Assessment of DDT and metabolites contamination of the Teltow Canal (Berlin) and polymer-induced desorption experiments

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Selbständigkeitserklärung

Hiermit versichere ich, die vorliegende Dissertation eigenständig und ausschließlich unter Verwendung der angegebenen Hilfsmittel, angefertigt zu haben. Alle Aussagen innerhalb der vorliegenden Arbeit, welche dem Wortlaut oder dem Sinne nach aus anderen Quellen entnommen wurden, einschließlich solcher aus elektronischen Medien, sind im Text kenntlich gemacht und befinden sich in einem vollständigen Verzeichnis.
Die vorliegende Arbeit ist in dieser oder anderer Form zuvor nicht als Prüfungsarbeit zur Begutachtung vorgelegt worden.

Datum und Unterschrift

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Summary

Even some 50 years after the ban of DDT in Europe and North America, DDT and its metabolites are still posing a severe problem due to the environmental persistence. According to the Stockholm Convention DDT is one of the “Dirty Dozen”, supposed to be phasing out in 2020. Industrial production sites and their surroundings still exhibit a high risk of contamination in recent years.

During the mid-1990´s a survey of different aquatic ecosystems revealed background information about the degree of contamination in North-East (NE) Germany, including the Arkona Basin in the Baltic Sea. The applied analytical approach provided basic data on trace metals and organic contaminants such as PCDD/F´s, PAH´s, PCB´s, DDX and HCH´s. The optimising of the analytical tool and extension to include non-extractable residues into the assessment led in combination with a non-target screening approach to the identification of the point source (Berlin-Chemie) at the Teltow Canal. Recent research activities have focused on this area contaminated by the effluents from this point source. Surface sediments, sediment cores, surface and ground water samples were extensively analysed and identified more than 30 different metabolites of DDT, among other pesticides and various industrial compounds.

As a result, in the 1990´s about 135,000 m^{-3} of contaminated sediment (approximately 180,000 t) were removed by dredging. The remaining sediment has been investigated with regard to the contamination state. Due to the improved water solubility of DDA through the polar carboxyl group, it is one of the best water-soluble DDT metabolites. The assessment of the maximum contamination potential in relation to DDX (in particular DDA and its precursor metabolites) was considered. Furthermore, the incorporation of metabolites into sediment was investigated by applying a five-step degradation procedure. Free available (**E**xtractable **F**raction) as well as easily (**E**asily **R**eleasable) and hardly available fractions of DDA and precursor metabolites were obtained and a maximum of 48 kg in the EF fraction (32 - 82 kg) and 1,360 kg in the ER fraction (11 – 4,010 kg) were estimated by application of a trapezoid model. Calculation using a column model resulted in 278 kg in the EF fraction (214 - 354 kg) and 9,800 kg in the ER fraction (250 - 29,000 kg). In both cases the mean values are applied and the variation is high, resulting in a very rough calculation. The comprehensive analysis scheme provides information on free accessible and potentially metabolised precursors also in the non-extractable residues (NER). This allows a quantitative assessment of the DDA contamination potential derived from DDT residues in the canal sediments close to the source. The remobilisation of sedimentary DDA under dynamic conditions such as dredging or shipping activities has been investigated. Hence, a high remobilisation and release potential of DDA was observed. The vast majority of the available DDA content has been released immediately resulting in a direct contamination potential for the aquatic environment.

Several precursor metabolites of DDA, e.g. DDD and DDMS, extractable from the sediment organic matter (SOM), revealed a high potential for a long-term formation of DDA, especially in the easily

releasable fraction (via hydrolysis) with a mean concentration of up to 11,000 µg g^{-1} dry sediment. The resulting DDA-contamination potential represents a significant contamination risk for the groundwater from a downstream waterworks area and by remobilisation into the whole ecosystem and adjacent rivers.

The application of the presented methods provides a tool for a quantitative assessment of the long-term release potential of DDA and similar compounds under different scenarios by a comprehensive analysis of contaminated sediments (and soils). This approach can be transferred to contaminants that are also characterised by a complex metabolism accompanied by NER-formation and, in combination with toxicological data and bioavailability tests, represents a more advanced and detailed evaluation approach.

This thesis should demonstrate the necessity to investigate not only extractable residues of sedimentary contamination but to consider the incorporation of contaminants and metabolites in particulate matter as well. Non-extractable residues in sediments can represent a long-term contamination potential for the environment. In most studies, the remobilisation of NER and their transformation reactions were widely neglected. In addition, released compounds can be transported to distant locations due to sorption on particles and colloids. The transport of released sedimentary compounds to the aquatic environment is neglected in literature as well.

An analytical approach resulting from the experience of the work is presented, where a distinction is made between the water phase and various particulate phases, including humic substances. The applied degradation scheme is integrated in the scheme. These separate extracts can be used for bioassays.

Differences in the analytical approaches and degradation techniques lead to further scientific questions about the formation of NER and the constituents involved. Combined analytical approaches with classes of SOM components (such as lipids, humic substances) are possible and the kinetics and dynamics of the NER formation and release process can be studied.

Natural attenuation is underway. To complete the evaluation potential of the instrument, desorption and bio-accumulation experiments can provide insights into the actual and potential contamination by the accumulated sediments.

Comparable contamination data were obtained in comparison to previous studies, indicating a still high contamination level and, by calculating the maximum contamination range, a continuous release potential into the water phase and the canal ecosystem.

Besides natural particulate sorbents such as humic substances and natural organic matter, synthetic polymers and plastic particles are an additional particulate sorbent in aquatic ecosystems. Plastic is a general term for a class of materials that is composed of different types of (synthetic) polymers. Such materials own beside the polymer often different additives at a low content, which optimise or adjust the properties during processing and application.

Plastic particles including micro plastic are widely detected in the environment today. Micro contaminants, especially very persistent organic compounds, are also detected in large parts in the (aquatic) environment resulting in many recent papers, dealing with interactions between organic contaminants and (micro) plastic particles in the environment, hypothesizing the function of plastic particles as a vector for bio-magnification, resulting in negative ecosystem effects.

In the present work such interactions between polymers (polyethylene (LD-PE) and hard polyvinyl chloride (H-PVC) and organic, persistent compounds (here: DDT, methoxychlor and dicofol) were investigated. A new and innovative experimental approach based on a static system similar to a burial in deeper sediment layers was investigated.

With the presented sorption test, it was possible to demonstrate the adsorption/incorporation of contaminants into the two polymers. The recovery of the three target compounds ranged between 2.0 - 2.4 % of the initial concentration for PE and 0.2 – 1.9 % for PVC, respectively. Differences between the two polymers are addressed. In the sorption experiments all the target compounds were detected in alignment with their hydrophobicity, resulting in a relative order of DDT > DMDT > Dicofol.

In the desorption experiments, diffusion of the contaminants out of a contaminated sediment on the polymers could be verified. In maximum 22 µg Σ DDX (DDD/DDE/DBP and DDMS) could be desorbed within one month in the PE-experiment. Relative to published data of the International Pellet Watch project (IPW) 180-460 ng Σ DDX/g PE-polymer were analysed. These are in the range of other more contaminated sites, except for a few very highly sites.

Differences in polymers are analysed and explained mainly by the glassy transition temperature with subsequent flexibility at room temperature. All three aspects differentiating LD-PE and H-PVC in polymer structure, polarity and properties, free volume and contaminant behaviour are obvious.

The rapid formation of a biofilm on the polymer surface limits the sorption capacity, even with highly contaminated material and compared to pellets and fragments. The ATR-FTIR analysis of the surface layers of the 3-month containers led to the identification of a water-rich surface layer consisting of hydroxy and aromatic structures. The differences between the two plastic polymers meet expectations, based upon the different glass transition temperatures (Tg).

The new experimental desorption approach shows an easy to handle alternative means for sorption and desorption experiments with (plastic) polymers as well as kinetic experiments. The limited capacity of pure polymers is demonstrated in the sorption experiments, including antagonistic effects due to differences in hydrophobicity. These complex issues are routinely not addressed in simple kinetic lab-experiments with a single substance approach.

The rapid formation of diffusion barriers at the polymer surface limits the sorption capacity, even for the highly contaminated material, demonstrating a more realistic approach for naturally contaminated systems with a huge number of different compounds and possible antagonistic effects on sorption.

The very low sorption capacity means that the possibility of remediation by plastic polymer material is very low and, together with the natural organic matrix, it has no function as a transport vehicle in natural ecosystems. Further investigations are urgently needed to verify the postulated effect as a vector.

A monitoring programme is strongly recommended, especially in the heavily contaminated area near the point source, considering the use of the Johannisthal waterworks as a protective well for the incoming bank filtrate from the Teltow Canal. The analysis of micro plastic in the Teltow Canal ecosystem is currently underway and the relative proportion of anthropogenic contaminants in these analyses can provide information about the relative proportion of micro plastic as a transport vehicle.

Zusammenfassung

Auch rund 50 Jahre nach dem Verbot von DDT in Europa und Nordamerika stellt DDT und seine Metabolite aufgrund der Persistenz in der Umwelt immer noch ein ernstes Problem dar. Nach der Stockholmer Konvention gehört DDT zu dem "Schmutzigen Dutzend", die 2020 auslaufen sollen. Industrielle Produktionsstätten weisen in den letzten Jahren immer noch eine große Kontaminationsgefahr auf.

Mitte der 1990er Jahre ergab eine Untersuchung verschiedener aquatischer Ökosysteme Hintergrundinformationen über den Grad der Kontamination in Nordostdeutschland, einschließlich des Arkonabeckens in der Ostsee. Der angewandte analytische Ansatz lieferte grundlegende Daten über Spurenmetalle und organische Schadstoffe wie PCDD/F, PAKs, PCBs, DDX und HCHs. Die Optimierung des Analysenschemas und die Integration nicht extrahierbarer Rückstände in den Bewertungsansatz führte in Kombination mit einem Non-Target-Screening-Ansatz zur Identifizierung der Punktquelle (Berlin-Chemie) am Teltowkanal. Jüngste Forschungsaktivitäten konzentrierten sich auf dieses Gebiet, das durch die Abwässer dieser Punktquelle kontaminiert ist. Oberflächensedimente, Sedimentkerne, Oberflächen- und Grundwasserproben wurden umfassend analysiert und mehr als 30 verschiedene Metaboliten von DDT, neben anderen Pestiziden und verschiedenen industriellen Chemikalien, identifiziert.

Infolgedessen wurden in den 1990er Jahren etwa 135.000 m^3 kontaminiertes Sediment (etwa 180.000 t) durch Ausbaggern nahe der ehemaligen Grenze in Berlin entfernt. Das verbliebene Sediment wurde im Hinblick auf den aktuellen Kontaminationszustand untersucht. Aufgrund seiner erhöhten Wasserlöslichkeit ist DDA durch die polare Carboxylgruppe einer der besten wasserlöslichen DDT-Metabolite.

Die Bewertung des maximalen Kontaminationspotentials erfolgte im Hinblick auf DDA, wobei alle DDT-Metabolite und die Vorläufer Metabolite berücksichtigt wurden, die sich in DDA umwandeln können. Darüber hinaus wurde die Bildung von nicht-extrahierbaren Rückständen durch Einbau von Metaboliten in das Sediment unter Anwendung eines fünfstufigen chemischen Degradationsprozesses untersucht. Es wurden sowohl frei verfügbare (**E**xtrahierbare **F**raktion) als auch leicht (leicht freisetzbare = **ER**) und schwer verfügbare Fraktionen von DDA und Vorläufer Metabolite erhalten und maximal 48 kg in der EF-Fraktion (32 – 82 kg) und 1.360 kg in der ER-Fraktion (11 – 4.010 kg) durch Anwendung eines Trapezmodells ermittelt. Die Kalkulation mit einem Säulenmodell führte zu 278 kg in der EF-Fraktion (278 – 354 kg) und 9.800 kg in der ER-Fraktion

(250 – 29.000 kg). In beiden Fällen wurden die Mittelwerte angewendet und die Variation war hoch, was zu einer sehr groben Abschätzung führte.

Das umfassende Analyseschema liefert Informationen über frei verfügbare und potenziell metabolisierbare Vorläuferverbindungen, auch in den nicht-extrahierbaren Rückständen (NER). Dies ermöglicht eine quantitative Bewertung des DDA-Kontaminationspotenzials, das aus den sedimentären DDT-Rückständen abgeleitet wird. Die Remobilisierung von sedimentärem DDA unter dynamischen Bedingungen wie Bagger- oder Schifffahrtsaktivitäten sowie eine mögliche Rückhaltung von DDA im Boden des Infiltrationsgebietes des Wasserwerkes Johannisthal wurde untersucht. Dabei wurde ein hohes Freisetzungspotential von sedimentärem DDA ermittelt. Der überwiegende Teil der verfügbaren DDA-Gehalte wurde sofort freigesetzt, was zu einem direkten Kontaminationspotential für die aquatische Umwelt führt.

Mehrere Vorläufer Metabolite, z.B. DDD und DDMS, die aus der organischen Substanz im Sediment (SOM) extrahierbar sind, zeigten ein hohes Potential für eine langfristige Bildung von DDA, insbesondere in der leicht freisetzbaren Fraktion (durch Hydrolyse) mit einer mittleren Konzentration von bis zu 11.000 µg g^{-1} trockenem Sediment. Das daraus resultierende DDA-Bildungspotential stellt ein erhebliches Kontaminationsrisiko für das Grundwasser eines flussabwärts gelegenen Wasserwerksbereiches und durch Remobilisierung in das gesamte Ökosystem und die angren-zenden Flüsse dar.

Die Anwendung der vorgestellten Methoden bietet ein Werkzeug für eine quantitative Bewertung des langfristigen Freisetzungspotenzials von DDA durch eine umfassende Analyse verschiedener Szenarien aus kontaminierten Sedimenten (und Böden). Dieser Ansatz lässt sich auf Kontaminanten übertragen, die ebenfalls durch einen komplexen Metabolismus mit NER-Bildung gekennzeichnet sind, und stellt in Kombination mit toxikologischen Analysen und Bioverfügbarkeitstests einen fortgeschrittenen und detaillierteren Bewertungsansatz dar.

Die vorliegende Arbeit soll die Notwendigkeit aufzeigen, nicht nur extrahierbare Rückstände sedimentärer Verunreinigungen zu untersuchen, sondern auch den Einbau von Kontaminanten in die organische Matrix zu berücksichtigen. Nicht extrahierbare Rückstände (NER) in Sedimenten können ein langfristiges Kontaminationspotential für die Umwelt darstellen. In den meisten Studien wurden die Remobilisierung von NER und ihre Umwandlungsreaktionen weitgehend vernachlässigt. Darüber hinaus können freigesetzte Verbindungen durch Sorption an Partikeln und Kolloiden an entfernte Orte transportiert werden. Auch der Transport von freigesetzten sedimentären und partikulären Verbindungen in der aquatischen Umwelt wird in der Literatur vernachlässigt.

Es wird ein aus den Erfahrungen der Arbeit resultierender analytischer Ansatz vorgestellt, bei dem zwischen der Wasserphase und verschiedenen partikulären Phasen, einschließlich Huminstoffen, unterschieden wird. Das angewandte Degradationsschema ist in den Ansatz integriert. Die separaten Extrakte können für Biotests verwendet werden.

Unterschiede in den analytischen Ansätzen und Abbaumethoden führen zu weiteren wissenschaftlichen Fragen über die Bildung von NER und die beteiligten Prozesse. Kombinierte analytische Ansätze mit Klassen von SOM-Bestandteilen (wie Lipide, Huminstoffe) sind möglich und die Kinetik und Dynamik des NER-Bildungs- und Freisetzungsprozesses kann untersucht werden.

Die natürliche Degradation der eingetragenen Kontaminanten ist fortgeschritten. Zur Vervollständigung des Evaluierungspotenzials des Instruments können Desorptions- und Bioakkumulationsexperimente Einblicke in die tatsächliche und potenzielle Kontamination durch die akkumulierten Sedimente geben.

Es wurden vergleichbare Daten relativ zu früheren Studien gewonnen, die auf einen nach wie vor hohen Kontaminationsgrad und durch die Berechnung des maximalen Kontaminationspotenzials auf eine kontinuierliche Freisetzung in die Wasserphase und das Kanalökosystem hinweisen.

Neben natürlichen partikulären Sorptionsmitteln wie Huminstoffen und natürlicher organischer Substanz, sind synthetische Polymere und Kunststoffpartikel ein zusätzliches partikuläres Sorptionsmittel in aquatischen Ökosystemen.

Kunststoff ist ein allgemeiner Begriff für eine Materialklasse, die sich aus verschiedenen Arten von (synthetischen) Polymeren zusammensetzt. Solche Materialien besitzen neben dem Polymer oft verschiedene Additive in einem geringen Gehalt, die die Eigenschaften bei der Verarbeitung und Anwendung optimieren oder einstellen.

Kunststoffpartikel, einschließlich Mikrokunststoffe, werden heute in der Umwelt weithin nachgewiesen. Mikrokontaminanten, insbesondere sehr persistente organische Verbindungen, werden ebenfalls in großen Teilen in der (aquatischen) Umwelt nachgewiesen, was zu vielen aktuellen Arbeiten geführt hat, die sich mit den Wechselwirkungen zwischen organischen Kontaminanten und (Mikro-)Kunststoffpartikeln in der Umwelt befassen und die Funktion von Kunststoffpartikeln als Vektor für die Biomagnifikation, die zu negativen Auswirkungen auf das Ökosystem führt, hypothetisieren.

In der vorliegenden Arbeit wurden solche Wechselwirkungen zwischen Polymeren (Polyethylen (LD-PE) und Hartpolyvinylchlorid (H-PVC) und organischen, persistenten Kontaminanten (hier: DDT, Methoxychlor und Dicofol) untersucht. Ein neuer und innovativer experimenteller Ansatz, der auf einem statischen System basiert, das eine Akkumulation in tieferen Sedimentschichten simuliert, wurde untersucht.

Mit dem vorliegenden Sorptionstest konnte die Adsorption/Inkorporation von Kontaminanten in die beiden Polymere nachgewiesen werden. Die Wiederfindung der drei Zielverbindungen lag zwischen 2,0 - 2,4 % der Ausgangskonzentration für PE und 0,2 - 1,9 % für PVC. Die Unterschiede zwischen den beiden Polymeren werden angesprochen. In den Sorptionsexperimenten wurden alle eingesetzten Kontaminanten in Übereinstimmung mit ihrer Hydrophobie nachgewiesen, was zu einer relativen Reihenfolge von DDT > DMDT > Dicofol führte.

In den Desorptionsexperimenten konnte die Diffusion von Verbindungen aus einem kontaminierten Sediment auf den Polymeren verifiziert werden. Maximal 22 µg Σ DDX (DDD/DDE/DBP und DDMS) konnte im PE-Experiment innerhalb eines Monats desorbiert werden. Relativ zu veröffentlichten Daten des International Pellet Watch Projekts (IPW) wurden 180 - 460 ng Σ DDX/g PE-Polymer analysiert. Diese Gehalte liegen im Bereich anderer, stärker kontaminierter Standorte, mit Ausnahme einiger weniger sehr stark kontaminierter Lokalitäten.

Die Unterschiede bei den Polymeren wurden registriert und hauptsächlich durch die Glasübergangstemperatur mit resultierender Flexibilität bei Raumtemperatur erklärt. Alle drei Aspekte, die PE und PVC in Polymerstruktur, Polarität und Eigenschaften wie freiem Volumen und Kontaminantenverhalten differenzieren, wurden offensichtlich.

Die rasche Bildung eines Biofilms an der Polymeroberfläche schränkt die Sorptionskapazität selbst bei dem stark kontaminierten Sedimentmaterial und im Vergleich zu Partikeln, Fasern und Fragmenten ein. Die ATR-FTIR-Analyse der Oberflächenschichten der 3-Monatsbehälter ergab die Identifizierung einer wasserreichen Oberflächenschicht, die aus Hydroxy- und Aromaten-Strukturen bestand.

Die Unterschiede zwischen den beiden Kunststoffpolymeren entsprechen den Erwartungen, basierend auf den unterschiedlichen Glasübergangstemperaturen (Tg). Der neue experimentelle Desorptionsansatz bietet eine einfach zu handhabende Alternative für Sorptions- und Desorptionsexperimente mit Kunststoffpolymeren sowie für Kinetik-Experimente. Die begrenzte Kapazität reiner Kunststoffpolymere wurde in den Sorptionsexperimenten demonstriert, einschließlich antagonistischer Effekte aufgrund von Unterschieden in der Hydrophobie. Diese komplexen Fragen werden in einfachen kinetischen Laborexperimenten routinemäßig nicht behandelt.

Aufgrund der raschen Bildung von Diffusionsbarrieren an der Oberfläche der Polymere ist die Sorptionskapazität auch bei stark kontaminiertem Material begrenzt. Dies ermöglicht einen realistischeren Ansatz für natürlich kontaminierte Systeme mit einer großen Anzahl verschiedener Kontaminanten und möglichen antagonistischen Effekte auf die Sorption.

Die sehr geringe Sorptionskapazität bedeutet, dass die Sanierungsmöglichkeit durch Kunststoff-Polymermaterial sehr gering ist und relativ zur natürlichen organischen Matrix keine Funktion als Transportvehikel in natürlichen Ökosystemen darstellt. Weitere Untersuchungen sind dringend erforderlich, um den postulierten Effekt als Vektor zu verifizieren.

