content determined in the leachates from the test fields (T1=dike cover exclusively build from marsh sediments, T2=dike cover partly constructed from METHA material) are compiled. For the calculation of the mean leachate content, values below the limit of quantification were set as equal the limit of quantification of the respective pollutant.

Table 8.3 Mean trace metal content determined in the leachates from the test fields (T1 and T2). Initial phase=2004-July 2006, transitional phase=August 2006-2009, final phase=2013-2015.

Parameter		**Test field cover**	
		Marsh sediment (T1)	**Marsh sediment and METHA material (T2)**
As	Mean leachate content - initial phase	1.0 µg/l	4.0 µg/l
	Mean leachate content-transitional phase	1.6 µg/l	1.2 µg/l
	Mean leachate content - final phase	1.1 µg/l	3.1 µg/l
Cd	Mean leachate content - initial phase	0.23 µg/l	0.35 µg/l
	Mean leachate content-transitional phase	0.18 µg/l	0.16 µg/l
	Mean leachate content - final phase	< 0.1 µg/l	< 0.1 µg/l
Cu	Mean leachate content - initial phase	5.8 µg/l	6.8 µg/l
	Mean leachate content-transitional phase	24.1 µg/l	20.0 µg/l
	Mean leachate content - final phase	10.3 µg/l	38.4 µg/l
Ni	Mean leachate content - initial phase	4.4 µg/l	41.5 µg/l
	Mean leachate content-transitional phase	13.4 µg/l	9.7 µg/l
	Mean leachate content - final phase	2.0 µg/l	3.8 µg/l
Pb	Mean leachate content - initial phase	< 0.1 µg/l	0.62 µg/l
	Mean leachate content-transitional phase	0.18 µg/l	0.26 µg/l
	Mean leachate content - final phase	< 0.1 µg/l	1.34 µg/l

Parameter		**Test field cover**	
		Marsh sediment (T1)	**Marsh sediment and METHA material (T2)**
Zn	Mean leachate content - initial phase	23 µg/l	37 µg/l
	Mean leachate content-transitional phase	12 µg/l	16 µg/l
	Mean leachate content - final phase	9 µg/l	31 µg/l

Since the leaching of contaminants from the test field partly constructed from METHA material was shown to occur according to the redox dynamics recognized by the redox-sensitive speciation of the main elements (Gebert and Gröngröft, 2010), three phases of contaminant leaching were distinguished for the assessment. First, the initial phase (2004-July 2006) in which reducing conditions prevailed in the dredged material. Second, the transitional phase (August 2006-2009) in which increasingly oxidizing conditions developed due to structure development of the material in the course of drying and root penetration. In this phase, sulfidically precipitated trace metals (e. g. cadmium, zinc, nickel) were released intermittently with the oxidation to sulphate. After their release these trace metals were in part fixed again by sorption on or association with iron (hydr)oxides due to the prevailing neutral pH value in the phase of continuing oxidative conditions (final phase: 2013-2015), or precipitation in the case of reoccurring reducing conditions.

The comparison of the trace metal contents of the leachates from test field (T1) build exclusively from marsh sediment with the contents determined in the leachates from test field (T2) which was partly constructed from METHA material shows:

- That the As contents in the leachate of T1 were determined below the test values (10 µg/l) for the soil-groundwater path of the BBodSchV (1999) for all three phases (comp. Table 8.3). This also applies to the leachates from the test field T2. In the final phase (2013-2015), the concentrations in the leachates of T2 are significantly higher than of T1. However, the As contents of the leachate can still be rated as very low and do not exceed the threshold value for the soil-groundwater path.
- That for Cd slightly but not statistically significant higher concentrations were determined in the leachate from T2 in the initial phase. However, the Cd contents in the leachates from both test fields were significantly below the threshold value specified in the BBodSchV (5 µg/l) for all three test phases.
- That the Cu contents of the leachate on average were below the test values (50 µg/l) for the soil-groundwater path of the BBodSchV (1999) for all three test phases. In some cases, significantly higher Cu concentrations (up to 96 µg/l) were determined. Cu is the only trace metal for which an increase in the leachate contents over time is determined. The Cu concentrations in the leachates from T1 where on the same level

in the first two test phases. In the final test phase, the Cu content determined in the leachates from T1 were significantly lower than from T2.

- That Ni concentrations in the leachates from T2 were significantly below the test values (50 µg/l) for the soil-ground water path of the BBodSchV (1999) for all three test phases and have decreased over time. In the leachates from T1, significantly lower Ni contents were determined in the first test phase. In the transitional phase and the final phase, the Ni contents in the leachates of T1 were not significantly different from those determined in the leachates from T2.
- That the concentrations of Pb in the leachates from T2 were determined with values significantly below the threshold value specified in the BBodSchV (25 µg/l) for all three test phases. For the leachates from T2, the Pb contents where almost always determined below the limit of quantification.
- That the Zn concentrations in the leachates from both T1 and T2 were determined with values significantly below the threshold value (500 µg/l) for all three test phases. In the final phase, significantly higher Zn concentrations were determined in the leachates from T2. However, these concentrations were still far below the threshold value.
- That the EPA-PAH contents in the leachates from both test fields were significantly below the threshold value (0.2 µg/l) for all three phases.

Overall, the results from the in-situ investigations on the emission of pollutants from a dike cover layer partly constructed from processed dredged material reveal the contaminants contained in the METHA material overall have a high binding strength to the solid. This is in a good agreement with the findings of the sequential extractions conducted in the present study, on the basis of which it was shown that the major proportion of trace metals are present in the processed dredged material in a moderately to hardly mobilizable form.

If the concentrations in the leachates are classified, e.g. using the threshold values of the BBodSchV for the soil-groundwater path, the mean concentrations in both the leachates from the test fields with and without METHA material are classified as "below threshold value".
This shows that the differences in pollutant emission i.e. the higher pollutant emission from the METHA material compared to the marsh sediments, does not imply a threat for the groundwater path.

The comprehensive investigation program carried out to examine the potential maximum leaching and thus also the long-term emission of contaminants (e.g. accelerated degradation of the organic substance, destruction of aggregates) did not reveal any realistic trends on the basis of which the pollutant emission from the dredged material would be rated more negatively in comparison to those from the marsh sediments.

9 Synthesis and outlook

Against the backdrop of the increasing demand for dike construction material and the limited availability of natural dike construction material, the utilization of processed dredged material for dike construction is considered an advisable option. The use of processed dredged material in dike construction requires the verification of the suitability of this material with regard to physical and chemical (pollutant-relevant) parameters.

The aim of the presented study is therefore to contribute to the clarification of the question of the suitability of processed dredged material from the Hamburg harbor (METHA material) for use in dike construction. To do so, two objectives were followed. Objective (1) was the assessment of the functional equivalency of the processed dredged material in comparison to traditional dike construction materials (aged fine-grained marsh sediments) in terms of chemical and physical properties, in particular the compactibility and the shrinkage behavior, which can be regarded as key properties for the impermeability of dike cover layers and thus for the long-term stability of dikes. Objective (2) was the assessment of the potential leaching of contaminants from the processed dredged material under given conditions, i.e. from fresh and ripened material and the potential maximum leaching under worst-case conditions. These investigations were carried out to clarify, whether contaminants leached from METHA material installed in dikes, may pose an imminent or future hazard to the environment.

By means of the very comprehensive investigation program conducted, it was possible to supplement the previous laboratory and field tests carried out with processed dredged material from Hamburg to investigate its suitability as dike construction material (Gebert and Gröngröft, 2010; Gröngröft et al., 2014) and to significantly expand the knowledge on properties and behavior of this material.

In particular, the following answers to the research questions given in the introduction (Chapter 1) could be derived:

How do dredged materials from the Hamburg harbor processed in the METHA-plant differ from traditional dike construction materials – fine-grained aged marsh sediments - in terms of their fundamental physical and chemical properties?

