Verbleib und Bioverfügbarkeit persistenter Organochlorpestizide nach diffusen und punktuellen Einträgen im Einflussgebiet der Sowjetunion

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Abkürzungsverzeichnis

AP	Arbeitspaket
AR	Aqua regia (lat.) – Königswasser
BRD	Bundesrepublik Deutschland
BMBF	Bundesministerium für Bildung und Forschung
DDD	Dichlordiphenyldichlorethan
DDE	Dichlordiphenyldichlorethen
DDR	Deutsche Demokratische Republik
DDT	Dichlordiphenyltrichlorethan
DDX	Sammelbezeichnung für die 4,4′- und 2,4′-Kongenere von DDT, DDD und DDE
DNA	Desoxyribonucleic acid (engl.) – Desoxyribonukleinsäure (DNS)
dSPE	Dispersive solid-phase extraction (engl.) – Dispersive Festphasenextraktion
eDNA	Environmental DNA (engl.) – Umwelt-DNA
EU	Europäische Union
GC	Gaschromatographie
HCH	Hexachlorcyclohexan
HS	Headspace (engl.) – Dampfraum
ICP-OES	Inductive coupled plasma–optical emission spectrometry (engl.) – Optische Emissionsspektrometrie mit induktiv gekoppeltem Plasma
IS	Interner Standard
ISO	International Organization for Standardization (engl.) – Internationale Organisation für Normung
JLU	Justus-Liebig-Universität (Gießen)
LOD	Limit of detection (engl.) – Nachweisgrenze
LOQ	Limit of quantification (engl.) – Bestimmungsgrenze
MAE	Microwave-assisted extraction (engl.) – Mikrowellengestützte Extraktion
MISOLEX	Miniaturized solid-liquid extraction (engl.) – Miniaturisierte Fest-flüssig-Extraktion
MPA	Median der prozentualen Abweichung vom Median
MS	Massenspektrometrie
OCP	Organochlorpestizid, auch chlororganisches Pestizid
PAK	Polyzyklischer aromatischer Kohlenwasserstoff
PCB	Polychloriertes Biphenyl
PCDD/F	Polychloriertes Dibenzodioxin/furan
PLE	Pressurized liquid extraction (engl.) – Druckunterstützte Flüssigextraktion, auch ASE, Accelerated solvent extraction (engl.) – Beschleunigte Lösungsmittelextraktion
POP	Persistent organic pollutant (engl.) – Persistenter organischer Schadstoff

QuEChERS	Quick, easy, cheap, efficient, rugged, safe (engl.) – Schnell, einfach, günstig, effizient, robust, sicher
RT	Retention time (engl.) – Retentionszeit
SPME	Solid-phase microextraction (engl.) – Festphasenmikroextraktion
SU	Sowjetunion
VarK	Variationskoeffizient, auch relative Standardabweichung
WFR	Wiederfindungsrate
WRB	World Reference Base for Soil Resources

Zusammenfassung

Viele Organochlorpestizide (OCPs) wurden aufgrund ihrer Toxizität, ihres bioakkumulativen Potentials sowie ihrer Persistenz als Gefahr für die Umwelt erkannt. Infolgedessen wurden sie durch die Stockholmer Konvention 2001 als persistente organische Schadstoffe (persistent organic pollutants, POPs) eingestuft und entweder verboten oder ihr Einsatz stark begrenzt.

In den Einflussgebieten der Sowjetunion (SU) wurden chlororganische Verbindungen – insbesondere Dichlordiphenyltrichlorethan (DDT), Lindan (HCH) und polychlorierte Biphenyle (PCBs) – in großen Mengen produziert und eingesetzt. Einige Gebiete verblieben großflächig und stark kontaminiert und stellen damit auch heute noch eine Gefahr für die Gesundheit von Mensch und Tier dar. Zu diesen Gebieten zählen u. a. die ehem. DDR sowie Georgien.

Zehn Seen im Norden Ostdeutschlands – ehemals ein Teilgebiet der DDR – wurden auf Änderungen in der Stoffkonzentration im Zeitraum der letzten hundert Jahre untersucht. Ziel war es, Hinweise auf den menschlichen Einfluss aus Industrie und Landwirtschaft auf die Umwelt, zu finden. Dazu wurden in jedem See Sedimentbohrkerne entnommen und segmentiert. Jedes Segment wurde datiert, sowie die Konzentrationen an Spurenelementen (As, Cd, Cr, Cu, Ni, Pb, S und Zn) und OCPs (DDT und HCH) bestimmt. Die Konzentrationsverläufe der einzelnen Spurenelemente mit der Zeit sind gleichförmig. Sie entsprechen der industriellen Aktivität und den politischen Entwicklungen im Westen Deutschlands und der Europäischen Union vor 1990 und nicht, wie erwartet, jenen in der DDR. Von den untersuchten OCPs wurden nur Transformationsprodukte von DDT gefunden. Die Konzentrationsprofile lassen Rückschlüsse auf regionale Besonderheiten sowie nationale Gesetzgebung und Maßnahmen zu. Der Konzentrationsverlauf spiegelt zudem den DDT-Einsatz in der DDR wider. Insgesamt wurden Hinweise auf die industrielle Revolution, die Nachkriegszeit und die Anfänge der Umweltbewegung der 1960er und 1970er Jahre gefunden.

Da für die Analyse der Sedimentproben nur begrenzte Mengen Probenmaterials zur Verfügung standen, wurde ein miniaturisiertes Extraktionsverfahren (miniaturized solid-liquid extraction, MISOLEX) auf Basis der Festphasenmikroextraktion (solid-phase microextraction, SPME) erprobt und einem vergleichbaren Verfahren gegenübergestellt. Die Validierung der MISOLEX ergibt eine generell gute Übereinstimmung der Qualitätsparameter Nachweisgrenze (LOD), Bestimmungsgrenze und Wiederfindungsrate mit den Standardanforderungen der Analytik. Sie erreicht solch niedrige LODs, dass der Einsatz im Bereich der Spurenanalytik möglich wäre. Die neue Methode erweist sich als schneller durchführbar als die Vergleichsmethode. MISOLEX ermöglicht es, zeit- und kostensparend, größere Mengen an Proben zu extrahieren. Die Methode eignet sich ebenfalls dazu, Informationen über die flächenhafte Verbreitung von OCPs zu sammeln, für die eine Großzahl an Proben benötigt wird. Die relativ einfache und kostengünstige Anwendbarkeit ist insbesondere in Regionen mit begrenzten (finanziellen) Mitteln von Vorteil.

Im dritten Teil der Promotion wurde auf einer kontaminierten Fläche in Georgien eine Vorstudie zur Erprobung einer Phytoremediationsmethode durchgeführt. Dazu wurden im Rahmen von durch mich betreuter Studienarbeiten erste Ergebnisse gesammelt. Diese dienen nun als Fallbeispiel für den Einsatz von MISOLEX. Aufgrund der Heterogenität und begrenzten Probenzahl sind weitergehende Auswertungen sowie Untersuchungen erforderlich.

Abstract

Because of their toxicity, bioaccumlative potential and persistence, many organochlorine pesticides (OCPs) where deemed a threat to the environment. Therefore, they were declared as persistent organic pollutants (POPs) by the Stockholm Convention 2001. They were either banned or their usage restricted.

In the former Soviet Union's sphere of influence, organochlorine compounds – in particular diclorodphenyltrichloroethane (DDT), lindane (HCH), and polychlorinated biphenyls (PCBs) – were produced and used in large quantities. Some areas remain extensively and heavily contaminated, posing a risk to human and animal health. These areas include the former GDR and Georgia (Caucasus).