Ein Monitoring Programm wird dringend empfohlen, insbesondere in dem stark kontaminierten Bereich in der Nähe der Punktquelle, vor allem vor dem Hintergrund der Nutzung des Wasserwerks Johannisthal als Abwehrbrunnen und zur Wasserhaltung für das einströmende Uferfiltrat aus dem Teltowkanal. Die Analyse von Mikrokunststoffen im Ökosystem des Teltowkanals ist derzeit im Gange und der relative Anteil anthropogener Kontaminanten in diesen Analysen kann Aufschluss über den relativen Anteil von Mikrokunststoffen als Transportvehikel geben.

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List of Abbreviations (the acronyms refer to the 4,4´-structure of the compounds)

ACS	American Chemical Society
ATR-FTIR	Attenuated Total Reflectance Fourier-Transformation Infrared Spectroscopy
BMBF	Federal Ministry of Education and Research
CSIA	Carbon-stable isotope analysis
DBP	2,2-Bis(chloro)benzophenone
DDA	2,2-Bis(chlorophenyl)acetic acid
DDCN	2,2-Bis(chlorophenyl)acetonitril
DDD	2,2-Bis(chlorophenyl)-1,1-dichloroethane
DDE	2,2-Bis(chlorophenyl)-1,1-dichloroethylene
DDEt	2,2-Bis(chlorophenyl)ethane
DDM	2,2-Bis(chlorophenyl)methane
DDMS	2,2-Bis(chlorophenyl)-1-chloroethane
DDMU	2,2-Bis(chlorophenyl)-1-chloroethene
DDNS	2,2-bis(p-chlorophenyl)ethane
DDNU	2,2-Bis(chlorophenyl)ethene
DDOH	2,2-Bis(chlorophenyl)-ethanol
DDS	2,2-Bis(chlorophenyl)sulfide
DDT	2,2-Bis(chlorophenyl)-1,1,1-trichloroethane
DDX	Sum of different 2,4´- and 4,4´-substituted congeners of DDT
DOC	Dissolved Organic Matter
EC_{50}	Half maximal effective concentration
GC x GC	2 dimensional Gaschromatography
GC/MS	Gaschromatography/Mass Spectrometry
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexanes
HRMS	High Resolution Mass Spectrometry
K_{OM}	Distribution coefficient organic matter
K_{OW}	Distribution coefficient octanol-water
LC-HRMS	Liquid Chromatogratography High Resolution Mass Spectrometry
LDPE	Low density polyethylene
LLBB	Federal Lab for Environmental Monitoring Berlin-Brandenburg
MDA	2,2-Bis(methoxy)acetic acid
MDB	2,2-Bis(methoxy)benzophenone
MDD	2,2-Bis(methoxy)-1,1-dichloroethane
MDE	2,2-Bis(methoxy)-1,1-dichloroethylene
MDT	2,2-Bis(methoxy)-1,1,1-trichloroethane
MOM	Macromolecular Organic Matter
MSFD	Marine Strategy Framework Directive
MS/MS	Tandem Mass Spectrometry
NCI	Negative Chemical Ionisation in Mass Spectrometry
NER	Non-extractable residues
NIST	National Institute of Standardisation (USA)
NOEC	No effect concentration
OCP	Organochlorine pesticides
PAH	Polycyclic Aromatic Hydrocarbons
PBT´s	Persistent Bioaccumulative Toxic Substances
PCB	Polychlorinated Biphenyls
PCDD/F	Dibenzo-p-dioxins and -furans

POP´s	Priority Organic Pollutants
POM	Particulate Organic Matter
PPCP	Pharmaceutical and Personal Care products
PVC	Polyvinyl chloride
SOM	Sedimentary Organic Matter/Sorbent Organic Matter
TED-GC/MS	Thermal-Extraction-Desorption Gaschromatography-Mass Spectrometry
T_{eq} acute LC_{50}	Toxicological equivalent of lethal concentration 50
TGA	Thermo-Gravimetrical-Analysis
TIC	Total Ion Chromatogram
TOC	Total Organic Matter
TOF-MS	Time of Flight Mass-Spectrometry
WFD	Water Framework Directive

Chapter 1. Introduction and scope of the dissertation

1.1 Introduction

Water is the elixir of life. Anthropogenic activities lead to the contamination of lakes, rivers, groundwaters and oceans. Natural substances (faecal indicators such as coprostanol, coprostanone; alkanes, and proteins) and anthropogenic substances (e.g. POP´s, PBT´s) were detected in the environment (Takada and Eganhouse 1998). More than 100 compounds should to be analysed in a single GC-MS analysis (Yunker et al.2014). Even the application of high-tech analysis such as multidimensional GC-MS (GC x GC – MS) reveals new compounds and metabolites not identified before (Manzano et al. 2013).

Aquatic sediments are the water archives and offer along with the hydrology through the geochronology a detailed memory of the water under undisturbed conditions (Zhang et al. 2018, Zalewska et al. 2020). They are thus sinks and can become sources during remobilisation (e.g. by flooding, professional shipping or excavation) (Fredrickson et al. 2003, Miller et al. 2010, Cho et al. 2010). In ecosystems it is warranted to investigate all systems components for a source and sink analysis (Roussiez et al. 2006, Smit et al. 2010, Combi et al. 2020) (see Figure 1.1). Differences in contamination patterns and behaviour through variable sources can be analysed and lead to a comprehensive view of the processes (Maletic et al. 2019, Kurek et al. 2019, Patel et al. 2019).

Beginning with the industrial revolution/production in the 19th century, the chemicals cocktail in the environment led to changed material cycles and modified microbiology. It started in 1831 with the synthesis of chloroform (Defalque and Wright 2000) and especially after the Second World War with the conversion of warfare agent production to pesticides and artificial fertilizers (see Figure 1.5). More than 167 million different chemicals are currently registered (Chemical Abstract Service of the American Chemical Society; 2020). Most anthropogenic substances do not have a counterpart in the geo-biosphere and cause changes in the material cycles or are transported in them (Schwarzbauer 2006).

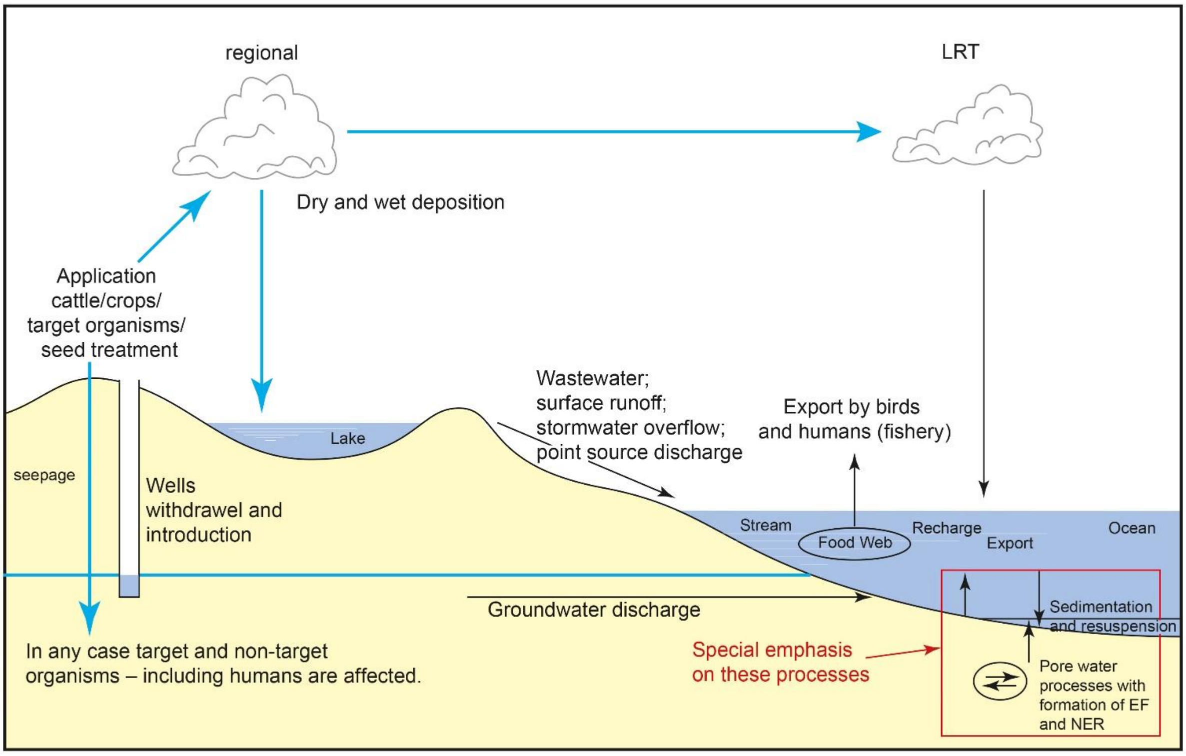

Figure 1.1: Scheme illustrating the sources and sinks for pesticides and contaminants (e.g. PPCP´s, PCB´s, PAH´s) in the environment including sources and sinks. The scheme concentrates on the topics of the dissertation with special emphasis on the sediment related processes (see extended box in the lower right).

Pesticides such as DDT were applied on crops during and after the second world war in the 1940´s and dispersed within all ecosystems (see Figure 1.1) and are still used in vector control against malaria (WHO 2019). Especially the decades of persistence of DDT have caused different patterns of distribution and accumulation in the environment, even if they are all distributed in the same way in particulate or dissolved form through air, water, soil, sediment and biota. The different persistence should be analysed and addressed to gain an understanding of the acute (bioavailable), chronic and long-term toxicity through the release of not actually bioavailable compounds via degradation of sorbents (Vasseur, Cossau-Leguille 2006, Chopra et al. 2011, Wang et al. 2019). The scheme in Figure 1.1 illustrates various fates through the application of pesticides (spray, granulate or seed treatment) and includes additionally the production as a contamination source for soil, groundwater and surface water with sediments. Through the direct application to plants or animals, the whole site is affected and additionally other areas via drift and the water cycle with a subsequent deposition and long-range transport on ecosystems not intended to spray/apply (US-EPA 2020) (https://www.epa.gov/reducing-pesticide-drift/introduction-pesticide-drift). Surface waters and oceans become contaminated unintentionally through the run-off from application areas and through the drift. Sediments act as a sink with burial in deeper layers (Taylor et al. 2019). Through resuspension and pore water diffusion, they serve as a potential source (Heim et al. 2005;

Miller et al. 2010). Differences in partition and conservation of compounds in the environment play a major role in the cycle of pesticides (Eganhouse et al. 2018).

The role of the climate shows a very retarded degradation in cold ecosystems relative to tropical/subtropical ecosystems (Ruus et al. 2010, Niu et al. 2018).

First publications on toxicology and ecosystem effects of DDT appeared in 1946/47 (Michelbacher et al. 1946, Linduska 1947) and especially through the egg shell thinning of the Bald Eagle (Ratcliffe et al. 1967, Faber and Hickey 1970, Cooke 1973, Peakall et al. 1973, Bowerman et al. 1995, Dykstra et al. 2019) combined with sophisticated analytical tools (e.g. capillary GC-columns and mass-sprectrometry) and increased public interest led in part to the establishment of environmental conventions (e.g. OSPAR and Stockholm Convention) and resulted in the EU Water Framework Directive and Marine Strategy Directive (Directives 2000/60/EC and 2008/56/EC). In 1972, the milestones were set for the establishment of the US-EPA and Germany Environment Agency and later the WFD/MSFD, which are implemented in national regulations such as the German Surface Water Ordinance (german Oberflächengewässerverordnung).

In routine analysis within these guidelines (EPA analytical methods, WFD, MSFD), only certain key parameters are analysed, e.g. twelve indicator congeners for PCB´s of a total of 209 theoretical congeners (EPA method 8082a – 2007). Of the PCDD/F´s with 75 and 135 congeners, respectively, only the 2, 3, 7, 8-substituted congeners are covered. In the case of polycyclic aromatic hydrocarbons, only 24 are routinely analysed (Commission Regulation (EU) 2011, extended by EPA-PAH compounds not included in the Commission Regulation), although this group comprises several hundred compounds (Howsam and Jones 1998). The same applies to pesticides such as HCH and DDT, where as a rule only five or six isomers and metabolites are analysed (Directive 2013/39/EU). Only the immediately bioavailable part of the contaminants is detected by extraction with solvents (Harwood et al. 2012). Due to the formation of non-extractable and bound residues, a large part of the contaminants becomes available only after degradation of the organic matrix, partly only after cleavage of the covalent bonds (Eschenbach et al. 1998). Chemical degradations are applied for this purpose (Gevao et al. 2000).

1.2 Natural Polymers

Natural polymers are proteins, starches, carbohydrates, cellulose, chiton, natural rubber and humic substances.

Non-extractable bound residues are essential for a comprehensive understanding of the transformation and distribution processes in the environment (Kästner et al. 2016). In risk management, the metabolites and the individual binding forms of the contaminants shall be considered. Transformation and transfer within the food web leads to bio-accumulation in fish and a potential contamination of food (Czub et al. 2008).

The chemical interactions of persistent bio-accumulative and toxic substances (PBT´s) with natural polymers in sediments and soils may result in strong binding and slow subsequent release rates that significantly affect remediation rates and endpoints. The underlying physical and chemical processes or phenomena potentially responsible for this apparent sequestration of PBT´s by natural polymers are only partially understood (Zhu et al. 2020). Recent observations suggest that PBT´s interactions with natural polymers comprise different organic and inorganic surfaces and matrices, and distinctions may be drawn along these lines particularly with regard to the roles of inorganic micropores (clay minerals or oxide coatings), natural sorbent organic matter components (SOM), combustion residue particulate carbon (soot), and spilled organic liquids. Definitely, SOM is not evenly distributed over all solid phases and not universally treatable as a well-defined organophilic phase with Δ K_{om}, as more than an order of magnitude difference in calculated fit between K_{om} and solubility or K_{ow} is recognised (Eganhouse and Pignatello 2008). Partition-like interaction with a "microscopic non-polar organic environment" is occurring with a humic membrane-like polar hydrophilic exterior structure and non-polar hydrophobic interior. The definitions are given in Figure 1.2, illustrating a vast variation of sorption interaction potentials for water soluble and particle-bound compounds. Plastic polymers (and micro plastic) serve as an additional particulate matter, not yet included into the scheme.

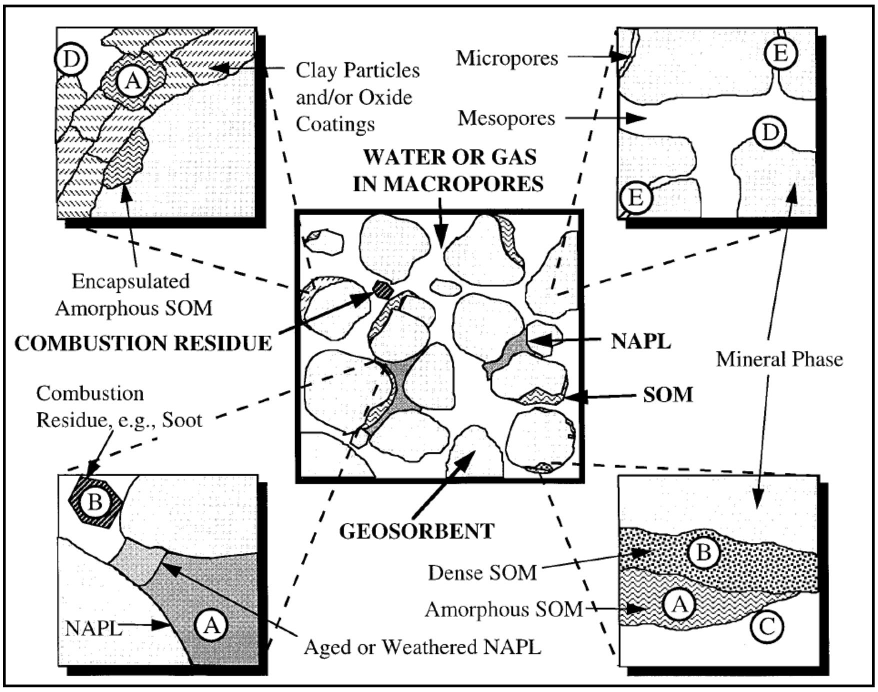

Figure 1.2: Definitions of natural polymers properties according to Luthy et al. (1997). Conceptual model of natural polymers = geosorbents. The circled letters refer to representations of the specific sorption mechanisms. The natural polymers include different forms of sorbent organic matter (SOM), combustion residue carbon particles such as soot, and anthropogenic carbon including non-aqueous phase lipids (NAPL).

The cases are: A - Adsorption into amorphous of “soft” natural organic matter; B - Absorption into condensed or “hard” organic polymer matter or combustion residues (e.g. soot); C - Adsorption onto water-wet organic surfaces (e.g. heterogeneous organic surfaces); D - Adsorption to exposed water – wet mineral surfaces (e.g. quartz); E - Adsorption into micro voids or microporous minerals (e.g. zeolites) with surface water at saturation < 100%. Details about the sorption isotherms and the processes are given in Luthy et al. 1997.

Important for the microbial degradation are the strength of the bonding and the degree of incorporation into the geopolymers. Toxicological effects are reduced due to a limited bioavailability of bound pollutants resulting in a higher persistence and modified degradation fates relative to laboratory model systems. Sequential chemical treatments are applied to selectively release compounds depending on the character and strength of incorporation. (Gevao et al. 2000, Kronimus et al. 2006, Zhu et al. 2019, Zhu et al. 2020).

The actual model of formation of non-extractable residues (NER) is illustrated in Figure 1.3 showing different release potentials due to the mode of incorporation. Physical entrapment and strong adsorption are reversible and covalently bound compounds are only released through covalent-bondage cleavage.

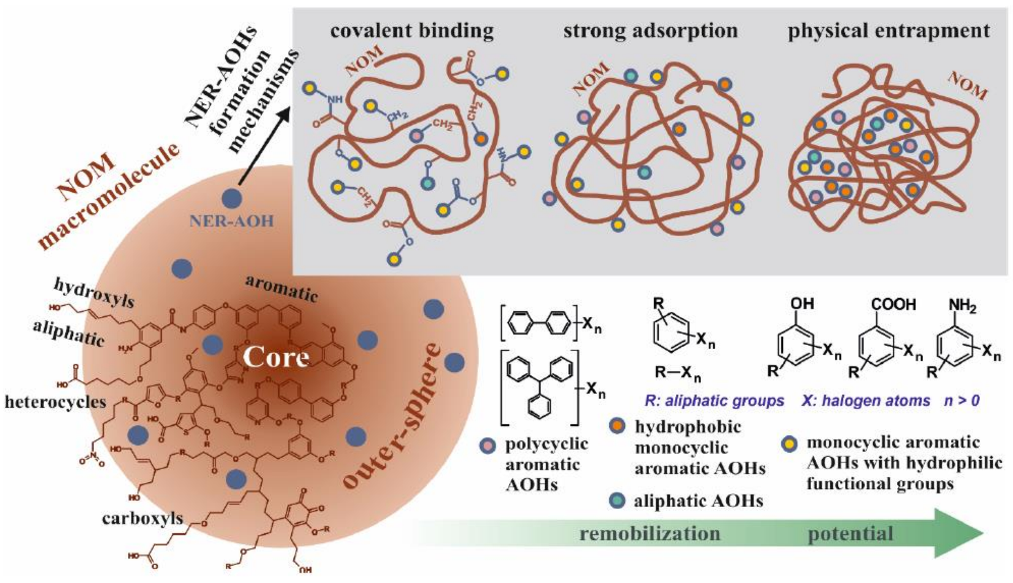

Figure 1.3: Processes of the formation of NER according to Zhu et al. 2020.

Through a comprehensive analysis, possible persistencies in the environment can be unambiguously determined, which are not represented in laboratory experiments under simple conditions. It is absolutely necessary and sensible to get a better/extensive understanding of the system. In the course of conversions in the water body (e.g. by extreme discharges, dredging measures, construction measures) the hydraulic conditions change and can lead to a remobilisation of the sediment-bound contaminants, including the pore water. As many metabolites as possible should be analysed to monitor the degradation of parent compounds and to illustrate the environmental path and the degree of metabolism. Geochronology including pore water analysis illustrates the contamination history (if not disturbed) and the pore water analysis displays release gradients out of the sediment or into the sediment. All processes should be considered and included in the risk assessment of the contamination. Important is the knowledge about the degradation of DDT in alignment with the Stockholm Convention on POP´s and the production history at the source – covering the co-contamination by other products (Pignatello et al. 2010, Eganhouse et al. 2018).

1.3 International legal requirements for monitoring

The Stockholm Convention

Most of the recalcitrant pollutants with public relevance and attention are the Dirty Dozen, regulated by the Stockholm Convention in 2004 (to be phased out in 2020) and by the EU WFD in 2002 (actually 33 priority substances plus 3 are regulated and a new list coming up including SCCA and BFR). DDT is also regulated by the OSPARCOM, ANNEX 34, ST2.

The priority organic pollutants (POP´s) are by definition organic compounds, which are highly halogenated and subsequently resistant to chemical, biological or photochemical degradation. They are passing readily through the phospholipid structure of biological membranes and accumulate in fat deposits in organism with the tendency to biomagnification through the food chain of ecosystems. Despite their bio-accumulation, an increased geo-accumulation rate is shown due to their high environmental stability, particle affinity and lipophilicity. Physical properties of greatest importance are typical water solubilities below 100 mg L^{-1}, a low vapour pressure < 100 Pa and a high $\log K_{ow}$-value ≥ 4 - > 9 (Blüthgen 2009).

All POP´s of the Stockholm Convention share the same molecular properties: high toxicity, persistence, evaporation into the air and travel subsequently long distances with a cold-trapping in higher altitudes and the arctic zones. The bio-accumulation is characterised by logKow ≥ 5 or BCF ≥ 5000 and a Taq acute LC50 ≤ 1 mg L-1, long-term NOEC ≤ 0.1 mg/L or a Tmammalian CMR or chronic toxicity.