To answer this question, comparative investigations on the inherent physical and chemical properties of different fine-grained marsh sediments originating from various locations in northern Germany and samples of processed dredged material representative for processed dredged material currently produced in the METHA in Hamburg were conducted.

Because the fine-grained aged marsh sediments samples exhibited a very wide range in their inherent soil properties, hardly any significant differences between these materials and the dredged material samples could be determined. The statistical analyses (Mann- Whitney

U tests) revealed only for the parameter TIC statistically significant differences between the METHA materials and the fine-grained aged marsh sediments. However, there were also differences in the organic matter contents and the particle size distribution of the investigated marsh sediments and processed dredged materials. The organic carbon contents of two of the four investigated fine-grained marsh sediments were markedly lower than those of the METHA samples. In comparison to the METHA materials, these two marsh sediments samples also contained markedly (by factor 2) lower proportions of clay. The sand content of the processed dredged material samples is controlled by processing in the METHA-plant. Although the METHA material contained between 21.4 and 46.9 % by weight of sand, this fraction consisted almost exclusively (on average 93 %) of fine sand. Contrary to that, some of the aged marsh sediment samples exhibited up to 17 % of medium sand. One of the marsh sediment samples examined was almost sand free. Since grain size distribution and organic carbon contents influence the consistency of the materials, there were also differences between the two material groups with regard to the parameters liquid limit, plasticity limit and plasticity index.

The METHA material is characterized by high liquid limits (mean 91.9 %) and moderately high plasticity limits (mean 49.5%) and thus exhibits a high plasticity index (mean 0.42). The majority of the marsh sediment samples showed considerably lower liquid limits (32-48 %) and especially the clay poor marsh sediments also considerably lower plasticity index values (0.08-0.16).

The assessment of the physical properties of the materials based on the criteria for the suitability of materials for construction of dike cover layers specified in EAK (200) reveal that the processed dredged material from the Hamburg harbor can overall be rated as suitable for the installation of dike cover layers. For some materials (METHA materials and marsh sediments), however, the suitability according to these criterion is to be rated as limited due to their elevated sand or water contents. However, since the EAK-criterions are recommendations, failures to comply these criterions do not mean that the utilization of these materials in dike construction is not possible. Furthermore, the water as well as the sand contents of the METHA material can, if necessary, be adjusted by changing the processing technology applied in the METHA plant. In addition, the water content can be adjusted after the processing in the METHA plant, for example when the material is stored in roofed depots and left to dry before use.

How do the materials differ in terms of their compactibility? Can the compactibility of the METHA processed material be improved by further processing measures?

The investigations on the compactibility revealed that there is no equivalence between METHA material and the investigated fine-grained marsh sediments with regard to this property. Both, the initial densities determined on the materials in the compaction test at original water contents and the Proctor densities achieved in the standard Proctor test differed markedly from each other. The initial densities of marsh sediments were determined with

1.37 g cm $^{-3}$ at average and were thus by a factor of 2.4 higher than the initial densities determined for the METHA materials. The Proctor densities achieved with the METHA materials ranged from 1.15 g cm^{-3} -1.38 g cm^{-3} and were shown to be significantly lower than the Proctor densities achieved with the fine grained aged marsh sediments (1.59 - 1.69 g cm^{-3}). Multiple regression analyses carried out to examine the effect of inherent soil properties (grain-size distribution, inorganic and organic carbon content) on the compactibility of the materials revealed a high significance of the organic and inorganic carbon content for the compactibility of the materials. Since the marsh sediments contain significantly less inorganic carbon than the METHA material and in some cases also less organic carbon, the differences in the compactibility of the materials can in part be ascribed to differences in the inherent chemical properties of the materials.

However, since water content and the extent of previous drying of sediments is known to be of vital importance for compactibility, it was assumed that these parameters are also responsible for the divergent compactibility of the materials. Therefore, it was hypothesized that a further dewatering of the METHA material prior compaction would allow higher bulk densities to be achieved and, hence, its compactibility would become more comparable to that of the fine-grained aged marsh sediments. To verify this hypothesis, Proctor tests were carried out with materials dried to different water contents. Furthermore, it was tested, whether compactibility can be improved by drying of the materials in an oven at higher temperatures (at 30°C and 105°C) and whether ripening, i.e., repeated drying and wetting of the dredged material under natural and laboratory conditions, can improve the compactibility.

The compaction tests with the further air-dried materials showed that the compactibility of the processed dredged material increases linearly with drying (up to a water content of 10 % DW). Compared to the Proctor densities achieved with the undried materials, an increase from an average of 45 % of the Proctor density to 98 % of the Proctor density could be achieved by drying to a water content of 10 % DW. Extrapolated from these findings, bulk densities of about 1.04 - 1.1 g cm^{-3} may be realized during the installation of dike cover layers when the METHA material is further processed by drying to water contents of less than 10 % DW and remoistened to optimal water contents before use.

Compared to air-drying, oven-drying at 30 °C and 105 °C did not improve the compactibility of the processed dredged material significantly. The results from the Proctor tests conducted with material that had ripened under laboratory or natural conditions showed that for this particular material the effect of ripening is inconsistent and do not enhance the compactibility of the processed dredged materials significantly either**.** For the selection of potential further processing options, this means that further drying has an increasing effect on the densities achievable when installing METHA material in dike cover layers, irrespective of the type and speed of drying. From these results it can be deduced that air-drying to water contents of less than 10 % DW is a useful and moreover practicable further processing step to improve the compaction behavior of processed dredged material and thus to obtain a better functional equivalency compared to fine-grained aged marsh sediments and to improve the suitability for dike construction.

How do the materials differ in terms of their shrinkage behavior? Is it possible to anticipate proportions of the shrinkage of the METHA material before installation in the dike and thus to achieve a better functional equivalency with the fine-grained marsh sediments?

For the comparative investigations on the shrinkage behavior of the materials, the shrinkage limits, the volumetric shrinkage rates and the coefficients of linear extensibility ($COLE_{rod}$) were determined. Furthermore, large-scale shrink-swell experiments were carried out to enable the investigation of the shrinkage behavior of large specimens of layerwise compacted materials in a scale in which naturally occurring structure formation upon drying was expected to occur. In these experiment, the materials were ripened, i.e. air-dried, until shrinkage almost ceased, remoistened until saturation and air-dried again.

Both small-scale shrinkage experiments conducted revealed that the METHA material exhibit a greater shrinkage than the marsh sediments. $COLE_{rod}$ values and volumetric shrinkage rates of the METHA materials were significantly higher than those of the fine-grained aged marsh sediment. During the first drying cycle in the large-scale shrinkage experiments, total shrinkage of the METHA specimens amounted 10.2 -19.3 Vol. % referred to their initial volume. The shrinkage of the marsh sediments was many times lower and amounted for 0.9 Vol. % and 3.1 Vol. % of the initial volume. By means of shrinkage curves derived from the data obtained in the large-scale shrink-swell experiment, it was shown that in contrast to the processed dredged materials, which exhibited initial (proportional) shrinkage and residual shrinkage during the first drying cycle, the fine-grained aged marsh sediments exhibited only residual and zero shrinkage in the investigated moisture range. The materials also differed in their swelling behavior at re-saturation. Contrary to the marsh sediments, where swelling of the samples after saturation with water yielded sample volumes equal or slightly higher than at the beginning of the first drying cycle, the volume of the processed dredged material after swelling did not reach the previous level. Thus, it could be shown that the shrinkage of the processed dredged material in the first drying cycle in contrast to that of the marsh sediments was only partly reversible. From the results obtained from the second drying cycle it could be shown that the shrinkage behavior of processed dredged material can be ameliorated by dewatering/ripening. Shrinkage in the second drying cycle amounted less volume than in the first drying cycle. Furthermore, as the marsh sediments in the first drying cycle, the METHA materials did not exhibit proportional shrinkage in the second drying cycle, at least in those cases where the material did not dry out further than in the first cycle. Dewatering to a greater extent than in the first drying cycle led to further proportional shrinkage. It can be concluded from the large-scale shrink-swell experiments that a change from an irreversible primary shrinkage behavior with pronounced proportional i.e. irreversible shrinkage to residual shrinkage behavior can be achieved by one single drying cycle to an average water content of 17 % DW. The amelioration of the shrinkage behavior by ripening was also confirmed by the small-scale shrinkage experiments conducted with materials sampled after the second drying cycle of the large-scale experiment. Compared to $\mathrm{COLE_{rod}}$ determined on the unripened materials, $\mathrm{COLE_{rod}}$ values of the ripened materials were found to be 30-80 % points smaller.