Ten lakes in the north of eastern Germany – formerly a part of the GDR – were examined for changes in the concentration of substances over the course of the last hundred years. The aim was to find evidence of human impact of industry and agriculture on the environment. To this end, sediment cores were taken from each lake and sliced. Each slice was dated and the concentrations of trace elements (As, Cd, Cr, Cu, Ni, Pb, S and Zn) and OCPs (DDT and HCH) were determined. The trend of concentration of the individual trace elements over time was uniform. It corresponded to industrial activity and political developments in West Germany and the European Union before 1990 and not, as expected, to those in the GDR. Of the group of OCPs, only transformation products of DDT were found. The concentration profiles allow conclusions to be drawn about regional characteristics as well as national legislation and measures. The concentration profile also reflects the use of DDT in the GDR. Overall, indications of the industrial revolution, the post-war period and the beginnings of the environmental movement of the 1960s and 1970s were found.

As only limited amounts of sample material were available for the analysis of the sediment samples, a miniaturized extraction method (miniaturized solid-liquid extraction, MISOLEX) based on solid-phase microextraction (SPME) was tested and compared with a comparable method. The validation of MISOLEX showed a generally good agreement of the qualitative measurement values, i.e., limit of detection (LOD), limit of quantification, and recovery rate with the standard requirements of analytics. It achieved such low LODs that it could be used in the field of trace analysis. The new method proved to be faster than the comparative method. MISOLEX enables extraction of larger quantities of samples in a time and cost-saving manner. It is also suitable for collecting information on the areal distribution of OCPs, for which a large number of samples are required. The relatively simple and cost-effective applicability is particularly advantageous in regions with limited (financial) resources.

The third part of this thesis, a preliminary study of the validation of a phytoremediation method was conducted on a contaminated pasture in Georgia (Caucasus). In the course of several student theses supervised by me, first results were obtained. These serve as example for the application of MISOLEX. However, because of the study site´s heterogeneity and a limited amount of samples, further investigations and analyses are necessary.

1 Erweiterte Zusammenfassung

1.1 Einleitung

Organochlorpestizide (OCPs, auch chlororganische Pestizide) sind Chlorkohlenwasserstoffe, die zur Schädlingsbekämpfung und im Pflanzenschutz eingesetzt werden. Zu ihnen gehören eine Vielzahl von Verbindungen. Ihnen gemein ist ein zumeist zyklisches oder aromatisches Grundgerüst sowie eine bis mehrere funktionelle Chlorgruppen. Bekannte Vertreter der Gruppe sind u. a. Lindan (Hexachlorcyclohexan, HCH), Dichlordiphenyltrichlorethan (DDT), Aldrin, Dieldrin, Endrin, Chlordan, Chlordecon, Heptachlor, Hexachlorbenzol (HCB), Mirex und Toxaphen (Blus 2003). Aufgrund der Halogenierung sind die meisten der genannten Verbindungen biologisch wie physikalisch schwer abbaubar (persistent). Da sie zumeist schädliche Nebenwirkungen auf Natur und Mensch aufweisen, sind sie als persistente organische Schadstoffe (POPs, von engl. persistent organic pollutants) deklariert und Einsatz sowie Produktion beschränkt oder verboten worden (UN 2001). Ausnahmen existieren für einige wenige POPs und lediglich für bestimmte Anwendungsfälle, z. B. für die Schädlingsbekämpfung (z. B. Läuse, Mücken, Zecken) zur Sicherung der menschlichen Gesundheit (Malariavektorkontrolle).

In der Sowjetunion (SU) wurden OCPs in großen Mengen produziert und ausgebracht. Dort gehörten DDT und HCH zu den am meisten produzierten Pestiziden der 1940er und 1950er Jahre (Kundiev und Kagan 1993). Aufgrund ihrer Persistenz verbleiben Rückstände dieser Substanzen in Böden und Sedimenten (Sharov et al. 2016). Unter bestimmten Umständen, wie z. B. erhöhten Temperaturen oder Flutereignissen, können sie remobilisiert werden (Ren et al. 2019; Crawford et al. 2022). Der landwirtschaftliche Verbrauch von HCH in der SU belief sich, Schätzungen von Li et al. (2004) zufolge, zwischen den Jahren 1950 und 1990 auf ca. 1.940 Kt technisches HCH und 40 Kt Lindan, welches das erstere kontinuierlich ersetzte. Im selben Zeitraum wurden ca. 250 bis 520 Kt DDT in der Landwirtschaft eingesetzt, der Großteil davon in den südlichen Regionen der SU (Li et al. 2006). Die DDR war in diesen Schätzungen nicht enthalten. In der Zeit von 1968 bis 1973 wurden dort laut Heinisch et al. (1993) ca. 21,5 Kt DDT produziert. Die DDR-Regierung war zwar bekannt dafür, an die Öffentlichkeit gerichtete Zahlen zu schönen, doch soll sie zu Daten der Pestizidverteilung in die verschiedenen Bezirke akribisch Buch geführt haben (Heinisch und Klein 1992).

Um Daten zu historischen Vorkommnissen und Sachverhalten zu prüfen oder zu rekonstruieren, bieten sich Abgleiche mit Umweltarchiven an, wie z. B. Torfbohrkernen, Wachstumsringen in Bäumen, Eisbohrkernen oder Seesedimenten (Waters und Turner 2022). Der Norden Ostdeutschlands zeichnet sich durch eine hohe Dichte an Seen aus. Sie liegen eingebettet in eine Landschaft, die durch über 80 Jahre intensive Landwirtschaft geprägt ist (Bauerkämper 2004; Sommer et al. 2008). Damit bietet diese Region optimale Bedingungen für die Untersuchung von Seesedimenten auf Hinweise von Pestizidnutzung und -verschmutzung aus den Zeiten der DDR. Obwohl solcherlei Untersuchungen in anderen Industrienationen durchgeführt wurden – z. B. Russland (Adams et al. 2018), Kanada (Kurek et al. 2019), Schweiz (Chiaia-Hernández et al. 2020) – gibt es dafür bisher keine Daten für Deutschland.

Zu den zuvor erwähnten südlichen Regionen der SU, in denen der Großteil der Pestizide eingesetzt wurde, gehört u. a. Georgien. Dort wurden zu SU-Zeiten jährlich ca. 25 bis 30 Kt Pestizide verteilt. Es gab 18 größere Pestizidlager mit einem Fassungsvermögen von je 21 Kt. Von diesen Zentral-

lagern aus wurden Lagerhäuser auf Bezirksebene versorgt, die zumeist von Kolchosen oder Sowchosen geführt wurden (d. h. genossenschaftlich bzw. staatlich geführte, landwirtschaftliche Großbetriebe). In den zwei Jahrzehnten nach 1990 sind diese Lager beinahe alle zerstört worden. Der Großteil der Einrichtungen und ihr Gelände liegt nun in privater Hand. Einige davon wurden schlichtweg sich selbst überlassen. Überreste von Pestiziden wurden entweder von Anwohnern entwendet oder mit der Zeit durch Witterungseinflüsse verteilt. Oftmals sind die ruinösen Gebäude nicht gesichert; grasendes Weidevieh kann die kontaminierten Gelände betreten oder es werden Feldfrüchte darauf oder in unmittelbarer Nähe angebaut. (Sopadze 2006; UN 2010).

Diese kontaminierten Flächen stellen eine Gefahr für Mensch und Umwelt dar: Einerseits über direkte Exposition, andererseits indirekt über die Nahrungskette (Feldfrüchte und Weidevieh). Es gibt zahlreiche Methoden, Kontaminationen zu bereinigen (Lee et al. 2024). Diese unterscheiden sich in Aufwand, Anwendungsdauer und Kosten. Die finanziellen Mittel der ländlichen Bevölkerung in Georgien sind begrenzt (Lud et al. 2022), weshalb simple und kostengünstige Methoden zu präferieren sind. Entsprechend bietet sich Phytoremediation als Sanierungsmethode an. Um diese Möglichkeit zu validieren, wurde eine Phytoremediationsstudie auf dem zuvor erwähnten Standort in Georgien durchgeführt.