The time scale of chemicals falling under the Stockholm Convention since 2004 is illustrated in Figure 1.4.

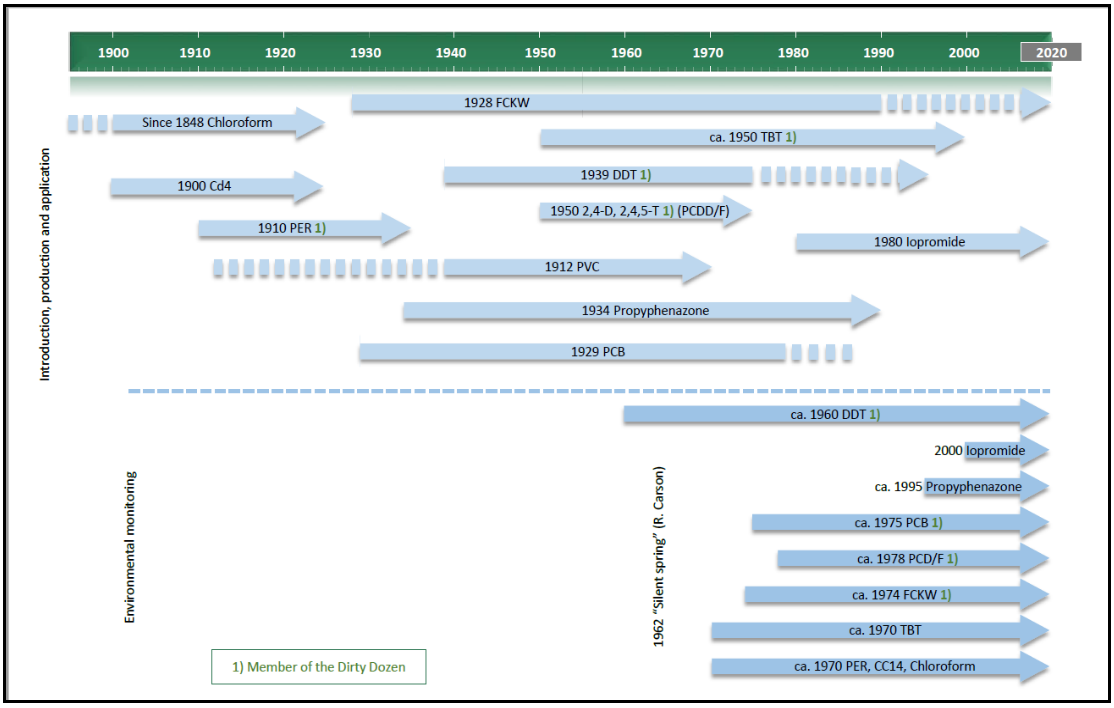

Figure 1.4: Timescale of the introduction and persistence of POPs, partially regulated by the Stockholm Convention (after Schwarzbauer 2006).

Due to the long-lasting nature they exist for years to decades (centuries) coming along with very slow rates of degradation into less harmful metabolites, posing up a legacy for next generations for more than a century (see Table in section 2.2 with current level data for DDX).

One of the most well-known representatives and well-studied compounds is DDT and its metabolites and analogues – Dicofol and DMDT). Figure 1.5 illustrates the invention and phasing out of DDT in Europe from 1939 until the 2020, with a peak at the end of the 1960´s – early 1970´s. DDT is still detected in many environmental compartments that currently represent a contaminated site (Kurek et al. 2019, Kivenson et al. 2019).

The annual production rates reached 40,000 tons worldwide in the early 1940´s. It was widely applied during World War II to protect troops and civilians from the spread of typhus and malaria, switching to agricultural applications and vector control in post-war times for hygienic purposes, such as malaria and typhus (WHO 1989, Heberer and Dünnbier 1999). Before 1970, 80% of the production (some 1 million tons since 1940) were used for treating cotton in the USA and for treating cereals and top fruits in Europe. DDT is still being produced in China, India, Mexico and North Korea in amounts of about 4,000 tons per year (Blüthgen 2009). DDT is additionally applied in antifouling paints in China (Lin et al. 2009). 2, 4´-DDD was produced and applied in human and veterinary medication as antineoplastic medicine (trade name: Lysodren).

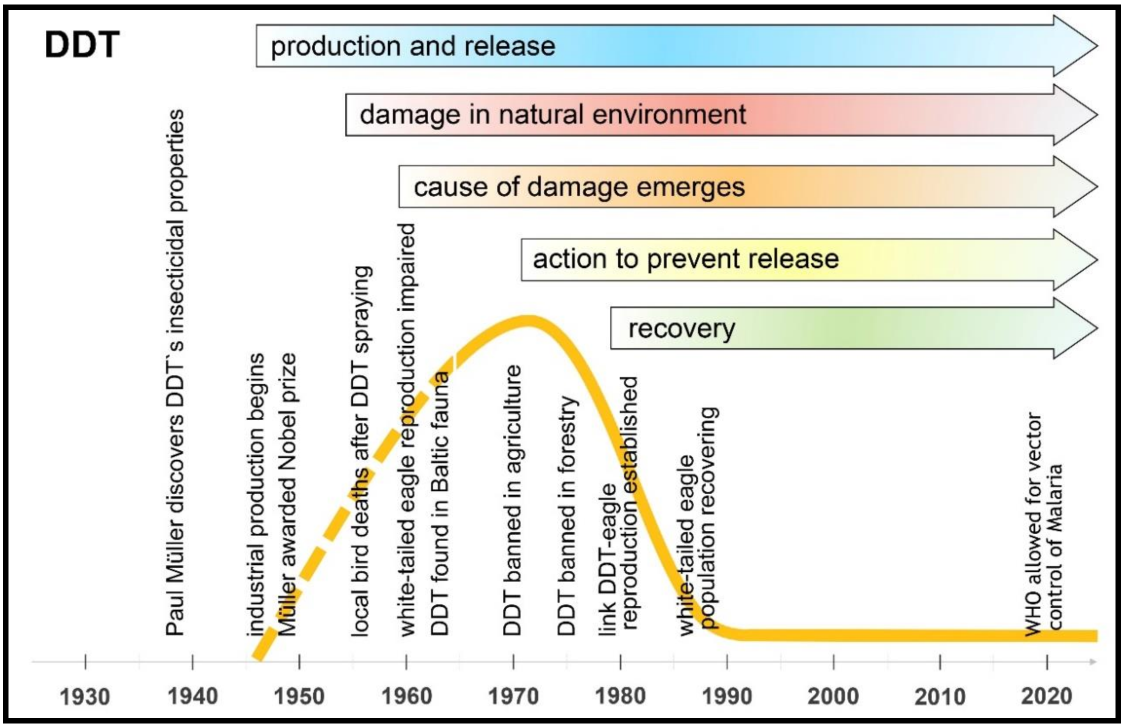

Figure 1.5: Historic overview of the DDT production and concern in Europe (Blüthgen 2009).

1.4 Scope of the dissertation

During the monitoring activities of the (West)-Berlin authorities in the 1980´s (Heinisch et al. 2005), a heavy contamination of SPM, sediments and eel from the Teltow Canal was discovered. Buchert et al. 1982 detected near the former border in West-Berlin in sediment samples of the Teltow Canal taken in 1979/1980 elevated concentrations of PCT (Polychlorinated Terphenyls with 54 % Cl), PCB (formulations A30/50/60), 4,4´-Methoxychlor, 4,4´-DDD, 4,4´-DDT, 4,4´-DDE, 4,4´-DDMU, 4,4´-DBP, CB´s and HCH´s, supported by elevated concentrations in Lake Griebnitz at the lower end of the Teltow Canal (Schwarzbauer et al. 2001, Ricking, M. 2003, unpublished). The analysis of non-extractable residues in grab samples resulted in a higher degree of contamination, not detectable by conventional solvent-extraction (Schwarzbauer et al. 2003). The addition of sequential chemical degradation methods to the conventional analysis gives information about the mode of incorporation of contaminants into the SOM and about the potential release behavior under different environmental conditions. Compared to non-influenced samples from the Berlin area and outside Berlin (with concentrations ≤ 10 ng g^{-1} S-DDX; Schwarzbauer et al. 2001), the sediment at the Teltow Canal is highly contaminated.

The main hypotheses of the thesis are:

1) DDX is far more persistent in the environment than extrapolated from laboratory experiments and different sources of contamination (pesticide application vs. Industrial wastewater) result in different patterns of metabolites and co-compounds; addressed by data about NE-Germany concerning POPs and trace metals including geochronology (Chapter 3)
2) An extensive analytical approach is necessary for an evaluation of the degree of contamination and the release potential back into the aquatic ecosystem; addressed by application of the chemical degradation scheme for the evaluation of the degree of contamination and first approximations of the release potential (Chapter 4)
3) Plastic particles and polymers may act as a carrier of POP´s such as DDX but the relative contribution to the fate of POP´s has to be evaluated and analysed in more detail; addressed by application of a new approach for studying the transfer of POP´s into two polymers from contaminated sediment (Chapter 5)

The analysis scheme (see Figure 4.3) is applied to sediment cores, grab samples and is assisted by analysis of water and ground water samples. The transfer between different compartments including the formation of NER results in recommendations for a more realistic approach on a contaminated site, including preliminary experiments to evaluate the release pattern out of the sediment through diffusion and remobilisation due to shipping activities and remediation. Therefore, the geochronology, porewater and water samples are analysed in addition to sediment samples.

One of the topics of this thesis was to figure out the degradation pathway of DDX in the Teltow Canal sediments via a non-target approach to include potential oxygenated DDX-metabolites, published photoproducts or aerobic degradation metabolites such as hydroxy-DDX (EAWAG 2020).

Plastic particles, pellets and fibres are suggested as a carrier of organic contaminants and trace metals within an ecosystem and (finally) to the sea. The experiments were performed to examine the maximum distribution of DDX and related compounds in a simple experimental set-up with only water and contaminants at the water solubility of three compounds (DDT, DMDT and Dicofol), differing by a factor of 800 in water solubility (1 µg L^{-1} – 800 µg L^{-1}). The results gave a more detailed insight into the transfer behaviour to polymers, expected to be different to the natural organic material. Polymers are characterised by surface absorption (in assistance with biofilms) and a limited contribution of polymers is possible via diffusion into the” free space” (absorption), depending on the degree of crystallinity (amorphous vs. glassy state).

The more realistic set-up was the second part, exposing contaminated sediment with a low content of TOC (1.1%) to the polymer surface. In natural systems the ratio of SOM to polymer is roughly calculated to be 1: 10^7-10^8: (Koelmans et al. 2016). The analysis includes both adsorption on the surface (including the biofilm) and diffusion into the "free space" of the polymer (absorption).

1.5 Areas of research of this thesis

The investigation area is NE-Germany with the last application in 1983/84 against *Lymantra monacha* L. (nun moth caterpillar) represented in the sampling locations except the Arkona Basin with a special focus on the contamination source (production site - TC) (see figure 1.6). To get background information about the degree and pattern of contamination through the direct application of the pesticide and the surface run-off into streams and lakes, and ultimately into the ocean, a set of sediment cores was analysed for a set of organic contaminants and trace metals, assisted by geochemical data and dating of the sediment cores (see chapter 3).

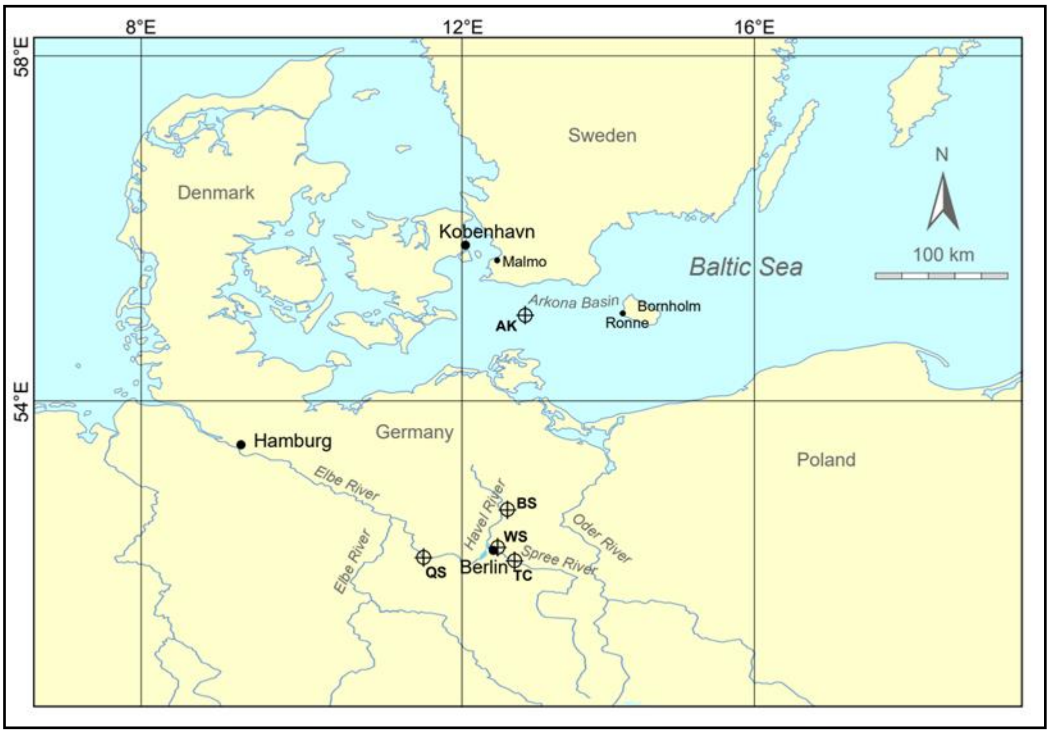

Figure 1.6: Map of the investigation area in NE-Germany with the sampling locations for dated sediment cores. Legend: (AK = Arkona Basin; BS = Lake Bugsinsee; QS = Lake Quenzsee; WS = Lake Weissersee; TC = Teltow Canal).

The waste water from the production site led to a contamination of the Teltow Canal (TC) and the Spree River including Lake Rummelsburger See (Reifferscheid et al. 2013; M. Ricking, unpublished) (see Figure 1.7).

1.5.1 Site description of the Teltow Canal

The Teltow Canal was built between 1901 and 1906 (http://www.wsa-b.de/) to connect the Dahme/Spree-River System with the Havel River (see figure 1.7).

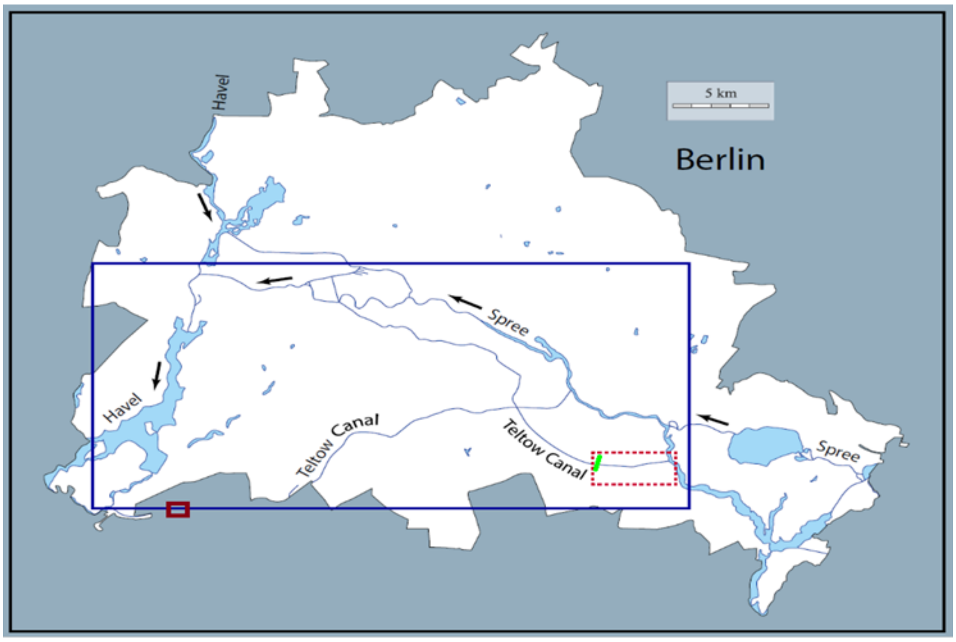

Figure 1.7: Map of the Teltow Canal connecting the Dahme and Havel River. The red rectangle marks the main investigation area at the Teltow Canal. The small red brackets locate the lock at Kleinmachnow.

The canal has a total length of 35 km and is characterized by a very slow flow (Q = 12 $m^3 s^{-1}$; 16 cm s^{-1}) and a gradient of 2 mm per km (http://www.wsa-b.de/). The average depth is 2 m with an average width of 50 - 60 m and parts of the near-bottom sediments are characterised by anoxic conditions at the sediment-water interface. Due to professional shipping activities, the main stream consists almost exclusively of sandy material at the surface.

Figure 1.8: View of the Teltow Canal at the inflow of the point source (photo: M. Ricking 2018).

The lock in Kleinmachnow (see Figure 1.7) regulates the shipping activity and hosts the gauge. In Table 1.1 the mean data for 2006 – 2015 are summarised. The mean discharge for the time period is 8.97 $m^3\ s^{-1}$ with the lowest mean discharge of 0.55 $m^3\ s^{-1}$ and the highest mean discharge of 23.4 $m^3\ s^{-1}$. The extremes are also given in the Table.

Table 1.1: Hydrological data for the Teltow Canal 2006 - 2015 (http://www.wsa-b.de/) at the lock in Kleinmachnow [$m^3\ s^{-1}$].

Teltow Canal Km	Lowest Low water discharge	Highest High-water discharge	Low water discharge	Mean Low water discharge	mean discharge	mean high water discharge	High water discharge
8.42	0.00	38.3	0.554	2.90	8.97	14.8	23.4

Using the data shown in Table 1.1 above, the transit time for a virtual particle of 8 days is roughly calculated. In fact, the passage time is extended by the shipping activity, which leads to a back and forth movement within the waters. Measurements of the German EA in 2019 showed almost no flow velocity near the measuring station Kleinmachnow in Brandenburg. The water quality parameters for 2000 – 2019 (April – October) at station 414 are: pH between 6 – 8, oxygen saturation 0 – 11 mg L^{-1} (minimum in June/July and maximum in April), conductivity 64 – 1,350 µS $cm^{-1}$with a mean of ~ 950 µS cm^{-1}, and water temperature between 7 – 22 °C (minimum in June/July and maximum in April) (https://www.berlin.de/senuvk/umwelt/wasser/ogewaesser).

Today, the canal is characterized by the fact that the sewage treatment plants in Waßmannsdorf, Ruhleben and Stahnsdorf discharge high percentages of sewage treatment plant effluents (WWTP) into the canal, as a result of which up to 50 % of the water is discharged into the canal in summer (~ 500,000 m^3 d^{-1}). The bank filtration is used by the waterworks Johannisthal and Beelitzhof at Lake Wannsee for groundwater enrichment. Due to remediation measures in the years 1994-1999, parts of the contaminated sediments were removed at the former border (see Figure 1.7).

The affected area by the point source is marked with the red rectangle. The spread of the wastewater was caused by the partial flow direction reversal of the Teltow Canal to the eastern side, which flows into the Rummelsburger See (Reifferscheidt et al. 2013) and the Spree River, which carries the contaminants into the Havel River (https://www.fgg-elbe.de/fgg-elbe.html; at Sophienwerder).

The production history is explained in more detail in the Annex. A short overview is presented here. The well-known source (Berlin-Chemie) produced DDT between 1949 and 1984 and until 1989 γ-HCH. In addition, HCB and methoxychlor were synthesised for about 10 years from 1973-1988, respectively. During the cleaning of the "production facilities", the plant site and the adjacent Teltow Canal were heavily contaminated with products and intermediates.
Since 1973, only 2 DDT formulations have been produced locally, the last time in the mid 1980´s (1983/84).
The production of crop protection products started during World War II in the early 1940´s (Schering Corporation), HCH followed in 1945. Dicofol was also produced locally (personal communication Dr. Beyer, Menari Corporation, 2007), no production information is available.

1.6 Main chapters of the dissertation

The main chapters are oriented according to the development of the analytical tools, combined with a non-target GC-MS screening approach and the proceeding analyses of different ecosystem parts, especially at the Teltow Canal. During the work, the analysis tools were optimised and applied to different ecosystem compartments.

Chapter 2 DDT compound

In chapter 2 information about the physico-chemical parameters of DDT and related compounds are presented along with an overview of current data related to sediment contamination by DDT. The degradation scheme is illustrated and some information about the toxicology of some metabolites and site-specific data are presented. Additional non-target screening results (tentatively identified) are given in Appendix B.

Chapter 3 (published in Marine Pollution Bulletin, 50, 1699-1705)

Ricking, M., Koch, M., Rotard, W. 2005: **Organic pollutants in sediment cores of NE-Germany: Comparison of the marine Arkona Basin with freshwater sediments**

The focus of the first publication is to present an overview of the degree of contamination of sediments with DDX and related compounds in NE-Germany where the last application was in 1983/84 and to provide an overview of the contaminants especially detected at the Teltow Canal in the solvent extractable fraction. A non-target screening resulted in the identification of a huge number of different DDX-compounds beyond the routinely analysed 6 isomers (2,4´- and 4,4´-DDT/DDD/DDE). The geochronology of the contamination is documented via radionuclide dating of the sediment cores and a detailed analysis of a set of halogenated compounds, PAC and trace metals. The core taken at the Teltow Canal revealed the highest contamination by various halogenated compounds, especially via for DDX. It was a part of the Elbe-2000 Program funded by the BMBF, resulting in several publications in the early 2000´s. The analyses resulted in a more detailed analysis of the hot spot at the Teltow Canal, especially in the development and application of a sequential chemical degradation to include the NER-fraction into a risk assessment.