According to the results of the shrinkage experiments conducted in the present study, the pre-drying intensity is vitally important for the shrinkage behavior. If the water content of soil specimens of material installed in the dike falls below the water content which was achieved in the pre-drying or further processing respectively, it is to be expected that irreversible proportional shrinkage occurs again. The intensity of pre-drying of the METHA material intended for the use in dike construction should therefore be greater than the drying intensity expected after installation in a dike. The evaluation of the in-situ water content measurements on the test fields showed a minimum water content of about 13 % DW at the dike slope and 18 % DW at the dike crest (Gröngröft et al., 2016). Based on these findings from the field tests and the results of the laboratory investigations on material-improving further processing options conducted in this study, it is recommended to pre-dry the METHA material to water contents of less than 12 % DW prior to use in dike construction to anticipate proportions of the shrinkage of the METHA material before installation and thus to achieve a better suitability of the material for dike construction.

Regarding the equivalency of METHA material with fine-grained aged marsh sediments traditionally used in dike construction, the results of the soil-physical and soil-mechanical investigations showed that the fresh METHA material is not equivalent to the examined marsh sediments in terms of compactibility and shrinkage behavior. However, the investigations carried out with further processed METHA material showed that the properties of the processed dredged material can be approached to those of the fine-grained marsh sediments and the suitability of the material for dike construction can be improved by further dewatering.

It is to be expected that coarse aggregates develop during further drying of the material on a technical scale - e.g. in roofed depots. Before installation, the aggregated material must be re-adjusted to a uniform moisture content of 30-40 % DW (optimum water contents as determined in the Proctor tests), which is more difficult to achieve with aggregated material. As to be expected, investigations on the influence of aggregate size and water content on the compactibility of the processed dredged material conducted in the laboratory have shown that compactibility tends to decrease with increasing aggregate size. According to the results of compactions tests conducted with materials of different aggregate size (< 2 mm, 2-20 mm, > 20 mm) and moisture content, coarse-aggregated materials can only be compacted to 81 % of the Proctor density when these materials are not remoistened to optimal water content (Oing et al., 2018a). Therefore, it should be examined in further experiments whether mechanical comminution of the aggregated material should be carried out to prevent the development of large aggregates and to ensure a uniform moisture distribution in the material before installation in the dike. Furthermore, it should be examined by means of an installation test under construction site conditions, how aggregated materials of heterogeneous moisture distribution can be compacted with the common installation methods.

The statistical evaluation of the data revealed significant inverse correlations between the organic carbon and the inorganic carbon content and the materialsˈ compactibility and shrinkage and, both the organic and the inorganic carbon content were shown to be correlated with the sand content i.e. both parameters decreased with increasing sand content. A higher sand content therefore has a positive effect on the compactibility of and shrinkage behavior of processed dredged material. Therefore, an estimation function for the derivation of the potential compactibility and shrinkage behavior was derived as a function of the sand content (Oing et al., 2018a).

The sand content of the METHA material is controlled by the technical processing of the dredged material in the METHA plant. In view of the relationships described above, a change in processing (omission of sand separation) may also be considered as an option to ameliorate the suitability of METHA material for the use in dike construction.

Which pollutant emissions are to be expected after installation in the dike under given conditions i.e. from fresh METHA material and from ripened METHA material?

The results from the batch-extractions and the percolation column tests conducted to estimate pollutant concentrations in the leachate occurring after installation of the processed dredged material in dikes showed that the release of most of the trace metals investigated (Zn, Cd, Ni, Pb) can preponderantly be classified as uncritical. However, for As and Cu, the results also revealed occasional breaches of the threshold values for the soil-groundwater path specified in the BBodSchV. Regarding the EPA-PAH, more frequent exceedances of the threshold value were observed in the assessment of the batch-extractions. In the percolation column tests occasional breaches of the threshold value were determined for the EPA-PAH.

When assessing a potential environmental hazard posed by dredged material used in dike construction on the basis of laboratory tests, the question arises whether and to what extend the laboratory results can be transferred to the field conditions. The calculation of the time periods in which L/S ratios similar to those applied in the laboratory leaching tests may develop under in-situ conditions in dikes showed that the L/S ratio of 2, which is to be used for the assessment of the results from the percolation column tests and to be applied in the batch-extraction according to DIN 19529, would be reached after 5 to 11 years, depending on the flooding frequency. An L/S ratio of 10 as it is applied in the 10:1 batch extractions would be reached after more than 50 years without any flood events. In the case of a repeated exposure to high water levels, this L/S ratio could develop after about 26 years. With regard to the transferability of laboratory results, it must be borne in mind that laboratory tests do not realistically reflect the conditions prevailing in the dike (redox conditions, permeability or contact surface water/material) and tend to overestimate the contaminant release observed in the field. The results of the percolation column tests for example, revealed the sensitivity of As to changing redox conditions. Contrary to the installation in the dike, where, as shown from the results of the investigations on the test fields in the Ellerholz canal (Gebert and Gröngröft, 2010; Gröngröft et al., 2016), oxidative conditions developed after ripening, in the column tests almost completely reduced conditions occurred leading to the mobilization of As. As shown from 11-years of leachate monitoring on the test-field partly constructed from METHA material, no release of As in amounts relevant to threshold values is to be expected once oxidized conditions have developed after dike construction. Also, for the EPA-PAH considerable discrepancies were found between the in-situ leaching behavior and the leaching behavior determined in the batch extractions and percolation column tests. Contrary to the results from the laboratory leaching investigations, in the leachates from the test field only occasionally EPA-PAH contents above the limit of quantification were determined. The threshold value of the BBodSchV was exceeded only once in 11-years of monitoring. Since only once an exceedance was determined and both the leachate from the test field built from marsh sediment and from the test field partly constructed from METHA material contained EPA-PAH in a concentration higher than the threshold value, the temporal parallelism and singularity of this measurement indicate a methodological artifact.

In view of the demonstrated limitations of the transferability of the laboratory results to the field conditions, it is recommended that the final assessment of the suitability of METHA material for use in dike construction should carried out on the basis of the results from the 11-year leachate monitoring conducted on the test fields in the Ellerholz canal. According to the results from the monitoring, Cu is the only contaminant whose elution behavior is not to be rated as uncritical. Some of the Cu concentrations determined in the test-field leachate were above discussed threshold values (GrwV, LAGA assignment citeria Z0) and most recently in May 2016 with a Cu content of 96 µg/l above the threshold value specified in the BBodSchV for the soil groundwater path. In addition to the copper contents, the nitrate and sulphate contents also exceeded the limit values (Gröngröft et al., 2016). For the assessment of the suphate and nitrate leaching, it must be taken into account that when these substances infiltrate the groundwater, nitrate is reduced to nitrogen, nitrite and ammonium due to the reducing physical-chemical conditions there. Due to the hydrogeological and geochemical conditions, the aquifer in the Elbmarsh in the area of Hamburg already naturally exhibits significantly increased ammonium concentrations. Furthermore, the nitrate loads calculated from the results of the leachate monitoring are considerably below the atmospheric deposition rates (Dèsi and Sucher, 2018). With regard to nutrients it should also be taken into account in the final assessment, that the nitrate and sulphate contents result from the naturally increased contents of organic matter and sulphur compounds contained in the sediments from the Elbe River. In the case of a utilization of METHA material in tidal river dikes in Hamburg both sulphate and nitrate would thus remain part of the original cycle, as the material would be used in a sedimentary characterized system (marsh of the Elbe River).