Ziel dieser Dissertation ist es, aufzuzeigen, welche Folgen der landwirtschaftlichen Praktiken aus der Zeit der SU noch heute fortdauern. Dem Einfluss auf dem Gebiet Deutschlands (formals DDR) wird in Kapitel 3 nachgegangen, während in Kapitel 1.5.3 die Folgen an einem Standort in Georgien dargestellt werden und eine Sanierungsmethode erprobt wird. Die Grundlage für die Analytik wird in Kapitel 2 gelegt.

1.2 Eigenschaften und Schicksal von Organochlorpestiziden

1.2.1 Chemische Eigenschaften

Dichlordiphenyltrichlorethan (DDT)

DDT ist ein günstig herzustellendes, persistentes, breit wirksames Kontakt- und Fraßinsektizid. Es wurde gegen Schädlinge in der Landwirtschaft, Obstplantagen, Gärten und dem Forst eingesetzt, oder auch um blutsaugende Insekten und Krankheitsüberträger (z. B. Mücken und Zecken) zu bekämpfen. Es ist eine der ersten synthetischen Chemikalien, die in großen Mengen produziert und weit in die Umwelt ausgebracht wurden (Li et al. 2006). Dabei hat vermutlich nur ein Bruchteil davon die Zielorganismen tatsächlich erreicht und sich der Großteil in Wasser und vor allem Boden angereichert (Somerville und Greaves 1987; Camenzuli et al. 2016).

Die erste Synthese von DDT fand 1874 durch Othmar Zeidler statt (Zeidler 1874). Erst 1939 entdeckte Paul Hermann Müller die insektizide Wirkung, wofür ihm 1948 der Medizinnobelpreis verliehen wurde (Nature 1948). Die schädlichen Eigenschaften und Auswirkungen auf die Biosphäre wurden erst später entdeckt, weshalb DDT sowie andere Stoffe durch die Stockholmer Konvention 2001 als POPs deklariert und ihr Einsatz stark eingeschränkt bis verboten wurde (UN 2001). Aber selbst nach dem Verbot wurde es noch bis 2009 in Antifoulingfarben für Schiffanstriche (Lin et al. 2009) sowie für die Produktion des Akarizids Dicofol bis 2019 genutzt (Tian et al. 2021).

DDT wird durch Kondensation von Chloralhydrat an Chlorbenzol in Anwesenheit von Schwefelsäure hergestellt (Zeidler 1874). Dabei entstehen die zwei Hauptkongenere 4,4′-DDT und 2,4′-DDT mit Anteilen von 65–80 bzw. 15–20 % (Haller et al. 1945), wovon lediglich das erstgenannte Kongener 4,4′-DDT die insektizide Wirkung trägt. Abb. 1 auf S. 4 gibt eine Übersicht über den strukturellen Aufbau der genannten Kongenere.

Das Hauptabbauprodukt von DDT ist unter aeroben Bedingungen Dichlordiphenyldichloroethen (DDE). Herrschen anaerobe Bedingungen vor, ist es Dichlordiphenyldichlorethan (DDD; Aislabie et al. 1997). Beim Abbau behalten die Kongenere ihre 4,4′- oder 2,4′-Konformation bei (Ricking und Schwarzbauer 2012). Für Erstere wurden höhere log K_{OW}-Werte bestimmt, womit sie eine höhere Lipophilität als Zweitere aufweisen (ATSDR 2022). Der logarithmierte Verteilungskoeffizient zwischen Wasser und organischem Kohlenstoff (log K_{OC}) liegt für 4,4′-DDT und 4,4′-DDD bei 5,18 (Meylan et al. 1992; ATSDR 2022) und für 4,4′-DDE bei 4,7 (Sabljic 1984), was darauf hinweist, dass sie stark an die Bodensubstanz sorbieren. Gepaart mit einer relativ geringen Wasserlöslichkeit (0,025, 0,12 bzw. 0,090 $mg \cdot L^{-1}$; Howard 1997), lässt dies vermuten, dass der Abfluss aus dem Boden zuvorderst an partikuläre Substanz gebunden vonstattengeht.

Per Volatilisation (Verdampfung) gelangt DDT aus den Kompartimenten Boden oder Wasser in das Kompartiment Luft. Die Neigung aus dem Wasser in die Luft zu wechseln, wird mit der sog. Henry-Flüchtigkeitskonstante (H_V) beschrieben. Sie liegt zwischen $5{,}9 \cdot 10^{-7}$ und $2{,}1 \cdot 10^{-5}$ $(atm \cdot m^3) \cdot mol^{-1}$ (Howard 1997). Die daraus abgeleiteten Volatilisationshalbwertszeiten aus einem Modellfluss lagen zwischen 3,3 und 10,5 d (Atlas et al. 1982). Für die Betrachtung von feuchten Bodenoberflächen kann als Näherung die sog. Dow-Methode angewandt werden, bei der die Henrykonstante durch den K_{OC} dividiert wird (Thomas 1996).

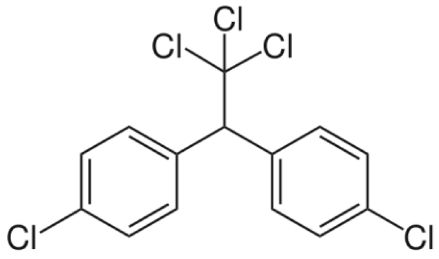
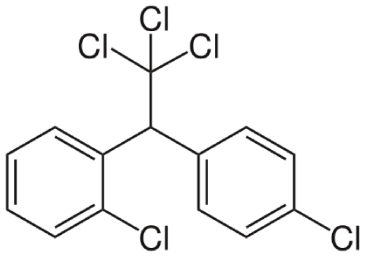
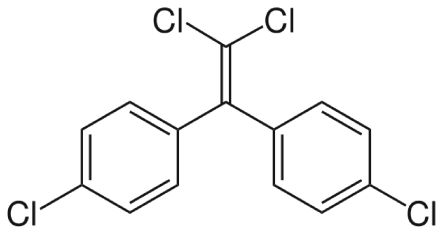
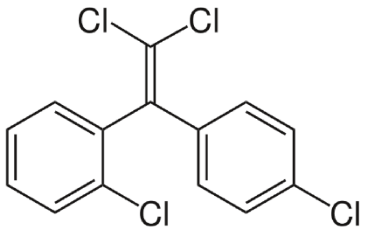
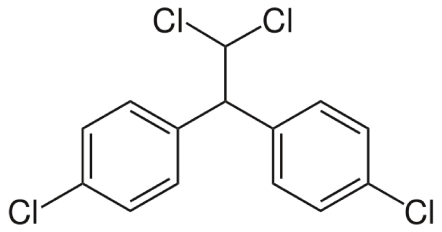
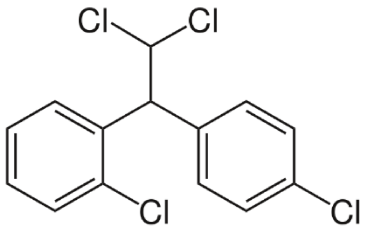
	4,4′-Kongenere	2,4′-Kongenere
Primärprodukte	 **4,4′-DDT**	 2,4′-DDT
Anaerobe Abbauprodukte	 4,4′-DDD	 2,4′-DDD
Aerobe Abbauprodukte	 4,4′-DDE	 2,4′-DDE

Abb. 1 – Kongenere von DDT und seiner zwei primären Abbauprodukte DDD und DDE. Der eigentliche Wirkstoff ist durch Umrahmung hervorgehoben. Abbildungen Leyo (2010), public domain.

Hexachlorcyclohexan (HCH)

Erstmals synthetisiert wurde HCH im Jahre 1825 von Michael Faraday (Ulmann und Blaquiere 1973). Die insektizide Wirkung hingegen wurde erst in den 1930er Jahren entdeckt (Vijgen 2006). HCH besteht aus einem einzelnen Kohlenstoffring (Cyclohexan), dessen Kohlenstoffatome jeweils eine Chlorgruppe aufweisen. Durch die jeweils zwei möglichen Anordnungen der Chloratome pro Kohlenstoffatom (axial oder äquatorial zur Ringebene) ergeben sich mehrere mögliche Isomere, die mit einem griechischen Präfix von Alpha (α) bis Theta (θ) deklariert werden. Das α-Isomer tritt zusätzlich als Enantiomer auf (s. Abb. 2 auf S. 5).