Contributions:

M. Ricking: Conceptualisation; Sampling; Preparation; Analysis of the POPs, Trace metals; Interpretation; Writing

M. Koch: Interpretation of the PCDD/F data; POPs data; Trace metal data (Chemometrics and Source Identification)

W. Rotard: Analysis of the PCDD/F

Chapter 4 (published in Journal Soils and Sediments, 21, 1275-1289)

Ricking, M. Frische, K., Schwarzbauer, J. 2021: **Sediment contamination of an urban canal– A case study approach for an integrated assessment of organic sediment contamination**

The focus of the second paper is a detailed assessment of sediment cores near the source for the extractable fraction and the non-extractable fraction (NER) while applying the developed analytical tools. The mapping revealed still contaminated sediment and the release potential is analysed by application of a sequential chemical degradation – extraction. The maximum contamination was investigated and indicators for a fate analysis are given. The anaerobic degradation was studied in more detail. The total DDA-formation potential was calculated and preliminary experiments indicate the release potential out of the sediment under anoxic and oxic conditions. Dicofol is detected only in water samples of a dated sediment core. The water phase is included in a more comprehensive overview of the degree of contamination.

Contributions:

M. Ricking: Conceptualisation; Sampling; Preparation, Extraction of the loosely bound fraction, Interpretation; Calculation of the Release Potential; Writing

K. Frische: Extraction of the Easy-Releasable Fraction; Analysis of the DDX-compounds; Release Experiments

J. Schwarzbauer: Interpretation; Co-Authoring

Chapter 5 (in final preparation for publication in Environmental Science and Pollution Research)

Ricking, M., Kerndorff, A., Obermaier, N., Zhu, X., Braun, U. & Bannick, C.G. 2022: **A simple model approach for the desorption of DDT and related compounds from contaminated sediment to plastic polymers**

The focus of the third paper is on the distribution of 3 DDX-related compounds (4,4´-DDT, 4,4´-DMDT and 4,4´-Dicofol) between polymers (PE, PVC) and the water phase at the highest concentration in pure water possible (at solubility). These experiments revealed the maximum “adsorption/distribution” on the surface and in the free space of the polymers in a simple experimental set-up. The second part of the experiment gave information about the distribution of compounds in a contaminated sediment relative to polymers. The contaminated sediments were exposed for up to 3 months in a static system to elucidate the contribution of polymers to the environmental fate. The focus was on the methodological approach.

Contributions:

M. Ricking: Conceptualisation; Sampling; Preparation, Extraction of the Containers and Water Phase; Analysis by GC-MS; Interpretation; Calculation of the Release Potential; Writing

A. Kerndorff: Sampling; Preparation and Performance of the Containers; Extraction of the Containers

N. Obermaier: Interpretation

X. Zhu: Analysis of the Contaminated Sedimentary

U. Braun: Conceptualisation; Interpretation of the IR-Spectra

C. Bannick: Interpretation

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DIRECTIVE 2008/56/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL; of 17 June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive); 1-31 https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1593613439738&uri=CELEX:52020DC0259

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Chapter 2. Chemistry of DDT and related compounds

2.1 DDT and Compounds

Artificial compounds (anthropogenic organ halogen compounds - AOHs) are introduced by man without a counterpart in the bio-geosphere (Zhu et al. 2020).

The first major identification of DDT as an environmental contaminant was initiated via the eggshell thinning of avian species at the end of the 1960´s (see chapter 1.1), referring especially to DDE, PCB and mercury.

In principle, DDT is used as a surrogate for a variety of compounds such as PCB´s with a di-halo-diphenyl backbone (such as methoxychlor, dicofol, perthane, metholochlor).

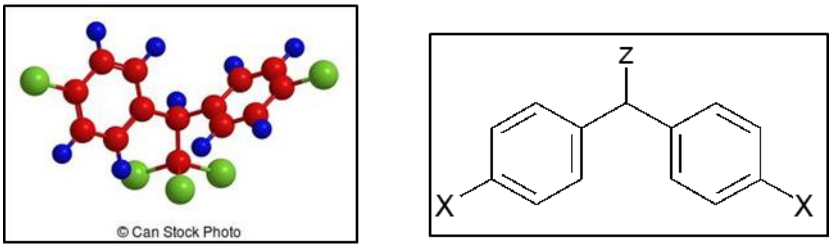

Figure 2.1: General formula of diphenyl-halogenated (X) compound with side chain (Z).
(Source: https://www.canstockphoto.com/ddt-molecular-structure-34228598.html)

The first synthesis was performed in 1874, DDT´s insecticidal properties were discovered in 1939 by the Swiss chemist Paul Hermann Müller (Ciba Geigy). DDT is synthesised via reaction of chloral (CCl_3CHO) with chlorobenzene (C_6H_5Cl) in the presence of sulfuric acid as catalyst (Blüthgen 2009) (see Figure 2.2).

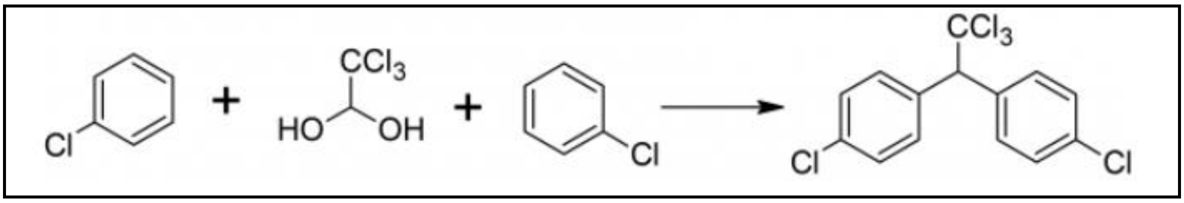

Figure 2.2: Synthesis of DDT (https://www.prepchem.com/synthesis-of-ddt).

Examples of trade names are Anofex, Cesarex, Clofenotane, 4,4´-DDT, Dicophane, Gesarol, Guesarol, Gyron, Neocydol and Zerdane.

DDT crystals are characterised by a high hydrophobicity, colourlessness and have a weak chemical odour. Due to its non-polar molecular structure (see Figure 2.4), it is highly soluble in fats, oils and organic solvents and almost insoluble in water. Due to the relatively low substitution selectivity of Friedel-Crafts acylation reactions technical DDT consists in varying percentages of 4,4´-DDT (up to 80%) and 2,4´-DDT (up to 21 %, see Tab. 2.1).

DDT was applied in the GDR in mixtures of pesticides (e.g. in combination with Dieldrin, Dicofol or γ-HCH) in an oily solution containing up to 17% of 4,4´-DDT. Tradenames of the formulated pesticides in the GDR were “bercema Aero-Super”, “bercema Spritz-aktiv” and “bercema Behosal” (Heinisch et al. 1993; only in german)

Although the toxicological risk is not limited to the main metabolites (Wetterauer et al. 2012), only very few studies have considered the wide variety of other metabolites and their contribution to the quantity and quality of DDT emissions (Schwarzbauer et al. 2001), so that despite the early detection of other metabolites, the overall degradation to CO_2 and H_2O has not yet been proven. A significant proportion of the real toxic potential is still underestimated. Only in the 1990´s the toxic enantiomer of 2,4'-DDT was identified as responsible for eggshell thinning in birds (Buser and Mueller 1995).

The organochlorine pesticide DDT exists with the general formula $C_{14}H_9Cl_5$ as 6 different isomers (2,2´-, 2,3´-, 2,4´-, 3,3´-, 3,4´-, 4,4´-) (see Figure 2.3 for the 4,4´-substitution), the main physico-chemical properties are summarised in Table 2.1

Table 2.1: Composition of technical DDT formulations.

2,2´-DDT	**2,4´-DDT**	**4,4´-DDT**	**2,4´-DDD**	**4,4´-DDD**	**4,4´-DDE**	**Additional compounds**	**Literature**
-	≤ 30	85	-	-	-		WHO 2009
0.1-1.0	8-21	63-77	-	-	-		WHO 1979
	17.5	79	0.35	1.2	0.2	Tris(4-chloro-phenyl)-methane	Buser and Müller 1995
	15.6	79	0.6	2.1	0.2	Tris(4-chloro-phenyl)-methane	Buser and Müller 1995
	19.0	66.7	-	0.3	-	Bis(p-chloro-phenyl)-sulfone (0.6)	Haller et al. 1945
	11.9	72.7	0.044	0.17	-	Bis(p-chloro-phenyl)-sulfone (0.034)	Haller et al. 1945

Methoxychlor (Bis(p-methoxyphenyl) tris(chloromethyl)methan) is another insecticide, quite similar in properties (see Figure 2.3) and was used to combat biting flies, houseflies, mosquito larvae, cockroaches, and chiggers. The application was realised on field crops, vegetables, fruits, stored grains, livestock, homes, gardens, lakes and marshes (ATSDR 2019). The technical mixture comprises 88-90 % of 4,4´-Methoxychlor, 4 % of 2,4´-Methoxyclor, 1.7 % of 1-methoxychlor-4

(1,2,2,2-tetrachlorethyl) benzene and 4,4´-Methoxychlor-olefin (MDE). The synthesis is carried out in a similar way to DDT by reaction of anisole and chloral in the presence of sulfuric acid or alumina chloride (Bionity 2020).

In addition, the acaricide dicofol, a hydroxylated derivative of DDT, is currently used in Europe, Turkey, Asia and the USA. Dicofol is synthesized by hydroxylation of DDT.

An overview on environmentally relevant properties of DDT and its main metabolites DDD and DDE is given in Tab. 2.2. However, such data have to be applied carefully. Recently, a review by Pontolillo and Eganhouse (2001) revealed a variation of published log K_{OW} for 4,4´-DDE in the range of 1-2 logK_{ow}-units.

Table 2.2: Summary of some physico-chemical data of DDT, DDD and DDE according to Lee et al. (1994; methoxychlor fact sheet and Dicofol fact sheet).

Compound	**DDT**	**DDE**	**DDD**	**DMDT**	**Dicofol**
Molecular Weight	354.5	318	320.1	345.7	370.5
Water Solubility [ppb at 25°C]	5.5 (4,4´-DDT) 26.0 (2,4´-DDT)	14.0 (4,4´-DDE)	20.0 (4,4´-DDD)	100 (4,4´-DMDT	800 (4,4´-Dicofol)
Vapor Pressure (mPa at 20/25°C)	0.0073 (4,4´-DDT) 0.055.0 (2,4´-DDT)	0.0 65.0 (4,4´-DDE) 0.062.0 (2,4´-DDE)	0.010.0 (4,4´-DDD) 0.019.0 (2,4´-DDD)	No data	1.87
LogK_{ow}	6.91	6.96	6.22	4.68-5.08	4.3
Log BCF (Fish)	4.52 (Fathead Minnow) 4.58	4.71 (Fathead Minnow) 7.26 Trout	5.24 (Estimate)	No data	No data

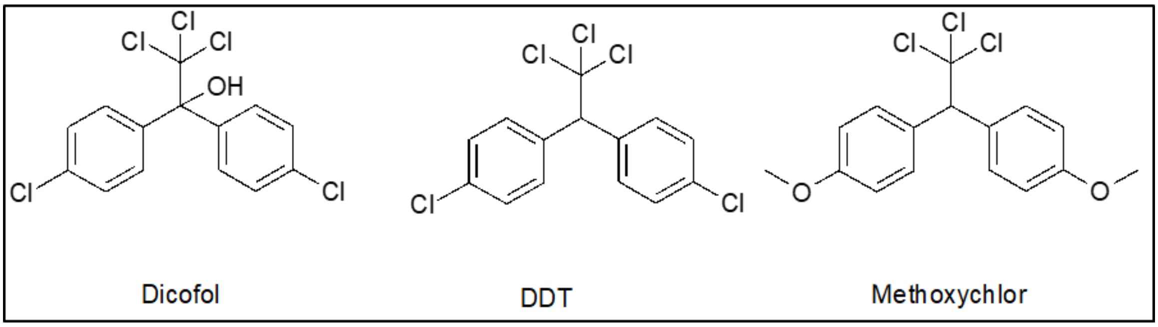

Figure 2.3: Molecular structure of DDT, an organochlorine insecticide. High structural similarity exists to further pesticides such as methoxyclhlor (insecticide) and dicofol (acaricide).

Methoxychlor was banned in the EU and USA in 2002/3.

The use of dicofol is restricted in the EU, USA, India and Australia. Its application in an antifouling coating for boats continues in China. The WFD established an annual Environmental Quality Standard (AA-EQS) for dicofol in the water phase for freshwater of 1.3 x 10^{-3} µg L^{-1} and 3.2 x 10^{-5} µg L^{-1} for marine water, respectively.

2.2 Current Levels of DDX-contamination worldwide with focus on production sites

DDT is still detected in very young sediment and suspended matter samples, reflecting decades of persistence in the environment (Kurek et al. 2019). Only recently, an offshore dumpsite in the deep basin at the Palos Verdes Shelf was inspected, indicating improper disposal of containers (Kivenson et al. 2019). Two sediment cores were analysed resulting in a very heterogeneous peak contamination of up to 257 µg g^{-1} Σ DDX, a factor of 40 greater than the highest surface sediment contamination at the Palos Verdes Superfund Site (Kivenson et al. 2019).
On June 12th, the ACS News Service Weekly PressPac recalled fifty years later, DDT still lingers in lake ecosystems.

An overview of current data is given in the Table 2.3, indicating there is still a legacy of DDT 50 years after the ban.

Table 2.3: Current data of the sediment contamination with DDT and metabolites [ng g^{-1} d.w.].

Location	**Matrix**	**4,4´-DDT**	**4,4´-DDD**	**4,4´-DDE**	**S-DDX**	**Reference**
Lake Weissensee, Berlin, Germany	sediment core				0.09-1597	Ricking et al. 2005
Teltow Canal, Berlin, Germany	sediment core				67.7-4163	Ricking et al. 2005
Teltow Canal, Berlin, Germany	sediment core	345 - 20620	3652 - 132676	1040 - 6725		Heim et al. 2005
Palos Verdes Shelf, USA	sediment		14200	28400		Liao et al. 2017
Palos Verdes Shelf, USA	sediment core	n.d. - 3130	69 - 7600	4120 - 42300	5420 - 91200	Kucher and Schwarzbauer 2017
Palos Verdes Shelf, USA	sediment core	96 - 11900	352 - 7410	3470 - 69300	6160 - 158000*	Kucher and Schwarzbauer 2017
Palos Verdes Shelf, USA	sediment core				7900 - 256000	Kivenson et al. 2019
Lauritzen Canal, USA	sediment				n.d. - 77000	Lee et al. 1994
Chinese Sea, China	sediment core	0 - 1600	0 - 950	0 - 120		Yu et al. 2011
Chinese Sea, China	sediment core	0 - 400	0.067 - 730	0 - 41		Yu et al. 2011
Chinese Sea, China	sediment core	1.0 - 12	0.86 - 7.3	0.68 - 4.3		Yu et al. 2011
Gulf of Naples	sediment	n.d. - 45.7	n.d.-81.4	n.d. - 4.03	n.d. - 131.13	Qu et al. 2018
Mediterranean Coast, Egypt	sediment				0.07 - 81.5	Literature cited in Qu et al. 2018
Cortiou, Marseille, France	sediment				2.01-255	Literature cited in Qu et al. 2018
Location	**Matrix**	**4,4´-DDT**	**4,4´-DDD**	**4,4´-DDE**	**S-DDX**	**Reference**

Keratsini harbour, Greece	sediment				9100 - 756000	Literature cited in Qu et al. 2018
Quanzhou Bay, China	sediment				0.21 - 7.83	Literature cited in Qu et al. 2018
Caspian Sea, All Neighbouring States	sediment	n.d. - 7.4			3.3 - 12	de Mora et al. 2004
Reservoirs in Texas and Boston, USA	sediment	n.d. - 13000			0.6 - 14080	van Metre et al. 2004
Lake Como, Italy	sediment	1 - 11	5 - 20	27 - 75	60 - 80	Bettinetti et al. 2016
Warsaw, Lakes, Poland	sediment	< 0.5 - 770	< 0.1 - 860	< 0.1 - 277	0.7 - 1990	Bojakoswka et al. 2018
Palos Verdes Shelf, USA	sediment				n.d. - 10007	Taylor et al. 2019
Palos Verdes Shelf, USA	sediment				108 - 90850	Taylor et al. 2019
Havel-Spree	surface sediment	n.d.	< 1 - 2900	3-180		Schwarzbauer et al. 2001
Teltow Canal	surface sediment	< 5 - 9700	9500 - 13000	3000 - 13000	48851 - 303860	Schwarzbauer et al. 2003

2.3 Degradation of DDT, DMDT and Dicofol in the environment

After release into the environment, DDT is mainly influenced by biotic transformation. The main degradation pathways under aerobic and anaerobic conditions have been intensively studied, published and combined in Wetterauer et al (2012). Usually, 3-/4-letter abbreviations are used to denote DDT metabolites. A detailed description of the anaerobic degradation pathway is shown in Figure 2.4 and can easily be summarised as follows:

1. Initial transformation processes affect the aliphatic moiety of the molecule forming de-halogenated intermediates with or without double bonds (DDD, DDE, DDMS, DDNS, DDMU, DDNU).

2. After dehalogenation a second group of metabolites is formed with functional groups at the position of the former trichloromethyl-group. These functional groups include hydroxyl-, carboxy- and nitrile-moieties (DDA, DDOH, DDCN).

3. Furthermore on biphenyl derivatives are formed by the loss of the 1-carbon atom forming either dichlorinated diphenylmethane (DDM) or dichlorinated benzophenone (DBP).

The principal degradation of DMDT follows the degradation of DDT. Identified metabolites are MDD, MDE, MDA and MDP (as analogous of DDT) (Schwarzbauer et al. 2001).

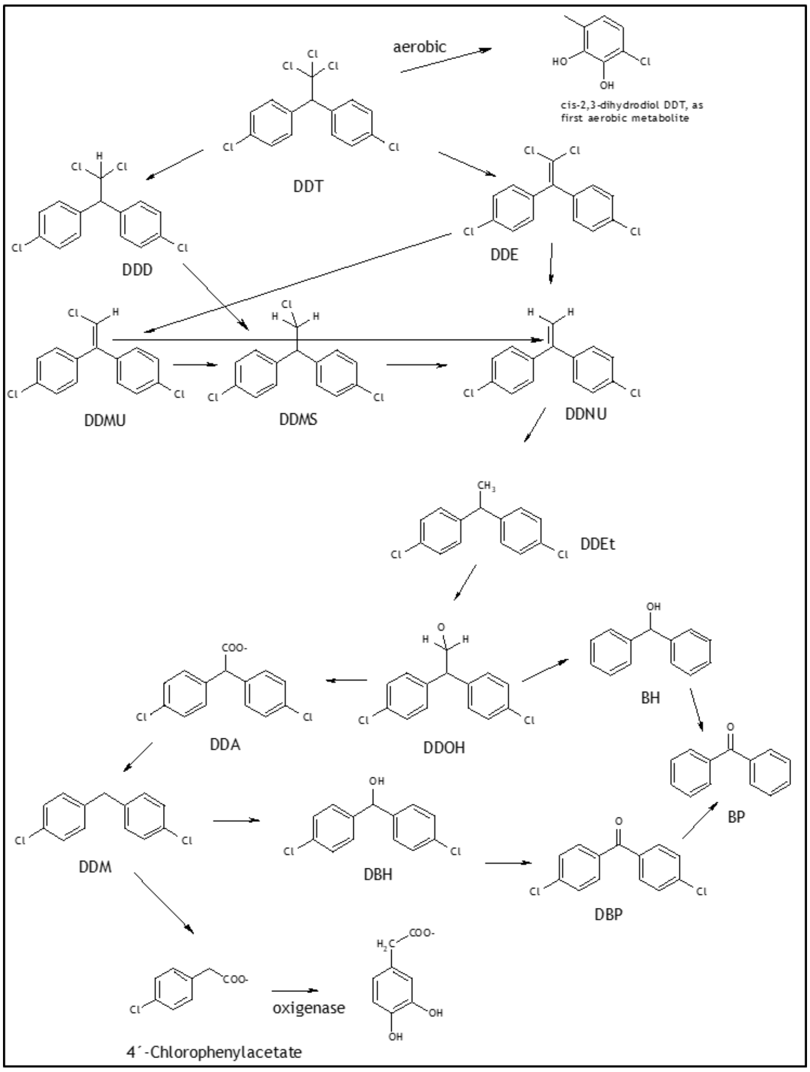

Figure 2.4: Simplified anoxic degradation pathways of 4,4´-DDT in aquatic systems (according to Sayles et al. 1997; Zeng and Venkatesan 1999; Eganhouse and Pontolillo 2008; Zook and Feng 2009 a,b,c,d; adapted by Ricking in 2011). The position of DDCN has only been partially enlightened through the direct pathway from DDT to DBP (Metcalfe 1973).

During all these anaerobic transformation processes the 2,4'- or 4,4'-substitution at the aromatic rings remains unaltered. The same accounts for the aerobic degradation pathway.

As the content and stability of the metabolites depend on the rate of formation and degradation, those metabolites with high formation rates but low degradation rates accumulate dominantly. Under anaerobic conditions the main metabolite is DDD, whereas under aerobic conditions DDE is the most representative metabolite, although the path has not been fully clarified and investigated.