To complement the assessment of the hazardous potential of contaminants contained in the processed dredged material with regard to another pathway that might be of relevance since dikes are normally grazed for maintenance purposes (Seijffert and Verheij, 1998; DWA, 2011), plant samples from the dikes partly constructed from METHA material (test field Ellerholzkanal, Drewer Hauptdeich) were analyzed. A comparison of the results of the trace metal and As determination with the feed limit values showed that none of the 13 samples analyzed exceeds the As, Cd or Pb feed limit values. Furthermore, the comparative analysis of plant material from dike areas in which no METHA material is installed has shown that the plants from areas with processed dredged material in the subsoil did not contain higher trace metal contents (Oing et al., 2018a).

Which potential maximum pollutant emissions are possible in the long-term of dike existence, i.e. after chemical changes of the dredged material?

In order to gain a deeper knowledge on the speciation of trace metals in the processed dredged material and to derive information on the potential impact of ripening and the mineralization of the organic substance contained in the dredged material on the speciation of trace metals in the materials, comparative sequential extractions were carried out.

Based on the sequential extraction of trace metals from unripened and unincubated dredged material samples, it was found that the majority of As (97.2 %) and Pb (99.8 %) was bound in the fractions that are considered to be moderately to not mobilizable, i.e. hardly or not at all capable of being released under natural conditions. In the case of Cd and Zn, the proportion of fractions that are moderately to not mobilizable is 79% and 78%. The percentage share of the mobile to easily mobilizable fraction of these trace metals was determined with about 20 %. Ripening led to a decrease in the proportions of the mobile and moderately mobilizable fractions of As, Pb, Cd and Zn. Regarding Cd, incubation led to an increase of the proportions associated with this fraction. Overall, the impact of laboratory ripening and mineralization of the organic substance on the trace metal distribution on the different fractions was low. In the sequential extraction of EPA-PAH, no significant effect of the mineralization of the organic substance could be observed as well.

The potential leaching of contaminants from altered materials was investigated by means of **worst-case scenarios**. The investigation on the impact of an acidification of the dredged material on trace metal leaching revealed the pH-sensitivity of trace metal mobility in soils and sediments. In the batch-extraction under acidic conditions (pH 5), leaching of Cd, Ni and Zn was significantly increased and the contents of these metals determined in the eluates exceeded the threshold values of the BBodSchV. In the percolation column leaching conducted with strongly acidified water (pH 2.9) as eluent, however, no significant increase in trace metal release could be determined, since the metals were re-adsorbed in areas within the columns where no acidification had taken place yet. The trace metal contents of the eluates from the percolation column tests were all below the threshold values by far. After incubation, i.e. partial degradation of about 10 % of the organic carbon contained in the dredged material, As, Ni and Zn leaching in the 10:1 was found to be significantly increased. However, the eluate contents of Ni and Zn did not exceed the threshold values (BBodSchV) for the soil-groundwater path. The threshold value for As was exceeded in some instances. Overall, the trace metal release from the samples after incubation was very low with less than 1 % of the total contents. PAH leaching from the samples was found not to be altered due to incubation in a statistically significant manner. As for the EPA-PAH contents of the eluates from the batch-extraction with unincubated material, the threshold value for PAH was found to be exceeded for most of the incubated samples investigated. However, also the leaching of EPA-PAH from the incubated samples was very low with less than 0.2 % of the total content on average.

Worst case studies serve to determine the maximum emission potential of pollutants from contaminated materials in a time-lapse effect. In order to intensify the potential release of contaminants, stronger eluents or more extreme release conditions are used than they occur under natural conditions over long periods of time are applied in these investigations. For this reason, the probability-of-occurrence of the experimental conditions must be taken into account when evaluating the ecological relevance of the results of such tests.

With regard to the effect of acidification of METHA material installed in dikes, the results of the determination of the acid neutralization capacity and the acid neutralization potential showed that an acidification relevant for a release of Cd and Zn (pH 6) is not expected to occur until after more than 12000 years. Acidification, which could lead to the mobilization of Ni (pH 5,5) may occur after 13000 years. A mobilization of As (limit pH: 4-4.5) or Pb (limit pH 4), would only occur after 15500 years according to the calculations. Since the actual total acid neutralization capacity of the dredged material is even higher than determined in the titration tests and because high tide induced inputs of bases such as Ca reduce acidification, these calculated time periods can be considered as conservative assumptions. According to the results of the worst-case approach acidification, a release of trace metal in reasonable periods of time is considered uncritical under natural conditions.

Compared to the laboratory incubation experiments, where mineralization of organic carbon was accelerated by applying higher temperatures and optimal moisture contents, the degradation of the organic substance is expected to be significantly slowed down under natural conditions. According to evaluations of the gas formation potential of the dredged material from Hamburg, the half time of the degradable organic substance contained in the dredged material under anaerobic conditions is 3.6 years assuming a mean soil temperature of 10 °C (HPA, 2012). Taking this half-life period into account, a degradation of about 10 % of the organic substance as achieved in the worst-case investigation would only be expected after more than 20 years. In assessing the probability of occurrence of the "degradation of organic matter" scenario, consideration should also be given to the question of whether the carbon turnover in soil could be accelerated by a change in climatic conditions in the course of climate change, in particular by an increase in temperature. Following the so-called Q10 rule, according to which biological activity doubles in the case of a temperature increase of about 10 °C, a degradation of 10 % of the organic substance would hence be possible after about 10 years. Taking these assumptions on the probability of occurrence of the "degradation of organic matter" scenario, a spatially and temporally concentrated release of contaminants from the processed dredged material due to the mineralization of organic matter is not to be expected. Hence, exceedances of the threshold values of the BBodSchV for the soil-groundwater pathway are not to be expected and the release of contaminants form the dredged material caused by a mineralization of the organic substance can be rated uncritical.

In summary, the worst-case scenarios which are considered to be realistic to occur under natural conditions showed that no increased leaching, i.e. leaching of threshold exceeding concentrations, will not occur in reasonable time frame due to acidification of the processed dredged material or the mineralization of the organic matter contained in the processed dredged material.

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Appendix

Table A1 Results of the physical and chemical characterization of the samples. DW=Dry weight, TIC=Total Inorganic carbon, TOC=Total organic carbon, N=Nitrogen, SD=Standard deviation.