HCH wird durch photochemische Addition von Chlor an Benzol hergestellt (LUBW 1993; Vijgen et al. 2011). Das bei der Synthese entstehende Isomerengemisch enthält folgende Hauptbestandteile: 55–80 % α-HCH, 5–14 % β-HCH, 8–15 % γ-HCH, 2–16 % δ-HCH und 3–5 % ε-HCH (Kutz et al. 1991). Ähnlich DDT, besitzt nur eines der synthetisierten Isomere, γ-HCH, die gewünschte, insektizide Eigenschaft. Die restlichen ca. 85 % sind unerwünschte Nebenprodukte. Dieses sog. technische Gemisch wurde entweder in dieser Form oder, nach Aufreinigung, mit γ-HCH-Gehalten von > 90 % eingesetzt. Diese konzentrierte Formulierung ist als sog. Lindan bekannt. Der Großteil der heute als verseucht geltenden Flächen ist entweder durch die bestimmungsgemäße Ausbringung von HCH oder Lindan auf landwirtschaftliche Flächen entstanden oder durch die unberechtigte Entsorgung der Nebenprodukte (Vijgen et al. 2011).

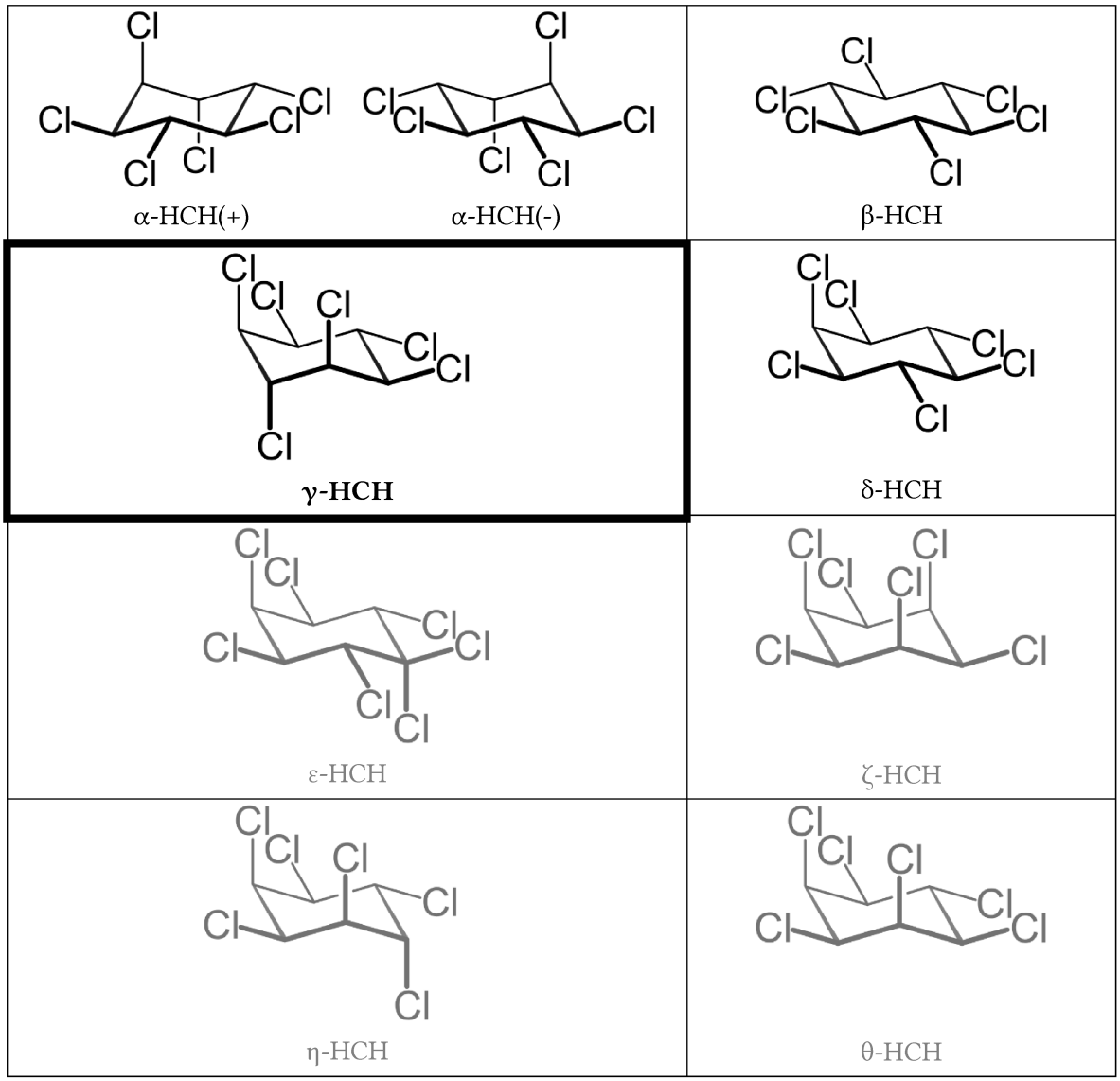


Abb. 2 – Isomere von HCH in Sesseldarstellung zur Verdeutlichung der Konformationsunterschiede. Der eigentliche Wirkstoff ist durch Umrahmung hervorgehoben. Die in dieser Arbeit nicht betrachteten Isomere sind grau gefärbt. Abbildungen Yikrazuul und NadirSH (2024), public domain.

In dieser Arbeit wurden von den bei der Synthese produzierten Isomeren die vier am häufigsten auftretenden untersucht: Alpha (α), Beta (β), Gamma (ɣ) und Delta (δ). Als Isomere besitzen sie das gleiche Molekulargewicht. Sie gelten als licht-, temperatur- und säurestabil (Ngabe et al. 1993). Worin sie sich unterscheiden, ist die Anordnung ihrer Chloratome. Dies ist wiederum für Unterschiede in den chemischen Eigenschaften verantwortlich. So sind die Isomere zwar allgemein gering wasserlöslich (Eichler 1983), ɣ- und δ-HCH sind allerdings um 1–2 Magnituden löslicher als α- und β-HCH.

Das reaktivste Isomer ist ɣ-HCH, gefolgt von α-HCH, δ-HCH und β-HCH. Letzteres besitzt – bedingt durch die thermodynamisch günstige äquatoriale Stellung der 6 Cl-Atome – eine größere thermodynamische Stabilität und Unpolarität als die anderen Isomere (DFG 1982; Eichler 1983).

Im Vergleich mit anderen OCPs, wie z. B. DDT, sind die HCH-Isomere generell wasserlöslicher und volatiler. Dies könnte erklären, wieso sie großflächiger verbreitet und in allen Umweltkompartimenten (Wasser, Sediment, Luft, Biota) anzutreffen sind (Chen et al. 2015).