For assessing the environmental mobility of DDT and metabolites, the knowledge on the chemical properties of the metabolites is an essential information. For example, all metabolites of the initial transformation processes under anaerobic conditions are highly lipophilic and tend to accumulate in particulate matter and biota. On the contrary, functionalized metabolites such as DDA have a higher polarity and thus a higher water solubility. Consequently, DDA has been identified and classified as a water relevant contaminant (Heberer and Dünnbier 1999, Frische et al. 2010). Further information on DDT and its environmental behaviour as well as its ecotoxicological and toxicological effects have been summarised by Zitko (2003) and are published in Wetterauer et al. 2012.

If the original isomeric composition is known, the change in isomeric ratios can be used to track these environmental processes. For DDT in particular, not only the 2,4' / 4,4' ratio itself, but also the modification of this parameter for the DDT metabolites has a high potential to track the environmental history of DDT contamination as a very key parameter (Kucher et al. 2019). For example, very little information is available on differences in isomeric persistence (Lichtenstein 1971; Fry and Toone 1981, Kucher et al. 2018). The interconversion of the isomers has been investigated early in the two possible directions from 2,4' -to 4,4'-DDX and vice versa (Abou-Donia 1968, Cranmer 1972). It is also noteworthy that it was recently shown that the ecotoxicological effects are different for the individual substitution positions in DDT. The 2,4'-isomer shows stronger estrogenic or anti-estrogenic effects compared to 4,4'-DDT (Wetterauer et al. 2012). Considering the fact that already in 1970 more metabolites were detected (Patil et al. 1970), only a few reports deal with DDA, DDOH, DDMS, DDNU etc. so far (Gossett 1988, Pereira et al. 1996) as DDX-metabolites in the environment. DDA was isolated from DDT in 1945 as a so-called universal metabolite. DDT is also easily converted into DDA by purely chemical reaction with zerovalent Fe or by photo-decomposition. Already in 1978 Marei et al. (1978) demonstrated DDA as an important metabolite in laboratory experiments when incubating DDT with sewage sludge. They also postulated the occurrence of DDA in the aquatic environment. Up to now only a few analyses have concentrated on the environmental fate of DDT and its metabolites. Pereira et al. 1996 additionally analysed DDMU, DDMS, DDNU and DBP. Although the principal breakdown products have been elucidated in the 1970´s (Patil et al. 1970; Albone et al. 1972; Jensen et al. 1972) and some metabolites have been tested for toxicity (Planche et al. 1979, Megharaj et al. 2000), toxicological and estrogenic data are still mostly missing.

The degradation of Dicofol in the environment is illustrated in Figure 2.5.

It resembles the degradation scheme of DDT with only one intermediate.

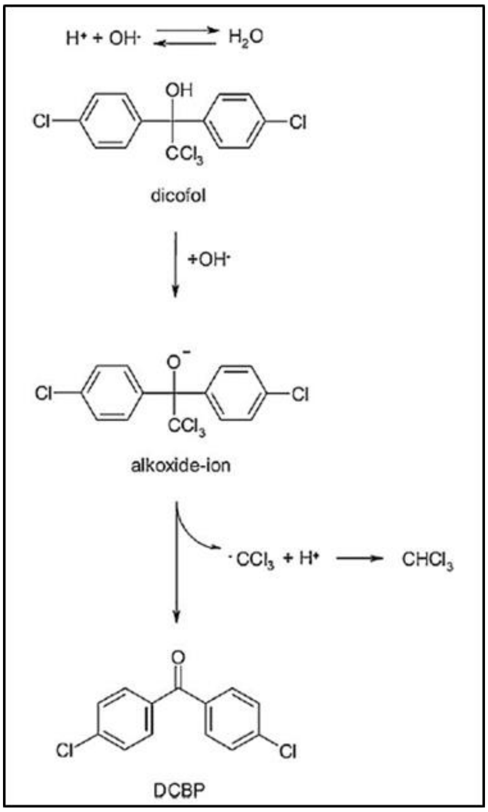

Figure 2.5: Degradation scheme of Dicofol (Thiel et al. 2011).

2.4 Toxicology and site-specific information about the Teltow Canal

Screening analysis of fish extracts (kindly provided by B. Pilz - LLBB) revealed only traces of DDMU and no further degradation metabolites due to the aerobic interior of the fish (Ricking, M. 2007, unpublished).

The acute toxicity of DDX compounds was low, the sediments exhibited acute toxicity by octameric sulphur due to the anaerobic conditions at the sediment-water interface (Svenson et al. 1998, Ricking et al. 2004). Two sediment samples with elevated DDX contents were included in the SCT project of the Federal Institute of Hydrology (Feiler et al. 2013), whereby no strong inhibition in nematodes and bacteria was detected.

Further investigations (algae test according to DIN 38412-L33 and *Daphnia magna* test according to DIN 38412, part 30) resulted in preliminary EC_{50} values of 0.23 mg L^{-1}, 24 mg $L^{-1}$and 16.4 mg L^{-1} for 4.4'-DDM, 4.4'-DDA and 4.4'-DBP in the algae test and 3.2 mg L^{-1}, 16.1 mg $L^{-1}$and 21.1 mg L^{-1}in the *Daphnia magna* test, respectively (U. Feiler 2018, personal communication). Toxicity tests of 4,4'-DDMU, 4,4'-DDMS, 4,4'-DDCN and 4,4'-DDA showed no dioxin-like activities in the RTL-W1 cells, but cytotoxic effects in the order of 2,4'-DDT > 4,4'-DDCN > 4,4'-DDMU > 4,4'-DDDMS > 4,4'-DDA. Endocrine effects occurred in the order of 2,4'-DDT > 4,4'-DDDMS > 4,4'-DDMU > 4,4'-

DDCN. 4,4'-DDA produced antiestrogenic effects. These effects represent a disturbance of normal reproductive and endocrine function in exposed organisms (Wetterauer et al. 2012).

Therefore, owing to the different effects on individual organisms and systems, a differentiation was actually made between the pure detection of a compound (contamination) and a measurable effect on biota (pollutant). In chapter 3 and 4 the original terminology was not updated.

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Chapter 3 Paper I

Organic pollutants in sediment cores of NE-Germany: Comparison of the marine Arkona Basin with freshwater sediments

Marine Pollution Bulletin
Volume 50, Issue 12, December 2005, Pages 1699-1705
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Chapter 4 Paper II

Sediment contamination of an urban canal: A case study approach for an integrated assessment of organic sediment contamination

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Chapter 5 Paper III

A simple model approach for the desorption of DDT and related compounds from contaminated sediments to polymers

5.1 Abstract

Plastics including micro plastic (MP) particles are widely detected in the environment today. Microcontaminants - especially very persistent organic compounds - are to a large extent also detected in the (aquatic) environment, which has led to a growing number of recent studies dealing with interactions between organic pollutants and (micro)plastic in the environment. The background of these investigations is the hypothesized function of plastic particles as a vector for bio-magnification, resulting in negative ecosystem effects.

In the present work, interactions between two common plastic polymers low density polyethylene (LD-PE) and rigid polyvinyl chloride (H-PVC) and three organic, persistent compounds, dichlorodiphenyltrichloroethane (DDT), methoxychlor (DMDT) and dicofol were investigated with a sorption test and desorption experiments. A new and innovative experimental approach based on a static system similar to a burial in deeper sediment layers was investigated. The experimental setup used additive-free plastic containers resulting in an easy to handle attempt instead of MP. It is assumed that the basic mechanisms of interaction are evaluated and material specific.

With the present sorption test, it was possible to demonstrate the adsorption/incorporation of contaminants into the two polymers. Differences between the two polymers are addressed. In the sorption experiments all the target compounds were detected in alignment with their hydrophobicity. In the desorption experiments, diffusion of the contaminants out of a contaminated sediment on the polymers could be verified. As expected, the sorption by PE was much higher. The differences between the two polymers meet expectations, based upon the different glass transition temperatures (Tg), and the polymer structure.

The simple approach is easy to handle and illustrates the limited sorption capacity of the two studied polymers. It eliminates possible sorption effects to glass walls and simulates the ecosystem situation of a multiple contaminant cocktail, usually not represented in laboratory experiments.

Keywords: polymers, transport vehicle, potential ad-/absorption, maximum loading, DDT, contaminated freshwater sediment, desorption into polymers

5.2 Introduction

First reports on plastic in the environment date back to the 1970´s (Carpenter et al. 1972, Colton et al. 1974). Macro plastic degrade into micro- and nano plastic particles and thus, plastic particles are reported in almost all ecosystem parts, even in deep-sea sediments (van Cauwenberghe et al. 2013, Woodall et al. 2014, Yao et al. 2019), remote marine gyres (Law et al. 2010, Maximenko et al. 2012, Pan et al. 2019), on remote islands (Crawford 2017, Schönlau et al. 2019) and in biota (Herzke et al. 2016). Very recently, the USA listed the topic (micro)plastic at position 2 of the most warranted research areas (Fairbrother et al. 2019).

Plastic is a general term for a class of materials that is composed of different types of (synthetic) polymers. Such materials own beside the polymer often different additives at a low content, which optimize or adjust the properties during processing and application.

In many publications, microplastic was sampled and analysed in general (Bannick et al. 2019, Duemichen et al. 2019) and for additives and contaminants adsorbed to the surface (Rios et al. 2010, Fernandez 2012, Crawford 2017, Camacho et al. 2019, Léon et al. 2019).

For this reason, many scientific papers are already dealing with the interactions between organic contaminants and (micro)plastic in the environment (e.g. Rochman et al. 2019, Laskar et al. 2019). The background of these investigations is the proposed function of plastic particles as a vector for bio-magnification, resulting in negative ecosystem effects. The applied research concepts and results provide very controversial information. The general approach is the use of microplastic powder for the distribution experiments (e.g. Bakir et al. 2014, Zhan et al. 2016, Hüffer et al. 2018, Liu et al. 2019). The ad/absorption of POP´s such as polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH) and Dichlorodiphenyltrichloroethane (DDT) is addressed in many scientific papers with the focus on plastic as a transfer vehicle to other ecosystems (Hartmann et al. 2017, Müller et al. 2018, Rochman et al. 2019).

For these experiments, previously manually isolated particles or model experiments on MP particles are performed, which lead to very different results. Due to the unspecific surface morphology and cryo-milling processes test specimen were taken for a better understanding of the model structure. In this case the interface is better defined and the permeation/penetration process is better evaluable.

These particles co-exist with suspended particulate matter, biota and sediments in a roughly calculated ratio of 1:10^7-10^8 (Koelmans et al. 2016). The relative contribution of plastic particles to the mass in suspended particulate matter is relevant for a realistic assessment of the role of microplastic as a vector (Bakir et al. 2016).

However, the range of plastic particles used and the respective shape vary greatly. The organic compounds used in the respective investigations are also subject to a wide range of variations. As far as small particles are used in water, the recovery of the loaded particles is relatively easy.

In the present study, which examines a contaminated aquatic sediment, a different approach was therefore pursued. Basically, it can be assumed that the same processes in organic matter work for the penetration into the free volume in microplastic and larger plastic structures. An amorphous polymer does not have an organized pattern in its molecular structure, whereas crystalline polymers show a regular line-up polymer molecule and are characterised by an ordered structure.

The concept of free volume is useful for explaining aspects of the chain mobility and permeability of polymers, even though its precise definition is subject to debate. Polymers that trap a large amount of interconnected free volume in the glassy state behave in many respects like microporous materials (Budd et al. 2005).

Permeation generally describes a process of mass transport of a molecule into or through a material (here: polymers). In order to be transported into the interior of polymers at all, the molecules must "dissolve" in the solid. The main mechanism of diffusion within a polymer is the "filling" of the free volume between the individual polymer chains. The "solution" in polymers is a thermodynamic process where the solubility is determined by the change in enthalpy of the solution of the respective molecule in the polymer matrix and the free volume available for occupation. A general assumption is that the surface reaches saturation at the time of exposure and the uptake rate is related to the diffusion rate of molecules adsorbed to the surface into the interior of the material (Duncan, et al., 2005).

A new approach is therefore chosen to bring the polymer (here: LD-PE and H-PVC) into contact with the organic compounds (here: DDT, methoxychlor – DMDT and dicofol) and to investigate a possible permeation into the polymer and desorption out of the sediment directly into the polymer. The advantage of this approach compared to the use of plastic in powder form is, for example, that no aggregates or conglomerates can occur in aqueous solution. The complex extraction of the microplastic particles from the sediment is not necessary, which could also have an influence on the distribution.

The distribution is mainly controlled by equilibrium partitioning and molecular diffusion (Mayer et al. 2000, O´Connor et al. 2016). The key process is the penetration of contaminants through the boundary layer (biofilm/coating) to the polymer surface and into the “free volume” within the polymer. Three important process parameters are the polarity of the polymer type, including fillers, the pores and voids, the free volume including temperature effects, as well as mechanical stress and possible irreversible absorption of the compound. The compound itself contributes to the processes with its solubility in the surrounding media, size and shape, concentration gradient in the media and degradation in the free volume in addition to the degree of sorption.

A differentiation between adsorption to the surface and absorption into the “free volume” of the polymer is necessary for assessing the short-time (adsorption) and long-time (absorption) release potential. Published boundary layer thicknesses are in the range of 10 – 100 µm (Berg et al. 1998, Smit et al. 2010, Fernandez et al. 2012, Endo et al. 2013).

In the present work, interactions between two very different polymers (here: polyethylene – LD-PE and polyvinyl chloride - H-PVC) and organic, persistent compounds (here: DDT, methoxychlor and dicofol) are investigated. PE is characterised by a glassy transition temperature at - 125 °C and PVC at ~ 85 °C (Pascall et al. 2005; Endo and Koelmans 2016).

The approach hypothesis is:

- DDT and related compounds are adsorbed on the surface and in the free volume of the polymer
- The maximum diffusion to the polymer is an indicator of the potential accumulation from the water phase
- After saturation of the ad- and absorption capacity, an equilibrium is reached between the surrounding phase and the polymer
- Sedimentary organic matrix is a concurrent sorbent relative to plastic material
- Antagonistic effects occur in multicomponent solutions
- The desorption is limited by the ad- and absorption capacity of the polymeric material

DDT and related compounds are examples of hydrophobic organic compounds such as PCBs, modern pesticides and PAH. It is possible to transfer the results to macro plastic and micro plastic particles while applying the same basic mechanisms.

The focus of the study is at first the distribution/permeation of 3 DDX-related compounds (4,4´-DDT, 4,4´-DMDT and 4,4´-Dicofol) between polymers (LD-PE, H-PVC) and the water phase at their maximum water solubility. These experiments give the maximum “adsorption/distribution” on the surface and in the “free volume” of the polymers in a simple experimental set-up. The experiment was conducted for 3 months along with the second experiment to assure an equilibrium distribution routinely achieved in hours to 10 days (EPA 2012). There was no formation of a biofilm/coating as indicated by a Raster Electron Microscope analysis (pictures not shown).

The second part of the experiment provides information on the distribution of the compounds in a contaminated sediment compared to polymers. The contaminated sediment was exposed in a static system for up to three months to demonstrate the contribution of polymers to the environmental behaviour of the compounds. The sediment, together with other pharmaceutical production chemicals, solvents and trace metals, was heavily contaminated with pesticide production wastewater for decades. The degradation of the initial effluents is proceeded, indicating a well-adapted microflora. This approach simulates burial in deeper sediment layers with pore water diffusion as a potential release process, besides the turbulence and resuspension caused by commercial shipping. The selected sediment was demonstrably analytically proven contaminated with all three different compounds used in the permeation experiment. Data for DMDT and metabolites were published in Schwarzbauer et al. 2001 and metabolites of Dicofol were published in Heim et al. 2005 for pore water samples. Dicofol itself was determined in these samples (data M. Ricking 2004, unpublished). All compounds used in the lab experiments were produced at the source.

To the best knowledge, only one publication treats the comparison of the adsorption of POPs (phenanthrene and pyrene) on polymers (PE, PS, PVC) and a sediment sample. The differences in TOC between polymers (> 80 % TOC) and sediment (10.4 % TOC) were addressed (Wang et al. 2019), resulting in a much higher sorption capacity of microplastic relative to the natural sediment. With increasing aqueous concentrations, the distribution coefficients of phenanthrene for the natural sediment decreased, leading to a lower release of the initially sorbed phenanthrene relative to the MP.

5.3 Material and Methods

5.3.1 Chemicals and containers

The PE and PVC containers (1 L) were purchased from Bürkle (Karlsruhe, Germany) and Roth (Karlsruhe, Germany), respectively, and pre-cleaned with demineralised water (aqua demin.) and solvents to remove production residues. All standards were of high purity (> 98 – 99 %; LGC Promochem, Wesel, Germany) and the solvents (ethyl acetate, n.-hexane, methanol, acetone) were of picograde quality (LGC Promochem, Wesel, Germany). The weight of the PE containers without lid is 93.4 g and the weight of the PVC containers is 53.4 g.

5.3.2 Sediment sampling

In total 31 cores were sampled by means of a tube coring system with a stainless-steel liner (Hydrobios, Kiel, Germany) in November 2018 at the Teltow Canal close to the source (Berlin-Chemie) on the right bank at a horizontal distance of approximately 3 m. The sandy surface layer of 20 cm was removed and the deeper layers at a sediment depth of 40 – 80 cm, containing contaminated sediments, were transported to the lab and stored at 4 °C in the dark. The complete sediment (30 L) had been sieved through a 1 mm mesh to remove the large debris prior to the experiments.

5.3.3 Determination of the loss-on-ignition (LOI) and extractable organic matter (EOM)

For homogeneity determination the loss on ignition was analysed in a furnace at 600 °C for 4 hours. The TOC has been calculated according to Fringipane et al. (2009) by multiplication of the LOI with a factor of 0.333.

The EOM was determined in duplicate by means of an extraction of 2 g dry sediment with 40 ml acetone/n-hexane (v/v) in an ultrasonic bath for 10 minutes (at 450 W). The residues were filtrated through a 0.45 µm glass fibre filter and evaporated to dryness. The EOM was determined on a microbalance and expressed in µg absolute and in % EOM of the dry sediment.

5.3.4 Determination of the particle size distribution of the sediment samples

The particle size distribution was determined by means of a laser particle analyser (Hoba L960, Retsch, Haan, Germany).

5.3.5 Analysis of the containers by ATR-FTIR

After the termination of the experiments, the pristine and the 3-month PVC- and PE-containers were analysed using ATR-FTIR regarding their polymer composition. A Nicolet iS50 was used (Thermo Fischer, Dreieich, Germany). An ATR Smart iTX Diamond was used with a DTGS detector. Eight scans were realised with a resolution of 4 cm^{-1}. All spectra were ATR and baseline corrected. for potential differences due to the sorption of contaminants and constituents of the diffusion barrier (biofilm/coating).

5.3.6 Sorption test

The sorption tests with the pure compounds were performed in triplicate in the dark at ~ 10°C without shaking. The containers were pre-extracted with aqua demin. and n-hexane to remove production remains.

Solutions of pre-sterilised aqua demin. have been saturated with 1 µg 4,4´-DDT, 100 µg 4,4´-DMDT and 800 µg 4,4´-Diclofol at the maximum water solubility level and left for 3 months to achieve an equilibrium after mixing for 24 hours. The composition of the solution was checked for possible degradation products through analysing the remaining solution via GC-MS.

5.3.7 Abrasion experiments

Initial tests indicated an abrasion of polymer material on an overhead shaker due to the sandy constituents still included in the sediment.
Due to the experience within the abrasion experiments, resulting in severe formation of micro polymer particles and the intention to simulate the burial in deeper sediment layers, the static approach is more comparable to the burial in the sediment body.

5.3.8 Desorption experiments

18 containers (9 x PE and 9 x PVC) were filled with the homogenised sediment and incubated in triplicate in the dark for 2 weeks, 4 weeks, and 12 weeks to get information about the principle process to be extrapolated to natural MP particles as no aged reference material was available. The approach was realised in the dark at ~ 10 °C.

After each time interval the sediment was removed from the containers, these were rinsed twice with 50 ml aqua demin. and the second rinse was checked for adsorption of contaminants on the surface and dried at 25 °C. Immediately, the containers were sequentially extracted with methanol and n-hexane for 24 hours on a horizontal shaker in the dark. The solvent was carefully decanted and reduced to dryness in a fume hood and re-dissolved in 500 µl ethyl acetate and fortified with 2 ng/µl of the internal standard Dicofol-D_8 and ISM-560 (Acenaphthene-D_{10}, Chrysene-D_{12}, 1,4-Dichlorobenzene-D_4, Naphthalene-D_8, Perylene-D_{12}, Phenanthrene-D_{10}) for selected analyses. An additional clean-up step was necessary due to high matrix in the extracts, especially for the PE-experiments. Hydrophobic compounds like alkanes and alkenes were removed by means of a Lichrolut EN mini-column (200 mg; Merck, Darmstadt, Germany) conditioned with n-hexane and eluted with n-hexane and ethyl acetate.

The possible sorption effects on glass walls, as mentioned already in the 1970´s (Picer et al. 1977) were eliminated by the experimental approach.

5.4 GC-MS analysis

5.4.1 GC-MS analysis of the experimental extracts

The GC-MS analysis was performed on an Agilent 6890 GC 5973 MSD (Agilent, Santa Clara, USA).

Starting with a pulsed spitless injection at 270 °C including a 2 minutes pulse at 50 psi. The GC-oven was ramped from 60 °C (5 min hold) to 300°C at 7 °C min^{-1} (10 min hold). The pressure was ramped from 14 psi at 0.5 psi min^{-1} to 20 psi (30 min hold).