Material group	**Sample**	**Water content**	**pH**	**Conductivity**	**Clay**	**Silt**	**Sand**	**Soil type***	**Particle density**	**TIC**	**TOC**	**N**	**Liquid limit**	**Plastic limit**
		% DW	**-**	**µS/cm**	**%**	**%**	**%**	**-**	$g\ cm^{-3}$	**%**	**%**	**%**	**%**	**%**
Technically processed dredged material (fresh)	METHA 1	66.84	7.2	795	25.1	41	34	Lt2	2.51	1.18	3.15	0.33	89.8	0.43
	METHA 2	72.20	7.2	842	29	48.4	22.5	Lt2	2.49	1.09	3.72	0.37	103.4	0.5
	METHA 3	47.46	7.2	279	15.5	37.7	46.9	Sl4	2.55	0.93	2.63	0.22	62.5	0.21
	METHA 4	54.09	6.9	504	20.4	45.1	34.6	Ls2	2.54	1.02	2.74	0.30	78.8	0.33
	METHA 5	72.93	7.2	649	27.4	50.5	22.1	Lu	2.52	1.19	3.76	0.40	104.3	0.5
	METHA 6	65.37	6.9	696	28.4	45.6	26	Lt2	2.5	1.15	3.49	0.40	97.2	0.39
	METHA 7	67.32	7.2	325	27.2	44	28.8	Lt2	2.49	1.03	3.61	0.36	95.8	0.51
	METHA 8	61.22	6.9	588	25.5	49.3	25.2	Lu	2.48	0.59	4.31	0.38	100.9	0.51
	METHA 9	70.89	6.9	1009	28.8	49.8	21.4	Lt2	2.52	0.64	4.12	0.38	94.5	0.44
	Mean	**64.26**	**7.1**	**631**	**25.2**	**45.7**	**29.1**	**-**	**2.5**	**0.9**	**3.5**	**0.35**	**91.9**	**0.42**
	SD	**8.62**	**0.2**	**231**	**4.28**	**4.08**	**7.8**	**-**	**0.02**	**0.21**	**0.54**	**0.06**	**12.7**	**0.09**

Continuation Table A1

Material group	Sample	Water content	pH	Conductivity	Clay	Silt	Sand	Soil type*	Particle density	TIC	TOC	N	Liquid limit	Plastic limit
		% DW	**-**	**µS/cm**	**%**	**%**	**%**	**-**	**g cm^{-3}**	**%**	**%**	**%**	**%**	**%**
Technically processed dredged material (ripened. natural conditions)	OD 1	27.73	6.8	240	21.7	45.2	33.1	Ls2	2.52	0.55	3.45	0.32	67.7	0.32
	OD 2	32.49	6.9	455	19.4	39.7	40.9	Ls3	2.51	1	2.83	0.28	71.3	0.45
	OD 3	28.10	6.8	396	23	41.5	35.5	Ls2	2.53	0.95	3.08	0.30	62.3	0.27
	Mean	**29.44**	**6.8**	**364**	**21.4**	**42.1**	**36.5**	-	**2.52**	**0.83**	**3.12**	**0.30**	**67.1**	**0.25**
	SD	**2.65**	**0.1**	**111**	**1.5**	**2.3**	**3.3**	-	**0.01**	**0.2**	**0.26**	**0.02**	**3.7**	**0.04**
	DC 1	53.71	7.5	692	18.7	35.7	45.6	Ls3	2.48	0.5	3.82	0.30	76.7	0.35
	DC 2	54.13	7.5	818	21.3	39.7	39	Ls3	2.57	0.64	4.03	0.35	88.5	0.32
	DC 3	47.78	7.5	987	18.5	41.1	40.4	Ls2	2.49	0.54	3.76	0.31	70	0.37
	DC 4	53.21	7.5	981	16.5	44	39.5	Slu	2.49	0.56	3.7	0.32	82.5	0.28
	DC 5	53.91	7.6	663	14.8	48.7	36.4	Slu	2.5	0.57	3.41	0.29	76.3	0.27
	DC 6	48.78	7.4	747	16.4	45.1	38.5	Slu	2.5	0.54	3.45	0.29	82.5	0.2
	Mean	**51.92**	**7.5**	**815**	**17.7**	**42.4**	**39.9**	-	**2.51**	**0.56**	**3.7**	**0.31**	**79.4**	**0.35**
	SD	**2.85**	**0.1**	**141**	**2.1**	**4.2**	**2.8**	-	**0.05**	**0.04**	**0.21**	**0.02**	**5.9**	**0.06**

Continuation Table A1

Material group	**Sample**	**Water content**	**pH**	**Conductivity**	**Clay**	**Silt**	**Sand**	**Soil type***	**Particle density**	**TIC**	**TOC**	**N**	**Liquid limit**	**Plastic limit**
		% DW	**-**	**µS/cm**	**%**	**%**	**%**	**-**	**g cm^{-3}**	**%**	**%**	**%**	**%**	**%**
Naturally processed dredged material (de-watering fields)	DF 1	56.56	7.1	932	21.3	26.8	52	Ls4	2.53	0.88	2.85	0.37	78.4	0.38
	DF 2	45.55	6.9	770	15.3	19.4	65.3	Sl4	2.54	0.55	2.41	0.30	64.4	0.28
	DF 3	58.89	7.3	704	24.3	34.4	41.3	Ls3	2.53	0.92	2.54	0.38	72.1	0.35
	Mean	**53.67**	**7.1**	**802**	**20.3**	**26.9**	**52.9**	-	**2.53**	**0.78**	**2.6**	**0.35**	**71.6**	**0.34**
	SD	**7.12**	**0.2**	**117**	**3.8**	**6.1**	**9.8**	-	**0.01**	**0.17**	**0.18**	**0.04**	**13.4**	**0.1**
Fine-grained aged marsh sediments	MS 1	22.37	7.1	32	27.5	49.2	23.3	Lt2	2.6	0.05	1.36	0.14	48.7	0.25
	MS 2	19.98	7.5	34	13.5	43.2	43.4	Slu	2.62	0.09	0.92	0.11	38.3	0.16
	MS 3	18.71	7.5	524	14	60.8	25.2	Uls	2.62	0.93	0.46	0.07	31.6	0.08
	MS4	55.96	3.8	89	64.4	34.5	1	Tu2	2.51	0.03	3.54	0.29	112	0.43
	Mean	**29.25**	**6.5**	**170**	**29.9**	**46.9**	**23.2**	-	**2.59**	**0.28**	**1.57**	**0.15**	**57.7**	**0.29**
	SD	**17.87**	**1.8**	**238**	**20.7**	**9.6**	**15**	-	**0.05**	**0.38**	**1.18**	**0.10**	**14.8**	**0.1**

* according to KA 5 (2005)

Table A2 Total trace metal content of the samples.

	Total content [mg/kg DW]						
Sample	**As**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Hg**
METHA 1	27.86	3.02	108.73	33.19	82.38	563.53	2.31
METHA 2	42.31	4.50	162.31	41.84	110.15	730.09	3.74
METHA 3	30.81	2.76	130.09	27.97	77.79	470.76	2.32
METHA 4	29.35	3.07	154.48	45.08	87.30	516.92	2.74
METHA 5	25.32	3.74	188.66	53.58	101.20	688.57	3.47
METHA 6	30.59	3.44	165.08	48.13	95.66	656.29	2.74
METHA 7	42.67	4.12	195.60	51.12	110.63	702.05	3.26
METHA 8	43.12	4.28	174.33	51.27	111.33	705.28	3.43
METHA 9	40.08	3.64	178.44	51.01	99.11	683.07	3.00
Mean	34.68	3.62	161.97	44.80	97.28	635.17	3.00
SD	7.22	0.60	27.80	8.91	12.57	93.63	0.51
DF 1	25.54	3.30	107.76	45.35	85.68	629.46	2.25
DF 2	27.41	2.91	120.76	42.58	84.17	578.12	2.08
DF 3	25.63	2.19	88.93	40.15	66.19	453.94	1.43
Mean	26.19	2.80	105.82	42.69	78.68	553.84	1.92
SD	1.05	0.56	16.00	2.60	10.84	90.24	0.43
OD 1	31.27	4.98	192.35	64.61	120.24	473.29	2.48
OD 2	28.88	5.14	197.04	63.35	126.04	475.56	2.81
OD 3	36.62	5.67	204.69	65.08	128.70	475.56	2.63
Mean	32.26	5.26	198.03	64.35	124.99	474.80	2.64
SD	3.96	0.36	6.23	0.89	4.33	1.31	0.17
DC 1	33.71	4.83	171.25	51.74	117.61	826.26	4.07
DC 3	37.67	6.75	233.26	79.51	163.94	658.61	4.44
DC 6	41.63	4.06	136.22	48.92	104.24	731.02	3.98
DC 7	38.28	4.13	136.29	49.42	102.97	736.74	3.98
DC 8	44.20	4.07	126.00	46.53	95.33	708.32	3.78
DC 9	34.16	3.93	118.98	46.19	92.31	685.18	3.52
Mean	38.28	4.63	153.67	53.72	112.73	724.36	3.96
SD	4.11	1.09	42.94	12.80	26.58	57.79	0.31
MS 1	21.41	0.44	22.07	39.66	32.10	98.91	0.11
MS 2	12.58	0.28	13.00	29.82	25.34	65.83	0.08
MS 3	7.98	0.04	3.32	21.80	4.65	31.07	< LOQ
MS 4	11.00	0.54	37.23	57.69	24.38	134.89	0.14
Mean	13.24	0.33	18.91	37.24	21.62	82.68	0.11
SD	0.68	0.30	6.04	5.77	4.00	16.40	0.17