1.2.2 Analytik

Für die Extraktion von Pestiziden aus Umweltproben existieren mehrere etablierte Methoden. Dazu zählen u. a. die Soxhletextraktion, die ultraschallverstärkte Extraktion, die mikrowellengestützte Extraktion (MAE, von engl. microwave assisted extraction) oder die druckgestützte Extraktion (PLE, von engl. pressurized liquid extraction; Ayala-Cabrera et al. 2021). Die Entwicklungen neuer Extraktions- oder Vorextraktionsmethoden orientieren sich heutzutage an den Prinzipien der sog. Grünen Chemie (Gałuszka et al. 2013). Es handelt sich deshalb meist um miniaturisierte Methoden mit geringen Probenvolumina und geringem Lösungsmittelverbrauch (Ali et al. 2019; Prosen 2019). Die QuEChERS-Methode (quick, easy, cheap, efficient, rugged and safe; engl. für schnell, einfach, günstig, effizient, robust, sicher; Anastassiades et al. 2003) ist ein Beispiel dafür. Ursprünglich für die Extraktion von Pestizidrückständen in Nahrungsmitteln entwickelt, ist sie mittlerweile für eine Vielzahl weiterer Matrices angepasst worden (Vera et al. 2013). Noch immer werden neue Methoden auf der Basis von QuEChERS oder der ihr zugrundeliegenden dispersiven Festphasenextraktion (dSPE, von engl. dispersive solid-phase extraction) veröffentlicht (Eyring et al. 2021; Park et al. 2021). So erfährt die Entwicklung von neuartigen Sorbentien Aufmerksamkeit (Li et al. 2021; Huang et al. 2020), aber auch der Einsatz neuartiger Extraktionsmaterialien (Lee et al. 2020; Llaver et al. 2021). Gleichwohl bleibt die Mikroextraktion weiterhin eine Methodenart der Wahl für die Extraktion oder Aufreinigung von Proben – ob mit Lösungsmittel (bspw. liquid-phase microextraction, LPME, engl. für Flüssigphasenmikroextraktion; Prosen 2019; Rutkowska et al. 2019) oder lösungsmittelfrei (bspw. solid-phase microextraction, SPME; engl. für Festphasen-mikroextraktion; Liang et al. 2019; Naccarato und Tagarelli 2019).

In dieser Arbeit wurde von der SPME intensiv Gebrauch gemacht. Sie wird als Extraktions- und Vorkonzentrationsmethode eingesetzt (Arthur und Pawliszyn 1990). Dazu wird eine mit einem Sorbens beschichtete Faser der Probe ausgesetzt. Dies kann entweder direkt in die Probe eingetaucht (engl. immersed) oder indirekt im Dampfraum (HS, von engl. headspace) der Probe geschehen. In der vorliegenden Arbeit wurde Zweiteres genutzt. Während der Exposition akkumuliert die Beschichtung der Faser verfügbare Stoffe im Dampfraum; darunter günstigerweise die gesuchten Analyten. Anschließend wird sie im Injektor eines Gaschromatographen thermisch desorbiert. Ein zusätzlicher Aufreinigungsschritt ist meist nicht notwendig. Nach Desorption steht die Faser für eine neue Extraktion zur Verfügung; sie ist mehrfach wiederverwendbar. Wenn die Extraktion im Dampfraum, anstatt direkt eingetaucht durchgeführt wird, kann man von einer erheblichen Reduktion von die Analyse störenden Matrixkomponenten profitieren. Zusätzlich wird die Wiederverwendbarkeit und damit die Lebensdauer der Faser erhöht (Zhang und Pawliszyn 1993; Zhang et al. 1994). Im Gegensatz zur herkömmlichen Flüssiginjektion, bei der meist nur ein kleiner Teil der Probe direkt injiziert wird, gelangt bei der SPME der Analyt nahezu quantitativ von der Faser in den Injektor. Wenn man von Festphasenproben mit entsprechenden Lösungsmitteln einen Extrakt generiert, kann man diesen mittels SPME aufreinigen (Hernandez et al. 2000; Fidalgo-Used et al. 2003).

Zur chromatographischen Auftrennung der Stoffe vor der Detektion steht klassischerweise für halb- und leichtflüchtige Stoffe die Gaschromatographie (GC) zur Verfügung. Doch erlangt in letzter Zeit die Flüssigchromatographie (LC, von engl. liquid chromatography) mehr und mehr Aufmerksamkeit, da mit ihr eine größere Flexibilität hinsichtlich untersuchbarer Arten von

Pestiziden gegeben ist und somit auch schwer- bis nichtflüchtige Stoffe in einem Lauf aufgetrennt werden können (Brinco et al. 2023).

Wurden zur Detektion von halogenierten Pestiziden früher vornehmlich die an die GC angeschlossenen Flammenionisations- und Elektroneneinfangdetektoren verwendet (FID bzw. ECD, von engl. electron capture detector), ist heute die (hochauflösende) Massenspektrometrie (MS) meist das Mittel der Wahl (Brinco et al. 2023).

1.2.3 Schicksal von Organochlorpestiziden in der Umwelt

Werden chemische Verbindungen, in diesem Fall organische Pestizide, in die Umwelt gebracht, hängt ihr Schicksal von den lokal herrschenden Bedingungen sowie ihren chemisch-physikalischen Eigenschaften ab. Als klassische Vertreter der POPs sind den hier betrachteten Stoffgruppen DDT und HCH eine gewisse Stabilität und Volatilität gemein. Beides zusammengenommen ermöglicht die Verteilung in der Umwelt über weite Strecken. Dabei verteilen sie sich zwischen den Umweltkompartimenten Boden, Luft, Aerosol, Wasser, Eis, Schnee und Biota entsprechend ihrer physikochemischen Eigenschaften (Wania und Mackay 1999; Scheringer 2008). Volatilere Stoffe werden schneller über die Atmosphäre verteilt, wohingegen weniger volatile Stoffe vermehrt mit Oberflächenmedien wie Boden, Wasser, Eis, Schnee und Vegetation interagieren und somit weniger schnell über weite Strecken transportiert werden (Scheringer 2008). Die Temperatur hat einen entscheidenden Einfluss auf physikochemische Eigenschaften wie Dampfdruck, Henrykonstante (H_V) und Oktanol-Luft-Verteilungskoeffizient (K_{OA}) der Chemikalien: Die zwei zuerst genannten sinken mit den Temperaturen ebenfalls, wohingegen der K_{OW} der hier betrachteten hydrophoben Verbindungen steigt. Dies führt dazu, dass die Chemikalien in kälteren Regionen wie in einer Kältefalle längere Zeit verweilen und angereichert werden können. Darüber hinaus stehen sie somit vermehrt der Aufnahme von Lebewesen zur Verfügung und können sich bei entsprechend vorherrschender Lipophilität in der Nahrungskette anreichern (Biomagnifikation). Insbesondere in arktischen Regionen wurde dies beobachtet (Lie et al. 2003), aber auch in Höhenlagen (Ren et al. 2017).

Auf die lokale Skala übertragen zeichnet sich ein analoges Bild, indem das Schicksal von den äußeren Einflüssen wie auch den Stoffeigenschaften bedingt wird. Sind organische Schadstoffe in einem Boden vorhanden, liegt es an ihrer Hydrophilität, ob sie sich im Bodenwasser lösen oder an der Bodenmatrix (z. B. Humus oder Ton) sorbieren. In beiden Fällen können sie direkt bzw. indirekt in tiefere Bodenschichten oder das Grundwasser gewaschen werden (engl. leaching). An die Bodensubstanz gebunden können sie per Erosion und Verdriftung durch Wind und Wasser auf horizontaler Ebene den Ort wechseln. Wie schon auf globaler Ebene beschrieben, können sie auch durch Verdampfung und Wind transportiert werden.

Abgesehen von reinen Ortsänderungen können Chemikalien auch Transformation unterliegen; zum einen physikochemisch (Hydrolyse oder Photolyse) und zum anderen biochemisch durch Mikroben unter aeroben oder anaeroben Bedingungen (Gavrilescu 2005). Zudem können sie von Organismen aufgenommen werden und somit in die Nahrungskette gelangen. Aufgrund der hohen Lipophilität werden sie im Fettgewebe angereichert (Kutz et al. 1991; Nolan et al. 2012). Von dort können sie in den Blutkreislauf remobilisiert und weiter in andere Organe oder z. B. die Muttermilch übertragen werden (Longnecker et al. 1997; Smith 1999; Stuetz 2006).

1.2.4 Sanierungsmethoden

Die Schadstoffaufnahme durch Organismen, genauer gesagt Pflanzen, lässt sich für die Sanierung kontaminierter Standorte nutzbar machen und fällt in die Kategorie der sog. Phytoremediation.