The chromatography was performed on a DB-5-ms column (30 m x 0.25 mm id x 0.25 µm ft; Agilent, Santa Clara, USA). Helium was the carrier gas at a velocity of 45 cm s^{-1}. The pressure program was realized at 17 psi constant pressure (2.2 ml min^{-1}).

The detection was carried out on an Agilent MSD 5973 in the EI-mode (70 eV). The source temperature was 230 °C and the quadrupole was maintained at 150 °C. The analysis was performed in the SIM-mode.

The SIM-parameters were (m/z): 139, 143, 250, 251, 258 for Dicofol, Dicholorobenzophenone and Dicofol-d_8; 227, 121, 308, 310, 344 for DMDT and metabolites; 246, 318 for DDE and 235, 237, 165 for DDD and DDMS.

The quantification was performed by means of a 4-point external calibration. The limit of detection (LOD) was 20 pg g^{-1} and the limit of quantification (LOQ) was 100 pg g^{-1} d.w.

Selected samples were additionally analysed in the SCAN-mode for the identification of degradation products and metabolites in the sorption experiments.

The degradation of DDT, DMDT and Dicofol was checked according to the US-EPA recommendation for the analysis of DDT. The degradation was < 15 %.

Procedural blanks of the experiments revealed no contamination by the target compounds.

Additional verification analyses were performed on an Agilent 7890 GC connected to a 5977 B Inert Plus MSD equipped with a TDU-2-System (Gerstel, Mühlheim, Germany), applying the micro vial technique. An aliquot of 20 µl was injected spitless at 25 °C with a temperature program ramped to 270 °C at 10 °C min^{-1}. The analytical parameters were identical to the above system.

Selected extracts of the desorption experiments were analysed in the SCAN-mode (m/z 40 - 650) for additional compounds, not targeted in the experiments.

5.4.2 GC-MS analysis of the sediment sample from the Teltow Canal

The analysis of the original sediment was performed according to Zhu et al. (2019). Briefly, the air-dried sediment was sequentially extracted with acetone, mixtures of acetone and n-hexane (1:1) and n-hexane via accelerated solvent extraction (Dionex ASE 150, Thermo Fisher Scientific, Waltham, USA) to obtain the solvent extractable fraction (EF). The extracts were dried with anhydrous sodium sulphate and fractionated according to Schwarzbauer et al. (2003). After fortifying with internal standards, the analysis was performed according to Zhu et al. (2019) on a GC-MS system.

5.5 Results and Discussion

The experiment revealed a sorption of the compounds and the desorption from the contaminated sediment into the polymer. All target compounds were detected in the sorption experiment while only DDT-related compounds were analysed in the desorption experiments, in accordance with the analysis of the contaminated sediment. Further compounds were identified via SCAN-analysis of the extracts.

5.5.1 Sediment characterisation

The particle size distribution of the sediment reveals a maximum particle size between 90 - 100 µm with the smallest particles in the range of 10 µm (see Figure 5.1). 50 % of the particles in the sample are ≤ 70 µm, indicating a partially fine-grained sediment composition. A larger number of particles in the range of 50 - 180 µm was analysed.

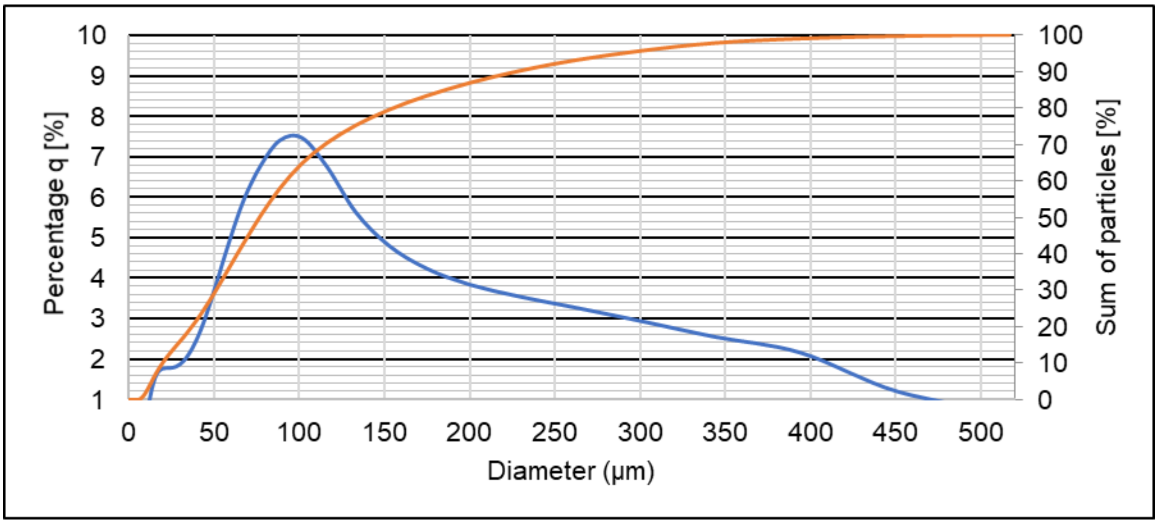

Figure 5.1: Particle size distribution of the contaminated sediment for the desorption experiment.

The Loss-on-ignition indicated a very homogeneous distribution of the OM throughout the experimental setup (3.3 ± 0.09 %) (data not shown). To compare the results with earlier investigations a conversion into TOC was performed by multiplying with a factor of 0.333 according to Frangipane et al. 2009 due to the slightly elevated temperature of 600°C relative to actual recommendations at 475 - 550 °C (DIN 18128). The TOC was in the range of a 1.1 % in accordance with earlier results at the same location (1.82 – 2.73 % TOC; Ricking et al. 2020).

The extractable organic material (EOM) was determined at 4.8 and 3.7 µg g^{-1} d.w., representing an EOM of 0.24 and 0.19 %, respectively for sample A and B (mean 0.21 %).

In total the sediment is a fine-grained sediment with a low TOC of 1.1 %. These two features favour the transfer of contaminants due to an expected low formation of non-extractable residues.

The GC-MS analyses of the contaminated sediment revealed a heavy contamination with DDT-related compounds (DDX) and no DMDT and Dicofol (see Table 5.1). Even the parent compounds 4,4´- and 2,4´-DDT were detected in accordance with earlier publications (Kucher et al. 2018, Zhu et al. 2019).

Table 5.1: Concentrations of different DDT-metabolites in the sediment sample used for the desorption experiment (ng g^{-1} d.w.).

Name	formula	MW	concentration ng g^{-1}
DDM	$C_{13}H_{10}Cl_2$	236	79
DDNU	$C_{14}H_{10}Cl_2$	248	321

DDEt	$C_{14}H_{12}Cl_2$	250	82
DBP	$C_{13}H_8Cl_2O$	250	320
2,4'-4,4'-DDCN	$C_{14}H_9Cl_2N$	261	13950
DDMU	$C_{14}H_9Cl_3$	282	3281
DDMS	$C_{14}H_{11}Cl_4$	284	22341
2,4´-DDE	$C_{14}H_8Cl_4$	316	55
4,4'-DDE	$C_{14}H_8Cl_4$	316	1328
2,4'-DDD	$C_{14}H_{10}Cl_4$	318	3079
4,4'-DDD	$C_{14}H_{10}Cl_4$	318	12778
2,4'-DDT	$C_{14}H_9Cl_5$	352	26
4,4'-DDT	$C_{14}H_9Cl_5$	352	592

5.5.2 Results of the FTIR-analysis

The composition of the polymeric materials was analysed using ATR-FTIR (Figure 5.2). Before the sorption experiments, the materials can be unambiguous determined as PE (characteristic bands at 2920 and 2855 cm^{-1}, 1475 and 1465 cm^{-1}, 731 and 720 cm^{-1}) and PVC (characteristic bands at 700, 617 cm^{-1}) with a minor part of carbonylic plasticizer (1733 cm^{-1}). After 3 months of incubation in both cases broad bands were added in both spectra between 3700 – 3000 cm^{-1}, as well as 1700 – 1500 cm^{-1} and 1200 – 800 cm^{-1}. Simultaneously the signals of the polymers are reduced. This indicates a surface layer of water-rich biofilm on the containers consisting of hydroxyl groups, aromatic structures and esters, respectively.

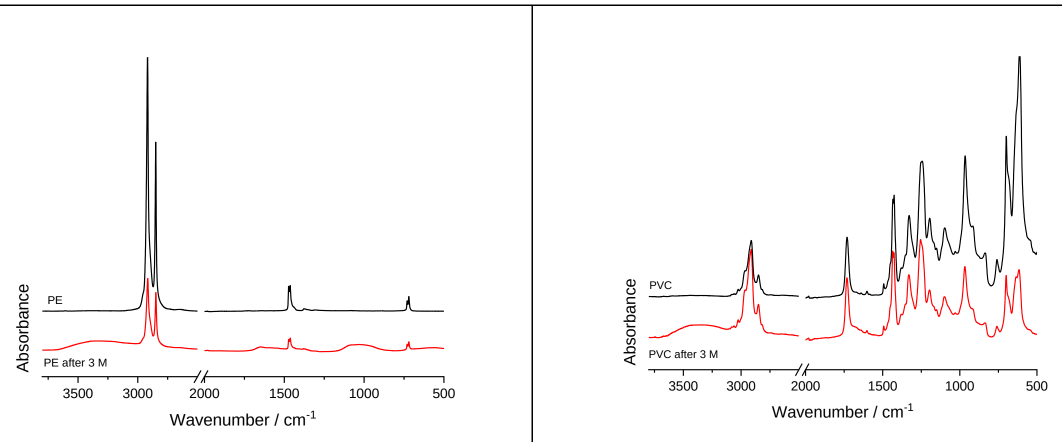

Figure 5.2: FTIR-spectra [Wavenumber cm-1 on the x-axis and Extinction on the y-axis] of the pristine polymer containers before and after the incubation within 3 months.

5.5.3 Sorption tests with the experimental set-up (only water and the polymers)

This simple approach illustrates the principal distribution between the water phase and the polymer. It ignores the formation of a biofilm/coating and the chosen equilibration was enough to approach an equilibrium. Compared to data in the literature 12 weeks are enough (EPA 2012, Bakir et al. 2014, Seidensticker et al. 2017, Hüffer et al. 2018). All three target compounds were detected in the extracts from the containers. A screening of the water phase via a Sorbstar™ revealed a slow degradation of the parent compounds and the detection of traces of metabolites (DDD, DDMS, DDE, MDE and DBP) for DDT, DMDT and Dicofol, respectively. There were no additional metabolites detected in the extracts.

In Figure 5.3 the mechanism of sorption/penetration into a polymer sheet is illustrated, not differentiating between adsorption and absorption. The red arrows illustrate the diffusion in and out of the polymer. A biofilm/coating is green schematically included and the boundary layer is in lighter blue drawn. PE is a partially flexible thermoplastic and semi crystalline and H-PVC is amorphous. The free volume is much lower in the glassy polymers (H-PVC) relative to the flexible polymer structure (PE) (Pascall et al. 2005; Omnexus 2020).

The size of the red arrows visualizes the results of the experiments, which showed a much higher sorption for PE. Differences in the surface properties that determine the sorption properties are in addition caused by the more hydrophilic properties introduced by the chlorine atoms of PVC.

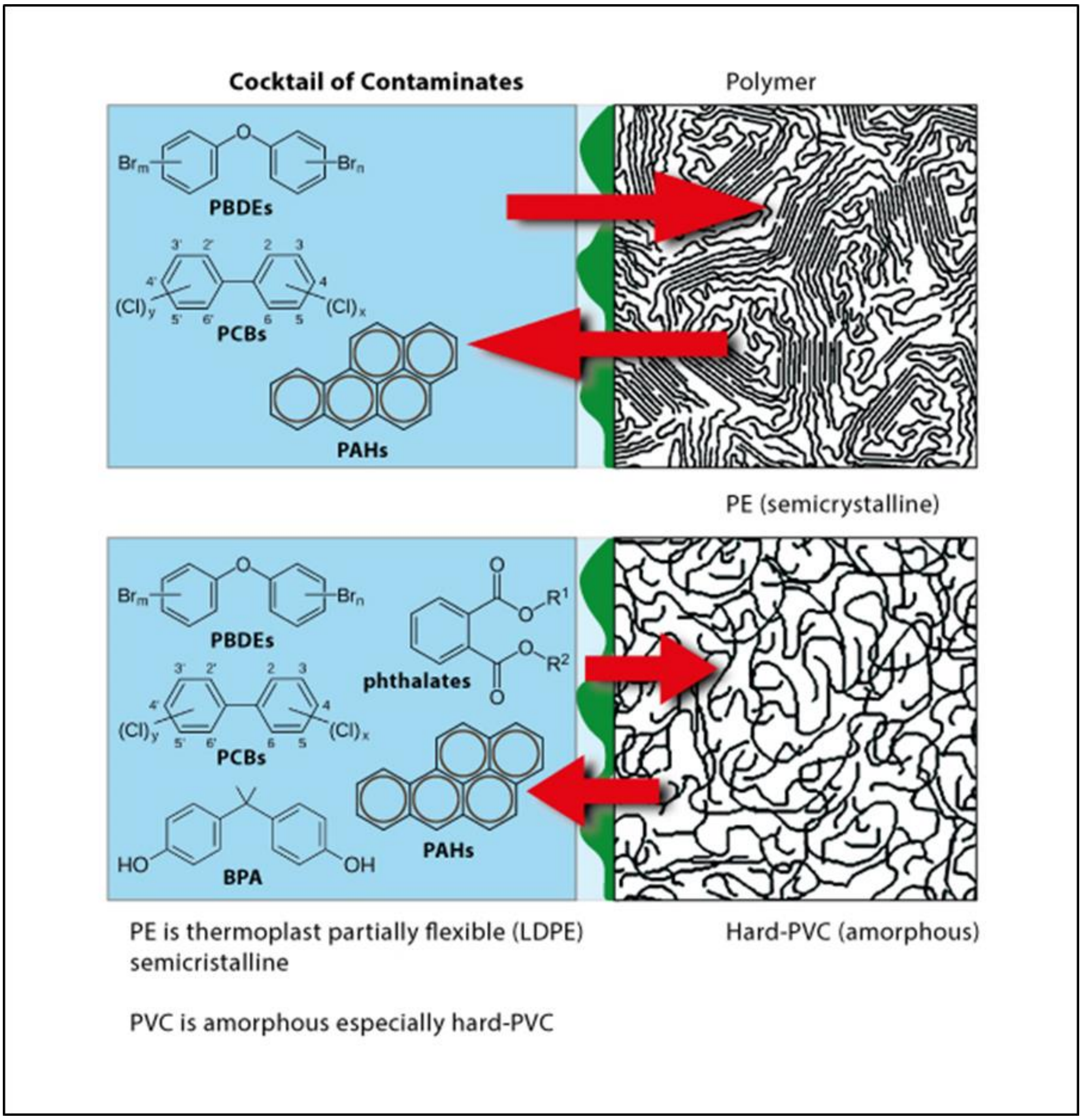

Figure 5.3: Schematic illustration of the processes of contaminant transfer into the plastic polymer and the release out of the polymer (graph: J. Evers, FU Berlin). (Abbreviation: PCB = Polychlorinated Biphenyls, PBDE = Polybrominated Diphenyl Ethers, BPA = Bisphenol A, PAH = Polycyclic Aromatic Hydrocarbons).

However, there are differences between the two polymers. The results indicate a higher “sorption capacity” for PE relative to PVC (see Table 5.2).

The recovery of the target compounds in the solutions extracted from the polymer containers was between 1.97 – 2.41 % for PE and between 0.21 – 1.46 % for PVC in relation to the total mass applied, reflecting the different polymer structure and glassy transition temperature. 4,4´-DBP as transformation product of 4,4´-Dicofol was analysed in a higher concentration in the PE experiments, indicating a higher transformation potential for PE, relative to PVC. The variation in the PVC experiments was much higher than in the PE-experiments. Details are given in the SI.

Table 5.2: Absolute mass in ng absolute of the three compounds and relative recovery in relation to the initial concentration of 1 µg L^{-1}, 100 µg L^{-1} and 800 µg L^{-1} for DDT, DMDT and Dicofol in the VE-sorption experiment for LD-PE and H-PVC, respectively.

[ng absolute]	**4,4-´DDT**	**4,4´-DMDT**	**4,4´-DBP**	**4,4´-Dicofol**	**Sum**
Mean PE	509 ± 63	11794 ± 1013	7309 ± 555	0.00	19612 ± 1630
Mean PVC	203 ±161	5229 ± 4374	354 ± 22	448 ± 420	6234 ± 4947
Recovery [%]	**4,4-´DDT**	**4,4´-DMDT**	**4,4´-DBP**	**4,4´-Dicofol**	
LD-PE 1	51.04	11.64	0.90		
LD-PE-2	58.49	13.10	1.01		
LD-PE-3	43.15	10.63	0.84		
H-PVC-1	5.74	1.38	0.05	10.62	
H-PVC-2	42.82	11.35	0.04	0.96	
H-PVC-3	12.42	2.96	0.04	4.70	

The highest relative recovery was determined as a function of water solubility and hydrophobicity for DDT > DMDT > dicofol. The DDT content compared to the other two target compounds was relatively low in relation to data from the Pellet Watch Project (see following chapter). Antagonistic effects are obvious due to the use of a cocktail of compounds with different water solubility.

5.5.4 Desorption experiments

Both polymers accumulated DDT-related compounds according to their polymer structure. The washing extracts (second aqua demin.) indicated no target compounds.

In the two week-samples no compound was detected due to the formation of a diffusion barrier at the surface, as indicated in the chromatograms of the extracts. The fast formation of coatings/biofilms was expected and is in alignment with published data of biofilm formation within minutes to hours (Loeb et al. 1975, Galloway et al. 2017, Rummel et al. 2017, Michels et al. 2018). These biofilms turned the polymer into a two-phase domain with an outer organic material shell and an inner polymer core (Endo and Koelmans 2016).

The results for the 1-month and 3-month experiments are listed in Table 5.3 and illustrated in Figure 5.5. Details are given in Table SI-5.1.

Table 5.3: Analysis of the detected compounds of the two experimental approaches [ng/container absolute].

compound [ng absolute)	DDD	DDE	DBP	DDMS
1 M PVC	495 ± 24	65 ± 65.02	85 ± 38.2	324 ± 24.9
3 M PVC	255 ± 124	62.5 ± 35.7	88 ± 47.7	117 ± 46.5
1 M PE	12671 ± 7656	2367 ± 1362	1236 ± 301	3549 ± 341
3 M PE	8041 ± 1521	1997 ± 194	2282 ± 681	6228 ± 1218

The data clearly demonstrate a desorption of the compounds from the sediment onto the polymer. Expected differences for PE and PVC are proven, resulting from the differences in crystallinity. The differences in flexibility at room temperature, related to the glassy transition temperature are obvious (- 125 °C for PE vs. 67 °C for PVC, Omnexus 2020), leading to absorption capacities varying by a factor of ~ 10. The higher capacity of PE is based upon the linear, non-competitive and mostly reversible sorption relative to the nano-pore filling within the PVC polymer (Endo and Koelmans 2016)

A differentiation into the methanolic and n-hexane fraction is shown in the Table SI-5.3. In all cases, the data show for PVC a higher content in the methanolic fraction (first extraction step). All quantified compounds are highly soluble in methanol (Pub Chem 2020). The increased content in the n-hexane fraction of PE indicates a possible diffusion into deeper polymer layers, which could not be extracted with methanol. The stronger sorption within three months (possible formation of non-extractable residues) is illustrated by the reversal of the relative contribution of the methanol and n-hexane fraction for the PE experiments.

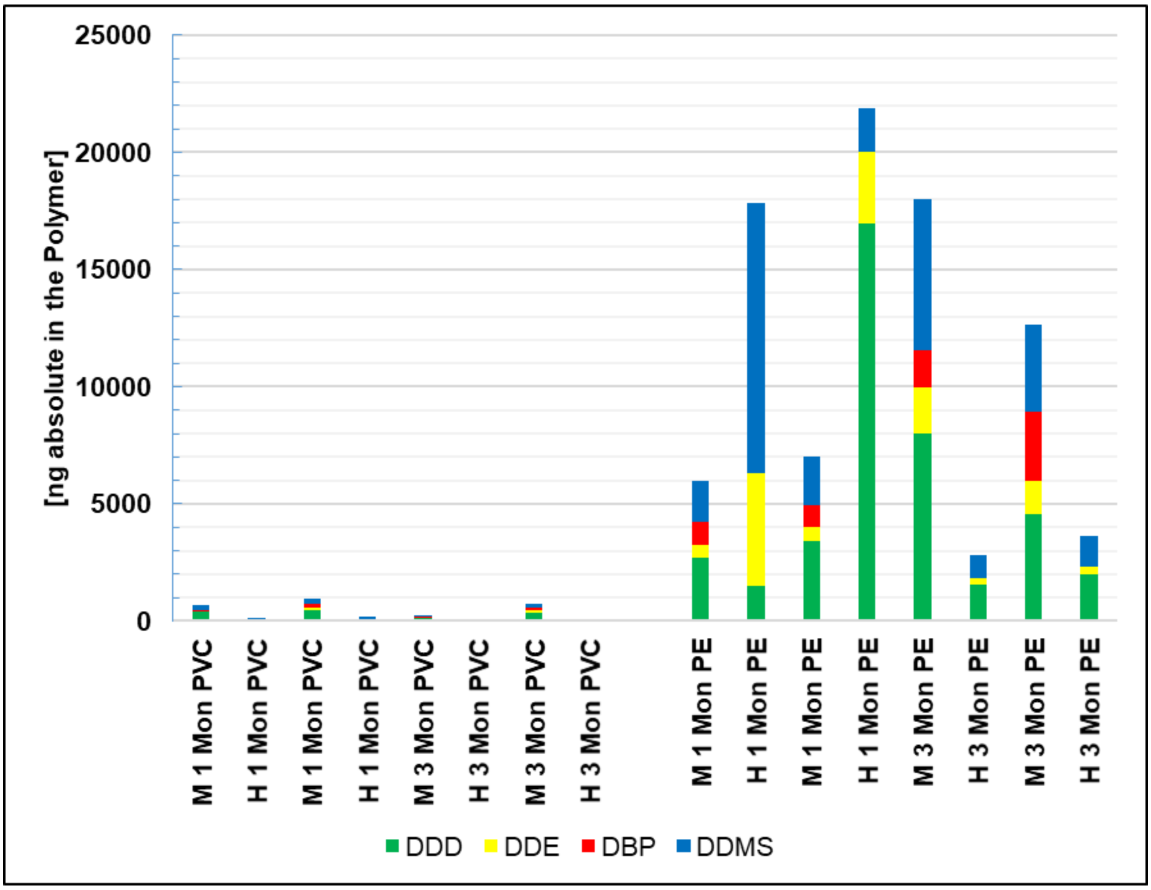

Figure 5.4: Detection of selected compounds in the methanolic (M) and n-hexane (H) extracts for 1 and 3 months [ng absolute].