Table A3 PAH content of the samples. DW= Dry weight. Nap=Naphthalene. Any=Acenaphthylen. Ace=Acenaphthen. Fln=Fluorene. Phen=Phentantrene. Ant=Antracene. Fth=Fluoranthene. Pyr=Pyrene. Baa=Benzo(a)anthracene. Chr=Chrysene. Bbf=Beno(b)fluoranthene. Bkf=Benzo(k)fluoranthene. Bap=Benzo(a)pyrene. Ind=Indenopyrene. Dah=Dibenzoanthracene. Ghi=Benzoghiperylene.

		PAH-Content [mg/kg DW]																
Sample		**Nap**	**Any**	**Ace**	**Fln**	**Phen**	**Ant**	**Fth**	**Pyr**	**Baa**	**Chr**	**Bbf**	**Bkf**	**Bap**	**Ind**	**Dah**	**Ghi**	**Σ EPA-PAH**
METHA 1	**Mean**	0.08	0.17	0.11	0.14	1.21	0.55	3.8	2.79	3.14	2.27	3.64	1.51	3.2	2.13	0.66	1.4	26.78
	Min	0.08	0.09	0.05	0.11	0.67	0.28	1.54	1.24	1.07	0.84	1.58	0.73	1.29	1.27	0.52	0.89	11.41
	Max	0.09	0.35	0.2	0.16	2.21	0.72	5.68	4.12	4.4	3.22	5.2	2.09	4.46	2.83	0.85	1.88	36.29
METHA 2	**Mean**	0.13	0.11	0.11	0.19	0.97	0.36	2.07	1.74	1.13	0.94	1.62	0.6	1.44	0.95	0.21	0.64	13.18
	Min	0.13	0.07	0.1	0.18	0.72	0.29	1.63	1.38	0.93	0.77	1.32	0.47	1.15	0.75	0.17	0.5	10.19
	Max	0.13	0.16	0.12	0.2	1.45	0.41	2.93	2.44	1.49	1.27	2.17	0.86	2	1.3	0.27	0.9	17.2
METHA 3	**Mean**	0.07	0.05	0.06	0.1	0.46	0.23	1.21	0.96	0.81	0.61	0.96	0.38	0.87	0.54	0.13	0.35	7.79
	Min	0.06	0.04	0.04	0.06	0.29	0.12	0.81	0.68	0.56	0.45	0.79	0.28	0.69	0.47	0.11	0.31	5.45
	Max	0.08	0.06	0.09	0.15	0.65	0.38	1.81	1.36	1.21	0.85	1.25	0.51	1.17	0.68	0.16	0.42	10.38
METHA 4	**Mean**	0.07	0.03	0.03	0.06	0.37	0.11	0.72	0.67	0.47	0.41	0.64	0.19	0.42	0.32	0.08	0.26	4.87
	Min	0.06	0.03	0.03	0.06	0.31	0.10	0.65	0.61	0.43	0.40	0.62	0.18	0.38	0.29	0.07	0.25	4.63
	Max	0.08	0.04	0.04	0.07	0.44	0.12	0.80	0.73	0.54	0.42	0.67	0.21	0.50	0.39	0.11	0.27	4.99
METHA 5	**Mean**	0.14	0.05	0.10	0.15	0.76	0.20	1.44	1.24	0.89	0.80	1.12	0.42	0.83	0.55	0.13	0.46	9.27
	Min	0.13	0.05	0.07	0.13	0.57	0.16	1.07	0.97	0.68	0.60	0.90	0.32	0.65	0.44	0.10	0.36	7.25
	Max	0.14	0.06	0.16	0.17	1.09	0.25	2.09	1.71	1.26	1.14	1.47	0.60	1.13	0.75	0.17	0.62	12.79
METHA 6	**Mean**	0.09	0.05	0.04	0.08	0.46	0.13	0.99	0.92	0.60	0.55	0.80	0.22	0.50	0.40	0.09	0.35	6.27
	Min	0.09	0.04	0.04	0.07	0.43	0.12	0.93	0.88	0.56	0.50	0.70	0.20	0.40	0.38	0.08	0.32	5.96

		PAH-Content [mg/kg DW]																
Sample		**Nap**	**Any**	**Ace**	**Fln**	**Phen**	**Ant**	**Fth**	**Pyr**	**Baa**	**Chr**	**Bbf**	**Bkf**	**Bap**	**Ind**	**Dah**	**Ghi**	**Σ EPA-PAH**
	Max	0.10	0.05	0.04	0.08	0.49	0.14	1.04	0.97	0.69	0.63	0.91	0.25	0.61	0.43	0.10	0.37	6.84
METHA 7	**Mean**	0.11	0.06	0.08	0.12	0.69	0.20	1.45	1.31	0.84	0.76	0.96	0.27	0.62	0.49	0.12	0.42	8.50
	Min	0.11	0.05	0.05	0.10	0.53	0.16	1.25	1.15	0.71	0.65	0.81	0.23	0.48	0.42	0.10	0.37	7.18
	Max	0.11	0.07	0.13	0.14	0.98	0.26	1.82	1.59	1.05	0.94	1.06	0.31	0.73	0.59	0.14	0.49	10.41
METHA 8	**Mean**	0.40	0.07	0.16	0.30	1.34	0.37	1.73	1.43	1.17	1.11	1.18	0.49	0.88	0.54	0.16	0.47	11.79
	Min	0.13	0.05	0.07	0.13	0.64	0.18	1.09	1.02	0.75	0.69	0.85	0.32	0.62	0.42	0.11	0.39	7.46
	Max	0.94	0.08	0.32	0.63	2.59	0.73	2.81	2.11	1.90	1.81	1.69	0.73	1.27	0.73	0.24	0.61	19.18
METHA 9	Mean	0.10	0.04	0.05	0.08	0.42	0.12	0.77	0.70	0.52	0.45	0.62	0.22	0.45	0.28	0.07	0.26	5.17
	Min	0.09	0.04	0.04	0.08	0.39	0.12	0.70	0.65	0.49	0.41	0.59	0.20	0.43	0.27	0.07	0.25	4.96
	Max	0.11	0.04	0.05	0.08	0.47	0.13	0.81	0.73	0.56	0.51	0.66	0.23	0.49	0.30	0.08	0.28	5.42
DF 1	**Mean**	0.08	0.03	0.03	0.06	0.31	0.08	0.47	0.43	0.33	0.30	0.48	0.16	0.33	0.24	0.06	0.20	3.58
	Min	0.08	0.03	0.01	0.06	0.29	0.07	0.43	0.40	0.31	0.28	0.45	0.15	0.30	0.21	0.05	0.18	3.32
	Max	0.08	0.03	0.04	0.07	0.34	0.08	0.49	0.46	0.34	0.31	0.50	0.17	0.36	0.26	0.06	0.22	3.74
DF 2	**Mean**	0.06	0.02	0.03	0.05	0.23	0.06	0.36	0.32	0.25	0.22	0.37	0.12	0.26	0.19	0.04	0.17	2.76
	Min	0.05	0.02	0.03	0.05	0.22	0.06	0.34	0.31	0.24	0.21	0.37	0.12	0.26	0.19	0.04	0.16	2.72
	Max	0.06	0.02	0.03	0.05	0.24	0.06	0.38	0.34	0.26	0.23	0.38	0.12	0.27	0.20	0.05	0.17	2.81
DF 3	**Mean**	0.05	0.02	0.03	0.05	0.26	0.05	0.37	0.32	0.24	0.23	0.35	0.13	0.25	0.16	0.04	0.15	2.71
	Min	0.05	0.02	0.02	0.04	0.24	0.05	0.33	0.29	0.24	0.22	0.33	0.12	0.23	0.15	0.04	0.14	2.54
	Max	0.05	0.02	0.04	0.05	0.28	0.06	0.43	0.36	0.25	0.25	0.38	0.15	0.27	0.18	0.04	0.17	2.98
DC 1	**Mean**	0.10	0.06	0.04	0.07	0.48	0.19	1.24	1.05	1.08	0.67	1.47	0.53	1.12	0.64	0.14	0.49	9.38