Sanierungsmethoden zielen darauf ab, einen aus biologischer Sicht akzeptablen Umweltzustand an einem kontaminierten Standort zu erreichen, der keine weiteren, zukünftigen Maßnahmen erfordert. Sie können generell in 4 Kategorien eingeteilt werden (Gavrilescu 2005):

1. Entfernung: physikalische Entfernung des Schadstoffs oder des durch ihn kontaminierten Mediums vom Standort
2. Abscheidung: Entfernung des Schadstoffs aus dem Wirtsmedium (Boden oder Wasser)
3. Zerstörung: biologischer oder chemischer Abbau oder Neutralisation des Schadstoffs, der danach z. B. als weniger toxisches Produkt vorliegt
4. Einkapselung: Hinderung oder gänzliche Immobilisierung des Schadstoffes

Je nach eingesetztem Prozess findet die Remediation vor Ort statt (in situ), oder das kontaminierte Medium muss andernorts behandelt werden (ex situ). Die Situation an einem kontaminierten Standort setzt sich aus den spezifischen Umweltbedingungen sowie aus dem Gemisch an Schadstoffen zusammen. Entsprechend muss für jede Situation individuell entschieden werden, welche und ob eventuell mehr als eine Sanierungstechnik zum Einsatz kommt. Eine Übersicht über Sanierungstechniken zur Behandlung kontaminierten Bodens gibt folgende Tabelle:

Tabelle 1 – Sanierungstechniken für kontaminierte Böden (nach Lee et al. 2024)

Methode	**In situ**	**Ex situ**
Thermisch	Thermisch unterstützte Bodenluftabsaugung Einspeisung von Heißdampf	Verbrennung Pyrolyse Thermische Desorption Verglasung
Physiko-chemisch	(Reaktive) Dichtwände Bodenspülung Bodenluftabsaugung	Bodenwäsche Lösungsmittelextraktion Chemische Dehalogenierung Chemische Reduktion und Oxidation Adsorption an Polymere
Biologisch	Natürliche Attenuation (passiv oder beschleunigt) Bioremediation Phytoremediation	Landfarming Bioreaktoren

Die Prinzipien der Nachhaltigkeit halten auch in den Bereich der Sanierungstechniken Einzug. Dadurch werden sie um die Aspekte der Umweltqualität und des Umweltschutzes erweitert. Es genügt nicht mehr, lediglich einen guten Bodenzustand zu erreichen. Zusätzlich muss dies mit so wenig Umwelt- und Klimaschäden wie möglich verbunden werden. Holistische Herangehensweisen verbinden sie mit soziologischen und wirtschaftlichen Aspekten (Grifoni et al. 2022; Lee et al. 2024).

Aus diesem Grund wurde sich in dieser Arbeit für die biologischen Sanierungsmethode der Phytoremediation entschieden, auch weil diese meist mit geringerem finanziellen, sowie technischem Aufwand zu bewerkstelligen ist. Unter Phytoremediation versteht man die Entfernung von Schadstoffen aus dem Bodenmedium durch Anbau von Pflanzen. Angefangen im Wurzelraum (Rhizosphäre) können Pflanzen z. B. über Wurzelexsudate den mikrobiellen Abbau beschleunigen (Rhizoremediation) oder die Immobilisierung von Schadstoffen bewirken (Phytostabilisierung). Je nach Lipophilität des Schadstoffes kommt es nach der Adsorption an das Wurzelgewebe zur Aufnahme in die Pflanze selbst (Extraktion). Dort werden die Schadstoffe weitertransportiert und entweder angereichert (Phytoakkumulation), abgebaut (Phytotransformation) oder eventuell wieder an die Atmosphäre ausgeschieden (Phytovolatilisation; Schnoor 1997; Singh und Singh 2017).

Um einen größtmöglichen Phytoremediationserfolg zu erreichen, bedarf es der sorgfältigen Auswahl geeigneter Pflanzenarten. Sie müssen selbst tolerant gegenüber den Schadstoffen sein, ein schnelles Wachstum aufweisen und dabei möglichst eine große Menge an Biomasse anlegen (Gerhardt et al. 2017; Zhu et al. 2024). Zusätzlich kann die Phytoremediation direkt durch die Schaffung optimaler Wachstumsbedingungen für die Pflanzen, oder indirekt durch mikrobiellen Abbau, verstärkt werden. Abgesehen vom reinen Remediationserfolg können auch weitere positive Effekte in Betracht gezogen werden. Zum Beispiel kann der Anbau der Pflanzen die Erosion auf der kontaminierten Fläche reduzieren (Chattopadhyay und Chattopadhyay 2015).

Für die Phytoremediation der Kongenere von DDT und seiner Abbauprodukte DDE und DDD (hiernach zusammenfassend DDX) im Speziellen haben sich Pflanzenarten der Familie der Kürbisgewächse (Cucurbitaceae) als starke Akkumulierer erwiesen, die DDX insbesondere in die oberirdische Biomasse einlagern (Lunney et al. 2004; Neitsch et al. 2016). Allerdings besteht beim Anbau von essbaren Pflanzenarten das Risiko, dass diese von Tier oder Mensch verzehrt werden. Daher müssen adäquate Sicherheitsmaßnahmen getroffen werden, um dies auszuschließen. Abgesehen von Kürbisgewächsen werden auch Grasarten – z. B. Vertreter der Süßgräser (Poaceae) – oft genutzt. Sie weisen nicht nur ein schnelles Wachstum auf, was mehrere Ernten im Jahr ermöglicht, sondern bilden zudem ein dichtes, faseriges Wurzelwerk aus, das einen großen Anteil des Bodenkörpers durchdringt. Zudem wurde gezeigt, dass sie polyzyklische aromatische Kohlenwasserstoffe (PAKs) und PCBs relativ zügig aus dem Boden entfernen können (Paul et al. 2015; Shahsavari et al. 2016).

Aus den genannten Gründen – und weil Saatmischungen unkompliziert und kostengünstig im Untersuchungsland Georgien zu erstehen waren – wurde sich auch in der vorliegenden Arbeit für die Nutzung von Gräsern entschieden.

1.3 Ziele

Mit dieser kumulativen Dissertation sollen Verbleib und Bioverfügbarkeit persistenter OCPs, die zu Zeiten der SU in deren Einflussgebiet aus punktuellen und diffusen Quellen in die Umwelt gelangt sind, untersucht werden.

Die wissenschaftliche Zielsetzung ist in drei Arbeitspakete (APs) aufgeteilt und liegt auf:

1. der Validierung und Erprobung einer miniaturisierten OCP-Extraktionsmethode auf Basis der SPME zur (flächenhaften) Erfassung von Belastungssituationen bei geringen Probenvolumina.
   Hiermit wird die Grundlage für alle weitergehenden Untersuchungen geschaffen.
   Hypothese: Die miniaturisierte Methode erfüllt die Mindestvoraussetzungen analytischer Methoden und liefert ein vergleichbares analytisches Ergebnis wie die Vergleichsmethode.

2. der Anwendung der miniaturisierten OCP-Extraktionsmethode auf Proben aus Sedimentbohrkernen aus Nordostdeutschland (vormals DDR) zur Rekonstruktion menschlichen Einflusses aus Landwirtschaft und Industrie auf die Umwelt.
   Hierbei liegt das Augenmerk auf dem *Verbleib* der organischen (und anorganischen) Schadstoffe.
   Hypothese: Aus den Schadstoffkonzentrationen der datierten Schichten lassen sich Rückschlüsse auf die menschliche Aktivität und ihren Einfluss auf die Umwelt ziehen.

3. der Durchführung einer Studie über eine erweiterte Phytoremediationsmethode zur Sanierung OCP-belasteter Ackerböden im Südkaukasus.
   Hierbei wird die *Bioverfügbarkeit* der Schadstoffe für Sanierungszwecke ausgenutzt.
   Hypothese: Die erweiterte Phytoremediationsmethode erzielt im Vergleich zu üblicher Phytoremediation höhere Aufnahmeraten in die Pflanzen und damit eine höhere Sanierungsleistung.