A slightly higher content of the total compounds in the three-month samples relates to a non-equilibrium process. The kinetics of the desorption require further attention, especially for the short-time processes.

Tables 5.2, 5.3 and Figure 5.4 clearly illustrate the differences between the polymers with an expected higher sorption capacity of LD-PE. The additional SCAN-analysis of the extracts revealed tetrachloro- and pentachloro-PCB, fluoranthene, pyrene, benz(a)anthracene and chrysene, beside alkanes (C_{16}-C_{24}), in accordance with prior investigations of the sediment (Heim et al. 2005, Ricking et al. 2020). The antagonistic processes for competitive sorption on limited sorption places have to be considered. Differences in contamination are obvious due to an inhomogeneous distribution of the contaminants in the 700 g (dry weight) sediment used for the experiments.

Table 5.4 and Figure 5.5 compare the relative loading of the polymers in the pure sorption experiments and the sediment desorption experiments assuming a relative similarity of the compounds and their physico-chemical characteristics. The loading of PE containers is much higher than that of PVC containers and is in the range of the sorption tests for PE. For PVC a slightly lower desorption load is indicated. The analytical details are given in the Tables SI-5.2 and

SI-5.3. Figure 5.5 illustrates the results per g of polymer for the comparison with other data in the literature.

Figure 5.5: Calculation of the concentrations of selected compounds [ng g^{-1} polymer] for comparison with the literature. Above are the VE-sorption experiments illustrated and below the desorption experiments.

Table 5.4: Comparison of the relative loading of the sediment desorption experiment for 1 month (1 M) and 3 months (3 M) relative to the sorption experiment.

Sorption experiment [ngg^{-1} polymer]	**4,4-´DDT**	**4,4´-DMDT**	**4,4´-DBP**	**4,4´-Dicofol**	**Sum**
PE	5.45 ± 0.67	126 ± 10.8	78.3 ± 5.94	0.00	210 ± 17.5
PVC	3.81 ± 3.02	97.9 ± 81.9	6.63 ± 0.41	8.40 ± 7.86	117 ± 93.2
Desorption experiment [ngg^{-1} polymer]	**4,4-DDD**	**4,4-DDE**	**4,4-DBP**	**4,4-DDMS**	**Sum**
1 M PE	204 ± 123	38.1 ± 21.9	19.9 ± 4.85	57.2 ± 5.49	319 ± 156
3 M PE	130 ± 24.5	32.2 ± 3.12	36.8 ± 11	100 ± 19.6	299 ± 58.2
1 M PVC	15.37 ± 0.74	2.00	2.62 ± 1.18	9.99 ± 0.77	29.9 ± 4.69
3 M PVC	7.86 ± 3.83	1.93 ± 1.10	2.71 ± 1.47	3.60 ± 1.43	16.1 ± 7.84

In comparison with published data for DDX within the International Pellet Watch project (IPW) in the range of n.d. - 198 ng g^{-1} S-DDT (Hirai et al. 2011), 1.1 – 42 ng g^{-1} S-DDT (Karapanagioti et al. 2011) and n.d. -140 ng g^{-1} S-DDT (Rios et al. 2007) the desorbed and analysed concentrations of DDX in the present study are of the same kind but lower than concentrations of 2 locations in California with contents of 1,000 and 1,100 ng g^{-1} S-DDT and two samples from an industrial in the USA with contents of up to 7,100 ng g^{-1} S-DDT (Rios et al. 2007). The data for comparison are given in Table SI-5.4.

The different geometry of the experiments (surface of the containers) versus three-dimensional pellets and fragments has to be considered. Information on the absorption in the plastic polymer is currently not available.

Differences in exposure (drifting vs. static) and analysis (the potential biofilm is in the Pellet Watch Project co-extracted) have to be considered. Additionally, the Pellet Watch Project analyses aged pellets and fragments relative to the pristine plastic containers applied in the current experiments. The published data reveal an obvious contamination of the marine pellets and fragments by aerobic metabolites of DDT (DDT and DDE) relative to anaerobic metabolites, expected in anoxic sediment samples. Besides, no DDT was analysed in the desorption experiments relative to a detection of DDT in the original sediment sample. The relatively low detection of only a few of the identified and quantified DDX-metabolites relates to the limited sorption capacity of the polymers, as already stated for the sorption experiments. Bakir et al. 2012 experienced the same differences in their kinetic sorption experiments with DDT and phenanthrene on PE and PVC. DDT is more prone to a tighter sorption into the pores of the plastic polymer relative to other compounds (Bakir et al. 2012).

Due to the diffusion barrier at surface of the containers (biofilm/coating) no attempt was made to refer the detected concentrations to the total sediment (assuming a homogeneous distribution) and to calculate the sediment layer thickness necessary to deliver the contaminants to the plastic polymer.

Polar metabolites (DDA, DBP, DDCN) are not expected to diffuse onto/into hydrophobic plastic polymer material. Another point is the potential competition for absorption sites with different capacities.

5.6 Conclusions

The new approach shows an easy to handle alternative approach for sorption and desorption experiments with LD-PE and H-PVC. The limited sorption/accumulation capacity of pure polymers is shown in the sorption experiments, including antagonistic effects for the compounds, rarely considered in experiments. Within the first week, a diffusion barrier or a biofilm formed on the polymer surface that can act as a sorbent for the substances, so that no compounds could be detected after the first-time interval. The differences in sorption between the 1-month and 3-month analyses give hints to further processes, not yet addressed in lab-experiments.

With the presented sorption test, it was possible to demonstrate the adsorption/incorporation of contaminants into the two polymers. The recovery of the three target compounds ranged between 2.0 - 2.4 % of the initial concentration for PE and 0.2 – 1.9 % for PVC, respectively. Differences between the two polymers are addressed. In the sorption experiments all the target compounds were detected in alignment with their hydrophobicity, resulting in a relative order of DDT > DMDT > Dicofol.

In the desorption experiments, diffusion of the contaminants out of a contaminated sediment onto the polymers could be verified. In maximum 22 µg Σ DDX (DDD/DDE/DBP and DDMS) could be desorbed within one month in the PE-experiment. Relative to published data of the International Pellet Watch project (IPW) 180-460 ng g^{-1} PE-polymer were analysed. These are in the range of other more contaminated sites, except for a few very highly sites.

Differences in polymers are analysed and explained mainly by the glassy transition temperature with subsequent flexibility at room temperature. All three aspects differentiating PE and PVC in polymer structure, polarity and properties, free volume and contaminant behaviour are obvious.

The rapid formation of a biofilm in the sediment limits the sorption capacity, even at the highly contaminated site and compared to pellets and fragments. The ATR-FTIR analysis of the surface layers of the 3-month containers resulted in an identification of a water-rich surface layers comprised of hydroxy and aromatic structures. The approach illustrates a more realistic approach for naturally contaminated systems with a large number of different compounds and possible antagonistic effects on sorption, especially for compounds with different and high log K_{ow}-values.

Further experiments on a much wider range of compounds and especially on short-term kinetics are recommended, as well as experiments with a higher TOC-content of the particulate phase due

to the formation of non-extractable residues (NER) and a much higher expected sorption capacity in the sedimentary organic matrix (SOM).
The very limited sorption capacity of plastic polymers, especially in natural ecosystems with rapid formation of biofilms/coatings, renders their function as transport vehicle/vector for POP´s low according to publications by Koelmans et al. 2016, Rodrigues et al. 2019 and Shi et al. 2020. The relative contribution of particle-bound transport of contaminants has been researched to a limited extent (e.g. Schwientek et al. 2013, Rügner et al. 2019) and especially flood events, which are the main transport of particulate material, require further research.

The results show a low desorption of contaminants. A patented remediation method from the USA has not yet been proven and peer-reviewed published.

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Table SI-5.1: Absolute mass in ng absolute of the three compounds and concentration per polymer [ng g^{-1}] for LD-PE and H-PVC.

ng Experiment	**4,4-´DDT**	**4,4´-DMDT**	**4,4´-DBP**	**4,4´-Dicofol**	**Sum**
PE 1	510.40	11644.70	7174.80	0.00	19330.00
PE-2	584.90	13102.90	8045.40	0.00	21733.30
PE-3	431.50	10634.60	6706.80	0.00	17772.90
Mean	508.93 ± 62.63	11794.07 ± 1013.20	7309.00 ± 554.66	0.00	19612.07 ± 1629.08
PVC-1	57.40	1377.80	383.30	94.20	1912.70
PVC-2	428.20	11346.10	347.10	1037.90	13159.30
PVC-3	124.20	2963.00	331.20	213.00	3631.30
Mean	203.27 ± 161.37	5228.97 ± 4373.61	353.87 ± 21.80	448.37 ± 419.67	6234.43 ± 4946.63
Experiment [ng g^{-1} polymer]	**4,4-´DDT**	**4,4´-DMDT**	**4,4´-DBP**	**4,4´-Dicofol**	**% of absolute mass**
PE 1	5.46	124.68	76.82	0.00	2.15
PE-2	6.26	140.29	86.14	0.00	2.41
PE-3	4.62	113.86	71.81	0.00	1.97
Mean	5.45 ± 0.67	126.27 ± 10.85	78.25 ± 5.94	0.00	2.18 ± 0.18
PVC-1	1.07	25.80	7.18	1.76	0.21
PVC-2	8.02	212.47	6.50	19.44	1.46
PVC-3	2.33	55.49	6.20	3.99	0.4
Mean	3.81 ± 3.02	97.92 81.90	6.63 ± 0.41	8.40 ± 7.86	0.69 ± 0.55

Table SI-5.2: Analysis results of the detected compounds of the two experimental approaches [ng/container absolute] and calculated relative to one g of the container polymer.

compound [ng absolute)	DDD	DDE	DBP	DDMS
1 M PVC	471.24	0.00	46.72	299.32
1 M PVC	519.41	130.04	123.19	349.13
Mean	495.33 ± 24.08	65.02	84.96 ± 38.23	324.22 ± 24.91
3 M PVC	130.68	26.84	40.29	70.22
3 M PVC	379.42	98.21	135.65	163.21
Mean	255.05 ± 124.37	62.53 ± 35.69	87.97 ± 47.68	116.71 ± 46.50
1 M PE	5014.14	1004.98	1536.98	3207.84
1 M PE	20326.85	3728.83	934.25	3889.65
Mean	12670.50 ± 7656.35	2366.90 1361.93	1235.61 ± 301.37	3548.75 ± 240.90
3 M PE	9562.17	2190.34	1600.72	7446.35
3 M PE	6520.23	1803.15	2962.90	5009.40
Mean	8041.20 ± 1520.97	1996.75 ± 103.59	2281.81 ± 681.09	6227.88 ± 1218.47
compound [ng g^{-1} polymer]	**DDD**	**DDE**	**DBP**	**DDMS**
1 M PVC	14.53	0.00	1.44	9.23
1 M PVC	16.01	4.01	3.80	10.76
Mean	15.27 ± 0.74	2.00	2.62 ± 1.18	9.99 ± 0.77
3 M PVC	4.03	0.83	1.24	2.16
3 M PVC	11.70	3.03	4.18	5.03
Mean	7.86 ± 3.83	1.93 ± 1.10	2.71 ± 1.47	3.60 ± 1.43
1 M PE	80.76	16.19	24.75	51.67
1 M PE	327.38	60.06	15.05	62.65
Mean	204.07 ± 123.31	38.12 ± 21.94	19.90 ± 4.85	57.16 ± 5.49
3 M PE	154.01	35.28	25.78	119.93
3 M PE	105.01	29.04	47.72	80.68
Mean	129.51 ± 24.50	32.16 ± 3.12	36.75 ± 10.97	100.31 ± 19.62

Table SI-5.3: Concentrations of the detected compounds of the two experimental approaches [ng/container absolute] differentiated into the methanol (M) and n-hexane (H) fraction.

Compound ng absolute	DDD	DDE	DBP	DDMS
M 1 Mon PVC	425.20	0.00	46.72	200.14
H 1 Mon PVC	46.04	0.00	0.00	99.18
M 1 Mon PVC	459.94	130.04	123.19	233.34
H 1 Mon PVC	59.47	0.00	0.00	115.80
M 3 Mon PVC	120.45	26.84	40.29	70.22
H 3 Mon PVC	10.24	0.00	0.00	0.00
M 3 Mon PVC	347.65	88.40	135.65	163.21
H 3 Mon PVC	31.76	9.81	0.00	0.00
Compound ng absolute	DDD	DDE	DBP	DDMS
M 1 Mon PE	2729.12	543.81	966.87	1733.33
H 1 Mon PE	1495.90	4830.76	0.00	11507.21
M 1 Mon PE	3388.11	618.01	934.25	2083.12
H 1 Mon PE	16938.74	3110.82	0.00	1806.53
M 3 Mon PE	8003.43	1945.68	1600.72	6462.34
H 3 Mon PE	1558.75	244.66	0.00	984.02
M 3 Mon PE	4554.35	1432.57	2962.90	3707.95
H 3 Mon PE	1965.87	370.59	0.00	1301.46

Table SI-5.4: Comparison of the relative loading in the sorption experiment to the sediment desorption experiment [ng g^{-1} polymer].

Experiment [ng g^{-1} polymer]	**4,4-´DDT**	**4,4´-DMDT**	**4,4´-DBP**	**4,4´-Dicofol**	**Sum**
PE 1	5.46	124.68	76.82	0.00	206.96
PE-2	6.26	140.29	86.14	0.00	232.69
PE-3	4.62	113.86	71.81	0.00	190.29
Mean	5.45 ± 0.67	126.27 ± 10.85	78.25 ± 5.94	0.00	209.98 ± 17.46
PVC-1	1.07	25.80	7.18	1.76	35.82
PVC-2	8.02	212.47	6.50	19.44	246.43
PVC-3	2.33	55.49	6.20	3.99	68.00
Mean	3.81 ± 3.02	97.92 ± 81.90	6.63 ± 0.41	8.40 ± 7.86	116.75 ± 93.19
compound [ng g^{-1} polymer]	**4,4-DDD**	**4,4-DDE**	**4,4-DBP**	**4,4-DDMS**	**Sum**
1 M PE	80.76	16.19	24.75	51.67	173.36
1 M PE	327.38	60.06	15.05	62.65	465.13
Mean	204.07 ± 123.31	38.12 ± 21.94	19.90 ± 4.85	57.16 ± 5.49	319.25 ± 155.59
3 M PE	154.01	35.28	25.78	119.93	335.00
3 M PE	105.01	29.04	47.72	80.68	262.46
Mean	129.51 ± 24.50	32.16 ± 3.12	36.75 ± 10.97	100.31 ± 19.62	298.73 ± 58.21
1 M PVC	14.53	0.00	1.44	9.23	25.19
1 M PVC	16.01	4.01	3.80	10.76	34.58
Mean	15.27 ± 0.74	2.00	2.62 ± 1.18	9.99 ± 0.77	29.89 ± 4.69
3 M PVC	4.03	0.83	1.24	2.16	8.26
3 M PVC	11.70	3.03	4.18	5.03	23.94
Mean	7.86 ± 3.83	1.93 ± 1.10	2.71 ± 1.47	3.60 ± 1.43	16.10 ± 7.84

6. General Discussion – Conclusion and Outlook

Summarising the chapters 3 – 5 the scientific achievements of the dissertation are:

Chapter 3 revealed during the survey in the mid-1990´s background data for DDT and related compounds in North-East Germany (NE-Germany) including the semi-final sink Arkona Basin in the Baltic Sea. The applied analytical approach provided geochronological basic data on trace metals and organic contaminants such as PCDD/F´s, PAH´s, PCB´s, DDX and HCH´s back to the turn of the 19th to the 20th century. Most sediment cores have recently recorded a decrease in contamination. The hot spot was identified in Berlin at the Teltow Canal, a production facility that manufactured and formulated chemicals including pesticides since the 1880´s (Berlin-Chemie). Production wastewater has been documented to have been discharged directly into the Teltow Canal since the 1950´s, contaminating the sediment in the discharge area. As a result, about 135,000 m³ of contaminated sediments (approx. 180,000 t d.w.), including ~ 65,000 t of highly contaminated material containing mainly DDT and HCH, were removed in the mid-1990´s before the reopening of the Teltow Canal for commercial shipping near the underwater threshold at the former border between West-Berlin and the GDR (Rauch 2020).

The identified point source triggered a comprehensive investigation of the contamination including non-extractable residues and a risk assessment presented in chapter 4. The remaining sediment after removal has been investigated with regard to the contamination state. Due to the enhanced water solubility of DDA (the acidic metabolite of DDT) a special focus was placed on DDA as a lead substance for the risk assessment and calculation of the release potential. Several precursor metabolites from DDT, e.g. DDD and DDMS, extractable from the sedimentary organic matrix (SOM) revealed a high potential for long-term formation of DDA, especially in the easily releasable fraction. The free available (extractable fraction) as well as the easily available (easily releasable via hydrolysis) and hardly available fractions of DDA and precursor metabolites were analysed and calculated. A maximum of 48 kg (32 - 82 kg) and 278 kg (214 - 354 kg) DDA-formation was estimated in the free available fraction by applying a trapezoid model with decreasing contamination in deeper layers and a column model with no decrease, respectively. The calculation of the easily releasable fraction via hydrolysis and uncoiling of the organic matrix resulted in 1,360 kg DDA-formation potential (11 – 4,010 kg) and 9,800 kg (250 – 29,000 kg) for the two models applied, respectively. In both cases the middle layer in area C contributed with approx. 75% to the estimated release potential of the DDA-formation from the easily releasable fraction (ER) downstream the source. Within the short canal section of 1,250 m close to the source, variations of the contents between not detected and maximum concentrations by a factor of more than 10 million were observed.

A preliminary release experiment indicated a rapid release potential within days, independent of the redox conditions. These estimations combined with the release experiments represent a significant contamination risk potential for the infiltration zone of a water works downstream the source and the whole ecosystem and adjacent water bodies.

In addition to natural particulate sorbents such as humic substances and natural organic matter, synthetic polymers and plastic particles are an additional particulate sorbent in (aquatic) ecosystems.

Plastic is a general term for a class of materials composed of different types of man-made synthetic polymers. In addition to synthetic polymers, these materials are often characterised by various additives with low content, optimising or adjusting the properties during processing and application. Plastic including micro plastic (MP) particles is widely detected in the environment today. Micro contaminants, especially very persistent organic compounds, are to a large extent also detected in the (aquatic) environment, which has led to a growing number of recent studies dealing with interactions between organic contaminants and (micro) plastic in the environment. The background of these investigations is the hypothetical function of plastic particles as a vector for bio-magnification, causing negative effects on the ecosystem.

In chapter 5 interactions between two common polymers (low density polyethylene (LD-PE) and hard polyvinyl chloride (H-PVC) and three organic, persistent compounds, dichlorodiphenyltrichloroethane (DDT), methoxychlor (DMDT) and dicofol were investigated with a sorption test and desorption experiment. A new and innovative experimental approach based on a static system similar to a burial in deeper sediment layers was investigated. The experimental setup used additive-free plastic containers resulting in an easy to handle attempt instead of MP particles and fibres. It is assumed that the basic mechanisms of interaction are evaluated and material specific.

With the presented sorption test, it was possible to demonstrate the adsorption/incorporation of contaminants into the two polymers. The recovery of the three target compounds ranged between 2.0 - 2.4 % of the initial concentration for PE and 0.2 – 1.9 % for PVC, respectively. Differences between the two polymers have been taken into consideration. In the sorption experiments all the target compounds were detected in alignment with their hydrophobicity, resulting in a relative order of DDT > DMDT > Dicofol.