		PAH-Content [mg/kg DW]																
Sample		**Nap**	**Any**	**Ace**	**Fln**	**Phen**	**Ant**	**Fth**	**Pyr**	**Baa**	**Chr**	**Bbf**	**Bkf**	**Bap**	**Ind**	**Dah**	**Ghi**	**Σ EPA-PAH**
	Min	0.08	0.05	0.03	0.07	0.43	0.18	1.17	1.00	1.01	0.64	1.38	0.48	1.08	0.61	0.13	0.47	8.84
	Max	0.11	0.07	0.04	0.07	0.54	0.22	1.34	1.12	1.19	0.72	1.57	0.58	1.20	0.66	0.15	0.51	10.07
DC 3	**Mean**	0.12	0.07	0.06	0.13	0.58	0.23	1.53	1.29	1.13	0.68	1.41	0.50	1.21	0.57	0.11	0.43	10.05
	Min	0.12	0.06	0.06	0.13	0.54	0.22	1.44	1.21	1.09	0.65	1.33	0.46	1.14	0.53	0.10	0.40	9.49
	Max	0.13	0.07	0.06	0.14	0.61	0.25	1.61	1.36	1.18	0.72	1.50	0.54	1.29	0.62	0.13	0.46	10.67
DC 6	**Mean**	0.08	0.05	0.03	0.06	0.49	0.17	1.02	0.81	0.85	0.53	1.15	0.39	0.91	0.50	0.10	0.38	7.51
	Min	0.08	0.04	0.02	0.04	0.33	0.13	0.75	0.63	0.67	0.44	1.01	0.33	0.76	0.44	0.08	0.34	6.10
	Max	0.08	0.07	0.04	0.10	0.77	0.25	1.45	1.11	1.18	0.70	1.43	0.50	1.16	0.61	0.13	0.44	10.00
DC 7	**Mean**	0.11	0.07	0.05	0.09	0.66	0.27	1.78	1.45	1.67	1.06	2.07	0.72	1.71	0.91	0.19	0.63	13.42
	Min	0.10	0.07	0.04	0.07	0.54	0.21	1.45	1.22	1.25	0.77	1.60	0.54	1.31	0.79	0.13	0.51	10.59
	Max	0.12	0.08	0.05	0.11	0.86	0.36	2.07	1.62	2.13	1.45	2.68	0.93	2.20	1.06	0.26	0.75	16.73
DC 8	**Mean**	0.10	0.06	0.05	0.08	0.72	0.24	1.38	1.11	1.17	0.69	1.51	0.53	1.23	0.66	0.13	0.49	10.15
	Min	0.09	0.05	0.03	0.05	0.42	0.14	0.92	0.76	0.80	0.50	1.16	0.41	0.89	0.52	0.09	0.40	7.21
	Max	0.11	0.07	0.07	0.12	1.19	0.38	1.97	1.55	1.60	0.93	1.96	0.67	1.64	0.86	0.18	0.61	13.91
DC 9	**Mean**	0.10	0.06	0.05	0.08	0.54	0.19	1.25	1.00	1.06	0.64	1.37	0.47	1.08	0.59	0.11	0.44	9.00
	Min	0.09	0.05	0.03	0.07	0.47	0.16	1.04	0.86	0.92	0.57	1.25	0.42	0.97	0.56	0.11	0.42	7.98
	Max	0.10	0.07	0.05	0.10	0.61	0.22	1.54	1.20	1.26	0.77	1.49	0.51	1.20	0.62	0.12	0.46	10.31
OD 1	**Mean**	0.06	0.03	0.03	0.04	0.25	0.09	0.57	0.46	0.50	0.35	0.72	0.25	0.64	0.35	0.09	0.29	4.69
	Min	0.05	0.03	0.02	0.04	0.22	0.09	0.50	0.41	0.44	0.31	0.64	0.22	0.56	0.30	0.08	0.25	4.14

		PAH-Content [mg/kg DW]																
Sample		**Nap**	**Any**	**Ace**	**Fln**	**Phen**	**Ant**	**Fth**	**Pyr**	**Baa**	**Chr**	**Bbf**	**Bkf**	**Bap**	**Ind**	**Dah**	**Ghi**	**Σ EPA-PAH**
	Max	0.06	0.04	0.07	0.05	0.29	0.27	0.65	0.51	0.55	0.40	0.80	0.28	0.72	0.40	0.11	0.32	5.52
OD 2	**Mean**	0.06	0.05	0.03	0.06	0.43	0.14	0.94	0.76	0.78	0.50	1.14	0.42	0.97	0.57	0.12	0.43	7.40
	Min	0.06	0.04	0.03	0.05	0.31	0.11	0.71	0.59	0.68	0.44	1.04	0.37	0.84	0.51	0.11	0.39	6.28
	Max	0.06	0.06	0.04	0.08	0.58	0.17	1.19	0.95	0.95	0.56	1.31	0.48	1.15	0.66	0.14	0.50	8.88
OD 3	**Mean**	0.06	0.05	0.03	0.05	0.30	0.13	0.68	0.59	0.67	0.43	1.02	0.36	0.87	0.48	0.10	0.36	6.19
	Min	0.06	0.05	0.02	0.05	0.27	0.12	0.62	0.54	0.62	0.42	0.99	0.33	0.84	0.44	0.10	0.34	5.81
	Max	0.06	0.06	0.03	0.06	0.34	0.15	0.72	0.62	0.69	0.44	1.07	0.39	0.91	0.50	0.11	0.38	6.51

Table A4 Contents of polychlorinated biphenyls (PCB) of the samples.

Sample	PCB 28 [mg/kg DW]	PCB 52 [mg/kg DW]	PCB 101 [mg/kg DW]	PCB 138 [mg/kg DW]	PCB 153 [mg/kg DW]	PCB 180 [mg/kg DW]	Σ PCB [mg/kg DW]
METHA 1	< LOQ	0.012	0.019	0.038	0.033	0.029	0.131
METHA 2	< LOQ	0.019	0.032	0.056	0.049	0.039	0.196
METHA 3	< LOQ	0.008	0.014	0.026	0.022	0.019	0.09
METHA 4	0.004	0.006	0.012	0.021	0.017	0.014	0.074
METHA 5	0.013	0.012	0.02	0.042	0.031	0.026	0.146
METHA 6	0.006	0.009	0.014	0.024	0.018	0.013	0.085
METHA 7	0.011	0.011	0.017	0.029	0.022	0.016	0.106
METHA 8	0.014	0.014	0.021	0.037	0.029	0.021	0.137
METHA 9	0.01	0.009	0.015	0.027	0.02	0.016	0.097
DF 1	0.005	0.005	0.008	0.019	0.014	0.012	0.064
DF 2	0.003	0.003	0.006	0.014	0.011	0.01	0.042
DF 3	0.007	0.005	0.009	0.019	0.016	0.012	0.068

Table A5 Contents of organochlorine pesticides of the samples.