1.4 Herangehensweise und Methoden

1.4.1 Validierung einer miniaturisierten Extraktionsmethode

Die analytische Herausforderung bei den hiesigen Arbeitspaketen lag in der stark begrenzten Probenmenge (vor allem AP 2) und in der hohen Probenzahl (AP 3). Da am Institut die Extraktion und Injektion mittels SPME etabliert ist, wurde mit dieser Technologie die traditionelle Fest-Flüssigphasen-Extraktion (sog. Schüttelextraktion; ISO 10382) miniaturisiert, um mit kleinen Probenvolumina – in diesem Fall 0,5 g – kompatibel zu sein. Damit sollte es zudem möglich sein, eine größere Zahl an Proben simultan zu extrahieren. Dies passt zu den heutzutage gängigen Entwicklungen neuer Methoden, welche den Prinzipien der sog. Grünen Chemie getreu mit geringeren Probenvolumina und niedrigerem Lösungsmittelverbrauch einhergehen (Ali et al. 2019; Prosen 2019).

Die Leistungsfähigkeit und damit die Eignung der Methode wurde anhand der Qualitätsparameter Wiederfindungsrate (WFR), Bestimmungsgrenze (LOQ) und Nachweisgrenze (LOD) sowie Reproduzierbarkeit mittels Variationskoeffizient (VarK) überprüft. Zudem wurde die Methode mit einer für Pflanzenproben modifizierten QuEChERS-Methode (Woldetsadik et al. 2021), welche ebenfalls SPME einsetzt, verglichen. Für diese Tests wurden einerseits dotierte Bodenproben mit verschiedenen organischen Kohlenstoffgehalten (1,25 %, 2,27 % und 2,75 %) genutzt, die typischerweise in den gemäßigten Breiten vorkommen. Sie wurden außerdem nach Dotierung 35 d im Kühlschrank bei 8 °C ruhen gelassen, um die natürliche Alterung eines Bodens in situ zu simulieren (Škulcová et al. 2017). Andererseits wurden Umweltproben eines gesichert kontaminierten Standorts (N41.444311, E44.76041) aus dem Dorf Tamarissi (Munizipalität Marneuli, Georgien) verwendet. Diese wurden 2018, im Rahmen des dritten Arbeitspakets, in der Nähe der Versuchsfläche gesammelt. Dazu wurden mittels eines Pürckhauer-Bohrstocks (Innendurchmesser 20 mm) drei Mischproben, bestehend aus fünf 10 cm langen Bohrkernen, aus je einer Teilfläche genommen. Der Extraktionserfolg der Methoden an diesen Proben wurde im Vergleich untereinander ausgewertet.

Beide Methoden bedienen sich einer relativ hohen Zahl isotopenmarkierter interner Standards (IS). Für die vier Analyten 2,4′-DDD, 2,4′-DDE, β-HCH und γ-HCH wurden keine Isotopologa sondern IS ähnlicher Kongenere genutzt (4,4′-DDD-D_8, 4,4′-DDE-D_8, δ-HCH-D_6, bzw. α-HCH-D_6). Gerade bei diesen vier Analyten wurden stark erhöhte, nicht plausible Konzentrationen und damit ebensolche WFRs gemessen. Da die IS-Korrektur als Ursache dafür angenommen wurde, wurden diese Analyten mit einer andere Methode korrigiert. Kurz gesagt, wurde die Retentionszeit (RT, von engl. retention time) eines Analyten als Indikator für die physikochemischen Eigenschaften desselben genutzt. Je näher die RTs zweier Analyten (oder eines Analyten und eines IS) liegen, desto näher müssten sich diese beiden Stoffe auch in ihren physikochemischen Eigenschaften sein – so die Annahme. Aus diesem Grund wurden die Korrekturfaktoren für jeden der genannten Analyten proportional zwischen den beiden einen Analyten umgebenden ISs berechnet. Dementsprechend wurden für 2,4′-DDD und 2,4′-DDE andere ISs als nach normaler Korrektur genutzt (4,4′-DDD-D_8 und ^{13}C-2,4′-DDT, bzw. δ-HCH-D_6 und 4,4′-DDE-D_8).

1.4.2 Bestimmung der Schadstoffgehalte in Seesedimenten Nordostdeutschlands

Die Rekonstruktion des menschlichen Einflusses auf die Region Nordostdeutschland geschah im Rahmen eines von der Deutschen Forschungsgesellschaft (DFG) geförderten und von Miklós Bálint geleiteten Projektes (Förderkennzeichen DFG BA 4843/2–1). Das Ziel seines Projektes ist die Untersuchung des Landnutzungswandels und dessen Widerspiegelung in der eDNA-Zusammensetzung der beprobten Seesedimente.

Als Indikatoren für den menschlichen Einfluss dienten die organischen Schadstoffe DDT und HCH sowie anorganische Elemente, wie die Metalle Cd, Cr, Cu, Ni, Pb, Zn, das Metalloid As und das Nichtmetall S. Dazu wurden 10 Süßwasserseen des betreffenden Gebiets untersucht (s. Abb. 3). Bei den Seen handelte es sich um 5 Seen aus Mecklenburg-Vorpommern (Feldberger Haussee, FH; Breiter Luzin, BL; Schmaler Luzin, SL; Carwitzer See, CR), 4 Seen aus Brandenburg (Stechlinsee, SL; Wummsee, WM; Oberuckersee, OR; Scharmützelsee, PL) und einen See aus Sachsen-Anhalt (Arendsee, AR). Der betrachtete Rekonstruktionszeitraum umfasst die letzten 100 Jahre.