In the desorption experiment, diffusion of the contaminants out of a contaminated sediment on/into the polymers could be verified. In maximum 22 µg Σ DDX (DDD/DDE/DBP and DDMS) per container could be desorbed within one month in the PE-experiment. Relative to published data of the International Pellet Watch project (IPW) 180 - 460 ng Σ DDX g^{-1} PE-polymer were analysed. These concentrations are close to other, more heavily contaminated sites, except for a few very severely affected sites. The rapid formation of a biofilm at the polymer surface limited the sorption capacity, even with the highly contaminated sediment and compared to pellets, fibres and fragments drifting in the water phase. The ATR-FTIR analysis of the surface layers of the 3-month containers resulted in an identification of a water-rich surface layer comprised of hydroxy and aromatic structures. As expected, the sorption of PE was much higher. The differences between the two polymers could be investigated to a large extent and mainly explained by **g**lass **t**ransition temperatures (**Tg**) and polymer structure with subsequent flexibility at room temperature. All three aspects differentiating PE and PVC in polymer structure, polarity and properties, free volume and contaminant behaviour were illustrated.

The simple approach is easy to handle and illustrates the limited sorption capacity of the two studied polymers. It eliminates possible sorption effects to glass walls and simulates the ecosystem situation of a multiple contaminant cocktail, usually not represented in laboratory experiments.

The very limited sorption capacity of plastic polymers, especially in natural ecosystems with rapid formation of biofilms/coatings, renders their function as a transport vehicle/vector for POP´s low.

The optimising of the analytical tool and extension to include non-extractable residues led in combination with a non-target screening approach (e.g. Schwarzbauer et al. 2001, 2003, Ricking et al. 2005) to the identification of the specific point source at the Teltow Canal. Recent research activities have focused on this area contaminated by the effluents from this point source. Surface sediments, sediment cores, surface and ground water samples were extensively analysed (Schwarzbauer et al. 2001, 2003, Ricking et al. 2005, Heim et al. 2005, Kronimus et al. 2006, Frische et al. 2010, Kucher et al. 2018, Zhu et al. 2019, Zhu et al. 2020, Ricking et al. 2020, Frische et al. 2020) and identified more than 30 different metabolites of DDT, among other pesticides and various industrial compounds.

Compared to Lake Weissensee with an unintentional contamination by DDT-application with airplanes in 1983/84, the metabolism/degradation of DDT in the Teltow Canal sediments is quite advanced. DDA as a more water-soluble metabolite was detected in traces in the sediments of Lake Weissensee (M. Ricking, data unpublished).

Geochronology (Ricking et al. 2005, Heim et al. 2005) displayed a strong contamination before and after the removal of most of the accumulated contaminated sediment near the former GDR border at the Teltow Canal. The dated sediment core taken in 1995 (chapter 3) represented the undisturbed long-term sediment contamination for nearly a century. In 1999, a dated sediment core reflected the recent contamination within the last 5 - 10 years (until 1999) with concentrations of up to 100,000 ng g^{-1} d.w. for 4,4´-DDD and 4,4´-DDMS in the extractable fraction (Heim et al. 2005). The contribution of 4,4´-DDA to the sum DDX was below 100 ng g^{-1} in all samples with no discernible trend in deeper layers. The sampling campaigns in 2007 and 2018 indicated a still high contamination with subsequent release potential into the water phase (Heim et al. 2005) via pore water diffusion and resuspension by commercial shipping. DDA was enriched in the particles of the fluffy layer, an indication of a release taking place from the sediment. In all analyses performed at the site no aerobic/oxygenated DDX were detected in the samples, indicating an immediately anaerobic condition.

Compared to the Palos Verdes Shelf (PVS) with aerobic conditions in the water column, NER-formation at the Teltow Canal is high and low at the PVS with a subsequent low DDA-formation

(Kucher and Schwarzbauer 2017). By comparing the isotope signature of the sedimentary DDX and groundwater samples from the production site and the bank filtration area in Johannisthal, sedimentary DDA-formation was identified as a source of contamination for surface water, possibly an indication of a source for bank filtration at the Johannisthal waterworks (Frische et al. 2020). $\delta^{13}C$ DDA-values from the sediment samples supported the assumption of surface water contamination by remobilisation from contaminated sediment material as the main source of DDA. Isotope values of the non-polar metabolites DDD and DDMS ranged from - 20.9 ‰ to - 27.7 ‰. The DDA-values in the samples ranged from -20.8 ‰ to - 22.2 ‰ in sediment samples and from - 17.6 ‰ to - 23.5 ‰ in water samples. No clear trend could be derived for DDT-degradation. In addition to the DDX-related compounds a large number of structurally diverse halogen-organic compounds was identified (Ricking et al. 2005, Frische et al. 2010, Kucher et al. 2018, Zhu et al. 2019, Appendix 2).

This thesis should demonstrate the necessity to investigate not only extractable residues of sedimentary contamination but to consider the incorporation of contaminants and metabolites in particulate matter as well. Non-extractable residues in sediments can represent a long-term contamination potential for the environment. Most studies have largely neglected the remobilisation of the NER and its transformation reactions and products. Furthermore, released compounds can be transported to distant places due to adsorption on particles such as colloids and in dissolved state. The transport of released sediment compounds into the aquatic environment is also scarcely discussed or analysed in the literature.

An analytical approach resulting from the experience of the work is shown in Figure 6.1, where a distinction is made between the water phase and various particulate phases, including humic substances. The applied degradation approach is integrated into the scheme. These separate extracts can be used for bioassays, considering elemental sulphur (S_8) as the main toxicant in the sediment assay of the anoxic sediments. Additional toxicity tests revealed synergistic and antagonistic effects (see chapter 2.4), highly recommending further analyses.

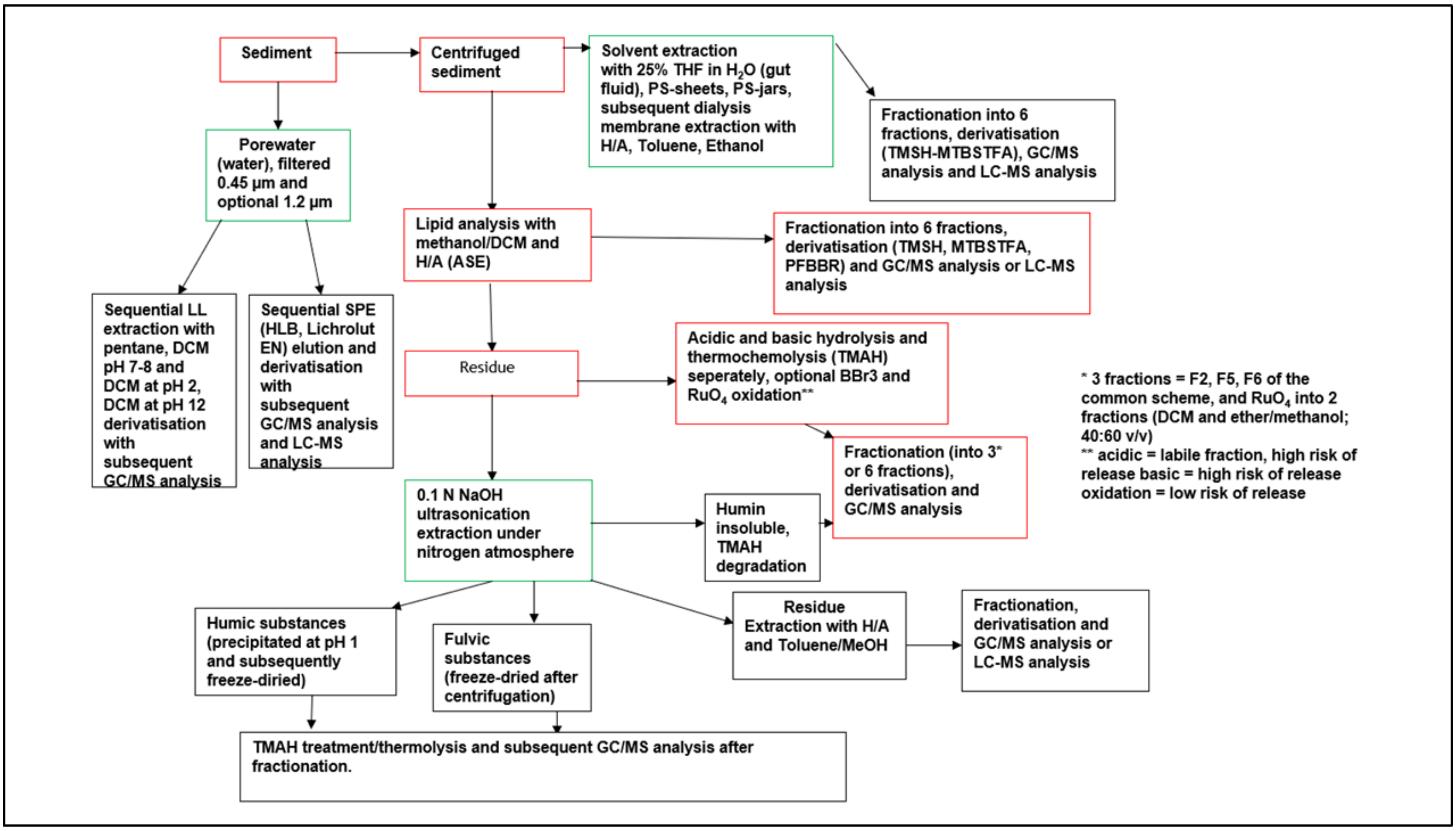

Figure 6.1: Analysis scheme of an extended evaluation approach.

To differentiate between the production process and the application, production source related compounds such as DDX ± Cl with an additional or missing chlorine atom (Kucher et al. 2018) are applicable. The analysis of three sediment samples from the source illustrated a relatively clean production process by the detection of DDT-Cl and DDD-Cl together with up to 700 times higher concentrations of the regularly chlorinated compounds.

Differences in the analytical approaches and degradation techniques lead to incomparable data and further scientific questions about the formation of NER and the constituents involved. Combined analytical approaches with classes of SOM-components (such as lipids, humic substances) are possible and the kinetics and dynamics of the NER-formation and release process can be studied. The method is currently being optimised to answer as many questions as possible (see current approaches in Zhu et al. 2019, Zhu et al. 2020), and a comparison between the NER and humic substances is useful and should be investigated. The acid hydrolysis has been removed in the meantime.

The EU is aware of the formation of NER (ECHA 2018), no recommendations are given for analyses of concentrations in NER. The release potential, especially from the ER fraction, is documented considering a sand layer of up to 15 - 20 cm, which is created by professional shipping when the sandy material is deposited on the banks.

Natural attenuation is occurring. To complete the evaluation potential of the presented approach, desorption and bio-accumulation experiments (Wang et al. 2019) can provide insights into the actual and potential contamination via the accumulated sediments.

The release potential from the sediment is supported by the carbon stable isotope analysis of DDA (Frische et al. 2020) and by the pore water analysis of a sediment core with a gradient from sediment to surface water (Heim et al. 2005).

The currently permitted discharge from the remediation of the source is 10 µg DDA L^{-1} (Kley 2014), mostly in the form of DDA methyl esters (Kley 2015, personal communication). No monitoring programme is carried out within the investigated channel water body and sediments. In surveillance wells at the production site, DDA was analysed as the most important DDX compound and in addition, DDA metabolites in the low mg L^{-1} range were identified as potential remediation markers for the effluents of the ongoing remediation at the point source (Frische et al. 2010). The WFD-EQS for total DDT [0.025 µg L^{-1}] (EU 2013) is far exceeded.

Zhu et al. 2019 illustrate the possible consequences of the release by reporting elevated concentrations along the canal, a “chromatographic system” indicated enhanced concentrations at the source and at the western end of the Teltow Canal near the Havel River. The relative contribution of the NER-fraction increased at the western end due to an elevated accumulation in organic-rich sediments at Lake Griebnitzsee.

Comparable data were obtained relative to earlier studies, indicating still a high degree of contamination and by the calculation of the maximum contamination range a continuous release potential into the water phase and Canal ecosystem.

Improvements in analytical tools are the application of MS-approaches with NCI, MS/MS, HRMS, GC x GC-TOF-MS and LC-HRMS. For the analysis of NER off-line pyrolysis approaches and TMAH-chemolysis or the application of TED-GC/MS are available, especially for the quick inclusion of NER-fractions due to the controlled pyrolysis via TGA (**T**hermo **G**ravimetrical **A**nalysis) of the TED-GC/MS-system. Additional sorbent material testing for the more hydrophilic compounds including derivatisation are currently in progress. For the CSIA-analysis the improvement of the resolution problem is possible through high-resolution fractionation.

The analysis of compounds/contaminants in humic substances, DOM, lignin and kerogen requires further efforts.

A recently published report summarised the potential of using plastic waste as an adsorbent to remove hazardous contaminants from aqueous samples (Zhang et al. 2019). Experiences with the methodological approach, which yielded a low recovery of the selected compounds, recommend further analyses to validate the tools as remedial agents. Removal of the contaminated sediment would result in an immediate release of the more water-soluble compounds, depending on the technique employed. Due to the maintenance of commercial shipping (on average 10-15 ships per day; http://www.wsa-b.de/), a sand cover is only possible near the shore. The results of experiments on desorption with plastic polymers from a heavily contaminated sediment revealed a low desorption of contaminants.

A monitoring programme is strongly recommended, especially in the heavily contaminated areas near the point source, notably in view of the use of the Johannisthal waterworks as a defensive well for the inflowing bank filtrate from the Teltow Canal. The relative contribution of particle-bound transport of contaminants has been researched to a limited extent (e.g. Schwientek et al. 2013, Rügner et al. 2019) and especially flood events, which are the main transport of particulate material, require further research.

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Appendix 1 Production history at the Source.

[t/yr] Year	DDT-Formulation	DDT-Synthesis
1949	173	10.33
1950	847	50.60
1951	996	59.50
1952	1960	117.08
1953	2511	150.00
1954	3405	203.41
1955	380	22.70
1956	1311	78.32
1957	1740	103.94
1958	1858	110.99
1959	2953	176.40
1960	2769	165.41
1961	2924	174.67
1962	5165	308.54
1963	5887	351.67
1964	3483	208.06
1965	3340	199.52
1966	3360	200.72
1967	3381	201.97
1968	3475	207.59
1969	3514	209.92
1970	2066	123.42
1971	1314	78.49
1972	598	35.72
1973	216	12.90
1974	175	10.45
1975	62	3.70
1976	16	0.96
1977	19	1.14
1978	23	1.37
1979	40	2.39
1980	8	0.48
1981	9	0.54
1982	8	0.48
1983	36	2.15
1984	112	6.69
1985	2	0.12
1986	6	0.36
Total Production	59852	

Appendix 2: List of unknown compounds detected in selected samples from the Teltow Canal, identified by means of MS-library search of Wiley 275-L, reference standards and by careful interpretation of mass spectra beside published mass spectra. The SRM samples are NIST SRM 1941 A (Reference material) and the hydrolysis is a basic hydrolysis.

Compounds	SRM 1941 A	SRM 1941 A hydrolysis	TEL79-85	TEL60-65	TEL 25-30
Anthropogenic compounds					
Halogenenated benzenes					
Chlorobenzene	-	-	+	+	+
1,3-DCB	-	-	+	+	+
1,4-DCB	-	-	+	+	+
1,2-DCB	-	-	+	+	+
1,3,5-TCB	-	-	+	+	+
1,2,4-TCB	+	-	+	+	+
1,2,3-TCB	-	-	+	+	+
1,2,3,5-/1,2,4,5-TeCB	+	-	+	+	+
1,2,3,4-TeCB	-	-	+	+	+
PeCB	+	(+)	+	+	+
HCB	+	(+)	+	+	+
Brombenzene	-	-	-	+	+
Dibrombenzene	-	-	+	-	-
Tetrabromobenzene	-	-	+	+	+
Pentabromobenzene	-	-	-	-	-
Chlorinated Styrenes					
Dichlorostyrene	-	-	3	2	2
Trichlorostyrene	-	-	2	2	2
Tetrachlorostyrene	-	-	-	-	-
Hexachlorostyrene	-	-	-	-	-
Heptachlorostyrene	-	-	-	-	-
Octachlorostyrene	-	-	-	-	-
Halogenated Toluenes					
Dibromotrichlorotoluene	-	-	-	-	-
Tribromodichlorotoluene	-	-	+	+	+
Tetrabromochlorotoluene	-	-	+	+	+
Pentabromotoluene	-	-	+	+	+
Chlorinated Anisoles					
Pentachloroanisole	-	-	-	-	-
Halogenated Anilines					
2,4,6-Tribromoanilin	-	-	+	+	+
Halogenated Naphthalenes					
2-Chloronaphthalene	-	-	+	+	+
1- Chloronaphthalene	-	-	+	+	+
1,3-Dichloronaphthalene	-	-	+	+	+
1,4- Dichloronaphthalene	-	-	+	+	+
1,5-/1,6- Dichloronaphthalene	-	-	+	+	+
1,7-/2,6-/2,7- Dichloronaphthalene	-	-	+	+	+

Compounds	SRM 1941 A	SRM 1941 A hydrolysis	TEL79-85	TEL60-65	TEL 25-30
1,2- Dichloronaphthalene	-	-	+	+	+
1,8- Dichloronaphthalene	-	-	+	+	+
Trichloronaphthalene	-	-	2	2	1
Tetrachloronaphthalene	-	-	-	+	-
Pentachloronaphthalene	-	-	-	-	-
Hexachloronaphthalene	-	-	-	-	-
Heptachloronaphthalene	-	-	-	-	-
2-Bromonapthalene	-	-	+	+	-
1-Bromonapthalene	-	-	+	+	+
Dibromonaphthalene	-	-	2	3	2
Chlorinated Biphenyls					
PCB-Mix, 2-9 chlorines per molecule	-	-	+	+	-
PCB-Mix, 3-7 chlorines per molecule	+	-	-	-	+
Deca-PCB (NCI)	**-**	**-**	**(+)**	**-**	**-**
PCT-Mix, 6-8 chlorines per molecule (NCI)	**-**	**-**	**(+)**	**-**	**-**
Polychlorinated dibenzo-p-dioxins					
TeCDD – OCDD			(-)	+	+
Polychlorinated dibenzo-p-furans					
TeCDF – OCDF			(+)	+	+
Polybrominated Diphenylethers					
Penta-BDE	-	-	-	-	(+)
Pesticides and Metabolites					
Pentachlorocyclohexene	-	-	+	+	-
α-HCH	-	-	+	+	+
β-HCH	-	-	+	+	+
γ-HCH	-	-	+	+	+
δ-HCH	-	-	+	+	+
2,4´-DDMU	-	-	+	+	+
4,4´-DDMU	+	-	+	+	+
2,4´-DDE	+	-	+	+	+
4,4´-DDE	+	-	+	+	+
2,4´-DDMS	-	-	+	+	+
4,4´-DDMS	-	-	+	+	+
4,4´-DDNS	-	-	+	-	-
2,4´-DDD	-	-	+	+	+
4,4´-DDD	+	-	+	+	+
2,4´-DDT	-	-	+	-	-
4,4´-DDT	-	-	+	+	+
4,4´-DDA-methyl ester	-	-	+	+	+
2,4´-DDCN	-	-	+	+	+
4,4´-DDCN	-	-	+	+	+
p-Chlorobenzaldehyde	-	-	+	n.a.	n.a.
2-Chlorobenzophenone	-	-	+	-	-
2,4´-Dichlorobenzophenone	-	-	+	+	+
x,x´-Dichlorobenzophenone	-	-	+	(+)	(+)
4,4´-Dichlorobenzophenone	-	-	+	+	+

Compounds	SRM 1941 A	SRM 1941 A hydrolysis	TEL79-85	TEL60-65	TEL 25-30
4,4´-Difluorobenzophenone	-	-	-	-	(+)
2-Bromobenzophenone	-	-	-	-	-
4,4´-Dibromobenzophenone	-	-	+	(+)	+
4,4´-Dichlorophenyl sulfone	-	-	+	n.a.	n.a.
1-(2-chlorophenyl)-1-(4-chlorophenyl)-ethene	-	-	-	-	-
1,1-Bis(4-chlorophenyl) ethene	-	-	-	-	-
Chlorfenson	-	-	+	-	+
Chlorofen	-	-	+	-	-
2,4´-Methoxychlor	-	-	+	+	+
4,4´-Methoxychlor	-	-	+	+	+
2,4´-MDE	-	-	+	-	-
4,4´-MDE	-	-	+	+	+
2,4´-MDD	-	-	+	-	+
4,4´-MDD	-	-	+	+	+
4,4´-MDA	-	-	n.a.	n.a.	n.a.
4,4´-MBP	-	-	n.a.	n.a.	n.a.
4,4´-Dimethoxybenzophenone	-	-	+	+	+
Bromopropylat	-	-	+	+	+
1,1-Bis(4-bromophenyl) acetic acid-iso-propylester	-	-	+	+	+
Chlorinated diphenylmethanes	-	-	-	-	(+)
Chlorinated triphenylmethanes	-	-	-	+	+
Chlorinated diphenylethers	-	-	-	-	-
Pentachlorophenole	-	-	+	+	-
α-and β-Endosulfane	-	-	-	-	-
Endosulfan ether	-	-	-	-	-
Endosulfan lactone	-	-	-	-	-
Hexachlorobutadiene	-	-	-	-	-
Aldrin	-	-	-	-	-
Dieldrin	-	-	-	-	-
Endrin	-	-	-	-	-
Isodrin	-	-	-	-	-
Heptachlor	-	-	-	-	-
Heptachlorepoxid	-	-	-	-	-
Technical Chlordane	-	-	-	-	-
Cis-Chlordane	-	-	-	-	-
Trans-Chlordane	-	-	-	-	-
Toxaphene (Melipax®)	-	-	-	-	-
Dichlorobenzoic acid (me)	-	-	-	-	-
Trichlorobenzoic acid (me)	-	-	-	-	-
Triclosan	-	-	-	-	-
Methyltriclosan	-	-	+	+	+

$^{(m)}$ = detected as methylester
(+) = tentatively identified