Sample	Pentachlor-benzene [mg/kg DW]	Hexachlor-benzene [mg/kg DW]	alpha-HCH [mg/kg DW]	beta-HCH [mg/kg DW]	gamma-HCH [mg/kg DW]	p.p-DDE [mg/kg DW]	p.p-DDD [mg/kg DW]	p.p-DDT [mg/kg DW]	Σ OCP [mg/kg DW]
METHA 1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
METHA 2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
METHA 3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
METHA 4	0.002	0.008	0.006	< 0.01	0.006	0.013	0.022	< 0.004	0.058
METHA 5	0.004	0.012	0.014	< 0.01	0.026	0.022	0.035	< 0.004	0.113
METHA 6	0.002	0.007	0.005	< 0.01	0.009	0.012	0.017	< 0.004	0.051
METHA 7	0.002	0.011	0.011	< 0.01	0.019	0.02	0.031	< 0.004	0.094
METHA 8	0.004	0.013	0.019	< 0.01	0.034	0.019	0.034	< 0.004	0.124
METHA 9	0.003	0.011	0.009	< 0.01	0.016	0.014	0.037	0.2	0.291
DF 1	0.002	0.006	0.007	< 0.01	0.012	0.009	0.013	< 0.004	0.049
DF 2	0.002	0.005	0.006	< 0.01	0.009	0.006	0.011	< 0.004	0.04
DF 3	0.002	0.006	0.006	< 0.01	0.008	0.007	0.013	0.015	0.058

Table A6 Contents of mineral oil hydrocarbons (MOH) o the samples.

Sample	**Σ MOH [mg/kg DW]**
METHA 1	1843.36
METHA 2	1644.59
METHA 3	455.96
METHA 4	783.77
METHA 5	1688.59
METHA 6	1270.61
METHA 7	1766.38
METHA 8	1948.37
METHA 9	1035.23
DF 1	839.66
DF 2	593.1
DF 3	532.45
DC 1	639.28
DC 2	894.33
DC 3	396.29
DC 4	434.38
DC 5	498.81
DC 6	513.88
OD 1	271.92
OD 2	413.83
OD 3	618.28

Table A7 Contents of organotin cations of the samples.

Sample	Mono-Butyltin (cation) [µg OZK/kg DW]	Di-Butyltin (cation) [µg OZK/kg DW]	Mono-Phenyltin (cation) [µg OZK/kg DW]	Tri-Butyltin (cation) [µg OZK/kg DW]	Mono-Oktyltin (cation) [µg OZK/kg DW]	Tetra-Butyltin (cation) [µg OZK/kg DW]	Di-Phenyltin (cation) [µg OZK/kg DW]	Di-Oktyltin (cation) [µg OZK/kg DW]	Tri-Phenyltin (cation) [µg OZK/kg DW]	Tri-Cyclohexyltin (cation) [µg OZK/kg DW]
METHA 1	38	34	<1	160	<1	59	<1	2.3	1.4	<1
METHA 2	110	95	<1	460	3.9	120	<1	9.8	8.9	<1
METHA 3	62	51	3.5	360	1.6	61	<1	2.6	2.8	<1
METHA 4	77	62	4.2	310	1.9	74	8.1	4.8	7.7	<1
METHA 5	130	88	2.9	450	3.6	120	1.8	6.6	10	<1
METHA 6	100	85	<1	910	1.8	97	<1	5.2	1.3	<1
METHA 7	180	110	4.6	630	4.3	110	1.3	7.9	11	<1
METHA 8	98	81	<1	380	2.6	110	<1	6.8	1.8	<1
METHA 9	100	97	1.5	360	3	77	<1	5	2.8	<1
DF 1	5	68	1.4	340	1.3	72	1.9	2.5	11	<1
DF 2	65	63	3.8	380	1.3	40	2	2	6.3	<1
DF 3	25	30	<1	200	<1	25	<1	1.2	1.4	<1
DC 1	41	56	<1	210	< 1	20	<1	2.7	1.5	<1
DC 2	180	140	<1	670	5.1	31	<1	4.9	1.6	<1
DC 3	19	32	<1	89	1.1	2.4	<1	1.7	< 1.0	<1
DC 4	34	55	<1	420	1.6	8.4	<1	2.9	< 1.0	<1
DC 5	25	36	<1	110	1.4	6.9	<1	3.1	< 1.0	<1
DC 6	28	47	<1	160	1.6	16	<1	2.1	< 1.0	<1
OD 1	36	39	<1	170	< 1	2.2	<1	1.5	< 1.0	<1
OD 2	40	44	<1	160	1.1	2.5	<1	1.5	1.2	<1
OD 3	62	84	<1	650	1.9	8.4	<1	2.2	4	<1

Table A8 Contents of dioxins and furans of the samples.

Sample	ΣPCDD/PCDF (I-TEQ NATO/CCMS) [ng/kg DW]	2.3.7.8-TetraCDD [ng/kg DW]	1.2.3.7.8-PentaCDD [ng/kg DW]	1.2.3.4.7.8-HexaCDD [ng/kg DW]	1.2.3.6.7.8-HexaCDD [ng/kg DW]	1.2.3.7.8.9-HexaCDD [ng/kg DW]	1.2.3.4.6.7.8.-HeptaCDD [ng/kg DW]	OctaCDD [ng/kg DW]	OctaCDF [ng/kg DW]
METHA 1	46	2	3	2.5	7	5.8	92	760	1100
METHA 2	81	3.3	5	4.3	14	9.5	160	1300	2200
METHA 3	53	2.8	3.8	2.4	8.4	6.2	95	720	1300
METHA 4	51	2.5	3	2.5	8.3	6.3	100	850	1400
METHA 5	65	2.9	3.9	4.1	12	8.2	140	1100	1600
METHA 6	55	2.5	4	3.7	9.8	7.3	120	940	1300
METHA 7	69	2.8	5.9	5	14	5	140	1100	1900
METHA 8	103	17	6.8	7.8	22	14	210	1400	2400
METHA 9	61	3.2	4.5	4	11	8.4	120	980	1500
DF 1	51	3.2	3.5	2.5	9.2	6.2	100	840	1200
DF 2	43	2.1	2.9	2.4	8.1	5.7	84	680	1000
DF 3	36	1.5	1.9	<2	6.4	4.6	66	530	890

Continuation Table A8

Sample	**2.3.7.8-TetraCDF [ng/kg DW]**	**1.2.3.7.8-PentaCDF [ng/kg DW]**	**2.3.4.7.8-PentaCDF [ng/kg DW]**	**1.2.3.4.7.8-HexaCDF [ng/kg DW]**	**1.2.3.6.7.8-HexaCDF [ng/kg DW]**	**1.2.3.7.8.9-HexaCDF [ng/kg DW]**	**2.3.4.6.7.8-HexaCDF [ng/kg DW]**	**1.2.3.4.6.7.8-HeptaCDF [ng/kg DW]**	**1.2.3.4.7.8.9-HeptaCDF [ng/kg DW]**
METHA 1	28	31	25	81	51	11	35	310	84
METHA 2	44	48	46	140	87	18	58	570	150
METHA 3	28	35	30	92	57	11	36	350	93
METHA 4	28	34	28	86	51	11	38	360	97
METHA 5	36	41	36	120	63	15	47	450	120
METHA 6	30	36	31	92	60	10	40	370	98
METHA 7	39	44	38	120	69	14	51	500	120
METHA 8	44	54	48	160	88	18	64	650	160
METHA 9	33	39	33	110	61	10	43	410	110
DF 1	24	34	28	90	51	8.7	37	340	92
DF 2	21	29	24	78	40	7.6	32	280	80
DF 3	19	24	21	66	34	7.7	27	250	66