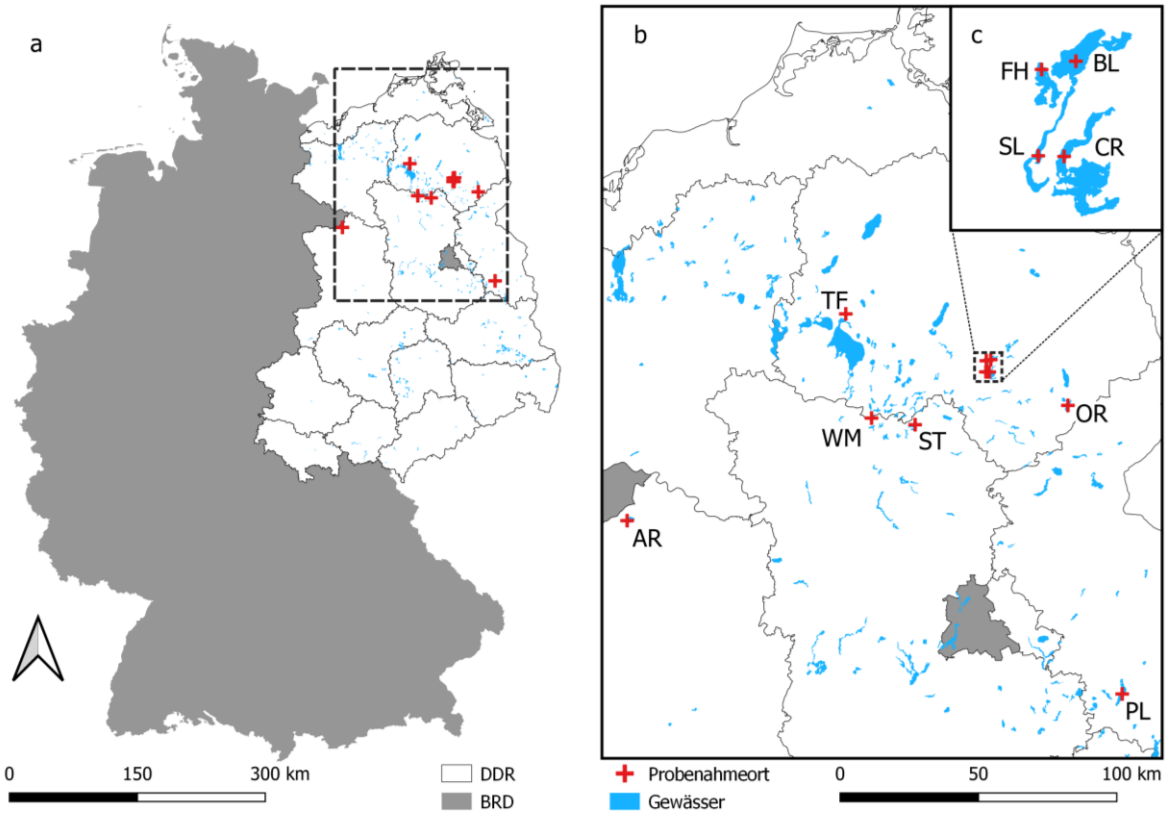


Abb. 3 – Karte des heutigen Deutschlands (a) geteilt in Westdeutschland (grau, BRD) und Ostdeutschland (weiß, DDR) mit den Bezirkseinteilungen der DDR. Blaue Flächen zeigen Gewässer, rote Kreuze die Probenahmeorte innerhalb der Seen. (b) zeigt einen vergrößerten Ausschnitt des Probenahmegebietes mit den Seen Arendsee (AR), Oberuckersee (OR), Stechlinsee (ST), Tiefwarensee (TF) und Wummsee (WM). (c) zeigt eine Detaildarstellung der untersuchten Seen der Feldberger Seenlandschaft: Feldberger Haussee (FH), Breiter Luzin (BL), Schmaler Luzin (SL) und Carwitzer See (CR). Abbildung ursprünglich publiziert in Simon et al. (2023), angepasst und übersetzt ins Deutsche.

In jedem See wurde ein 1 m langer Sedimentbohrkern an der tiefsten Stelle des Sees mittels eines Schwerelots (90 mm Durchmesser, UWITEC, Mondsee, Österreich) gefördert. Die Kerne wurden an Ort und Stelle in Segmente unterteilt (5 mm oder 10 mm, je nach Sedimentationsrate), bei 4 °C

ins Labor transportiert und dort bei −20 °C bis zur Weiterverarbeitung gelagert. Jede Sedimentscheibe wurde mittels der Radioisotope ^{210}Pb und ^{137}Cs datiert (Appleby und Oldfield 1978). Die Elementkonzentrationen wurden nach mikrowellengestützter Königswasserextraktion (MAE-AR, von lat. aqua regia) mittels optischer Emissionsspektrometrie mit induktiv gekoppeltem Plasma (ICP-OES; von engl. inductive coupled plasma–optical emission spectrometry) bestimmt (Methode nach Öztan und Düring 2012). Die Konzentrationen an OCPs wurden mit der unter AP 1 validierten Methode MISOLEX auf Basis von HS-SPME-GC-MS extrahiert und analysiert.

Aus den resultierenden Konzentrationen wurden Zeitreihen erstellt und anhand von historischen Daten zu Emissionen und Einsatz der betreffenden Analyten eingeordnet.

1.4.3 Vorbereitung und Durchführung einer Phytoremediationsstudie

Mit dem dritten Arbeitspaket soll eine Methode beleuchtet werden, mit welcher ein zuvor festgestellter menschlicher Einfluss – die Kontamination mit Schadstoffen – reduziert werden kann. Die hier dargestellten Vorergebnisse wurden mit der in AP 1 beschriebenen Methode MISOLEX ermittelt und dienen in diesem Zuge als Fallbeispiel für die Anwendung auf Umweltproben und für den Einsatz in einer wissenschaftlichen Studie. Die Arbeiten fanden im Rahmen des vom Bundeministerium für Bildung und Forschung (BMBF) geförderten Projekts „Environmental Health Risks of POP contaminated Soils in the South-Caucasus Region: Monitoring and Mitigation (POPcont)“ (engl. für „Umweltgesundheitsrisiken von POP-kontaminierten Böden in der Südkaukasusregion: Überwachung und Risikominderung“) statt (Förderkennzeichen: 01DK17030A). Das Ziel war die Erprobung eines erweiterten Phytoremediationsverfahrens.

Die eigentliche Studie bestand aus mehreren Teilaspekten und -schritten:

- Desorptionsversuche zur Ermittlung der geeigneten Remediationsbedingungen
- Durchführung der Studie auf dem Versuchsfeld in Georgien
    - Konzentrationsänderung im Boden
    - Konzentrationen in den Pflanzen
- Monitoring des Versuchsfeldes im Nachgang
    - Konzentrationsänderung im Boden

Die Art der Erweiterung der Phytoremediation ist an dieser Stelle bewusst vage gehalten, da die abschließende Auswertung und vor allem Veröffentlichung der Ergebnisse zum Zeitpunkt der Abgabe der Dissertation noch aussteht. Aus zeitlichen Gründen finden diese keinen Eingang in die Endfassung der Arbeit.

Der Feldversuch fand in der Vegetationsperiode des Jahres 2018 in der ca. 30 km südlich der Hauptstadt Georgiens (Tiflis) gelegenen Gemeinde Tamarissi, Teil der Munizipalität Marneuli statt (N41.444311, E44.76041). Sie liegt in einer Region, die nach Köppen-Geiger als aride, kalte Steppe (BSk) klassifiziert wird (Beck et al. 2018). Laut Lydolph (1977) herrschen dort milde Winter mit alternierendem Frost- und Tauwetter, sowie lange, heiße Sommer vor. Klimadaten für die Periode 2003–2019 der ca. 15 km westlich gelegenen Klimastation der Stadt Bolnissi (N41.450000, E44.566667) zeigen eine Jahresmitteltemperatur von 13,4 °C, sowie eine mittlere Jahressumme des Niederschlags von 544,2 mm (DWD 2024).

Die Versuchsfläche lag auf einer Brachfläche hinter der Ruine eines ehem. Pestizidlagers (vgl. Kapitel 1.4.1 sowie Abb. 4).

Abb. 4 – Oben: Frontseite der Ruine eines ehem. Pestizidlagers in Tamarissi (Munizipalität Marneuli, Georgien; N41.444311° E44.76041°). Blick in Südrichtung. Unten: Versuchsfläche auf der Rückseite der Ruine. Teilausschnitt der Versuchsfläche von Osten aus gesehen. Eigene Aufnahmen aus 2018.

Die Korngrößenverteilung des Bodens ergab im Bereich von 0–30 cm Tiefe im Median einen Sandanteil von 15,36 %, einen Schluffanteil von 26,33 % und einen Tonanteil von 53,10 %, womit sich als Bodenart nach Bodenkundlicher Kartieranleitung ein lehmiger Ton (Tl) ergibt (Hartmann et al. 2024). Der organische Kohlenstoffgehalt lag im Median bei 2,64 %. Der Boden wurde nach Word Reference Base for Soil Resources (WRB) als Vertic Kastanozem klassifiziert (IUSS Working Group WRB 2022).

Die eigentliche Versuchsfläche war ein 108 m^2 großer, eingezäunter Bereich, welcher in Vorbereitung der Aussaat der Versuchspflanzen gemäht und gepflügt wurde (März 2018; s. Abb. 4 auf S. 14). Die Aussaat einer lokal handelsüblichen Grasmischung (*Lolium perenne*, *Festuca arundinacea*, *Poa pratense*) erfolgte ca. einen Monat später. Zu diesem Zeitpunkt wurde die Fläche in 3 × 6 Parzellen zu je 9 m^2 unterteilt. Jede Parzelle bestand aus einer 0,5 m breiten Pufferzone und dem eigentlichen 4 m^2 großen Arbeitsbereich im Zentrum, aus dem die Proben entnommen wurden und der unterschiedlich behandelt wurde, um die Phytoremediation zu beeinflussen (s. Abb. 5). Die Pufferzone diente dazu, den Arbeitsbereich vor etwaiger Drift bei der Behandlung der umliegenden Flächen zu schützen.

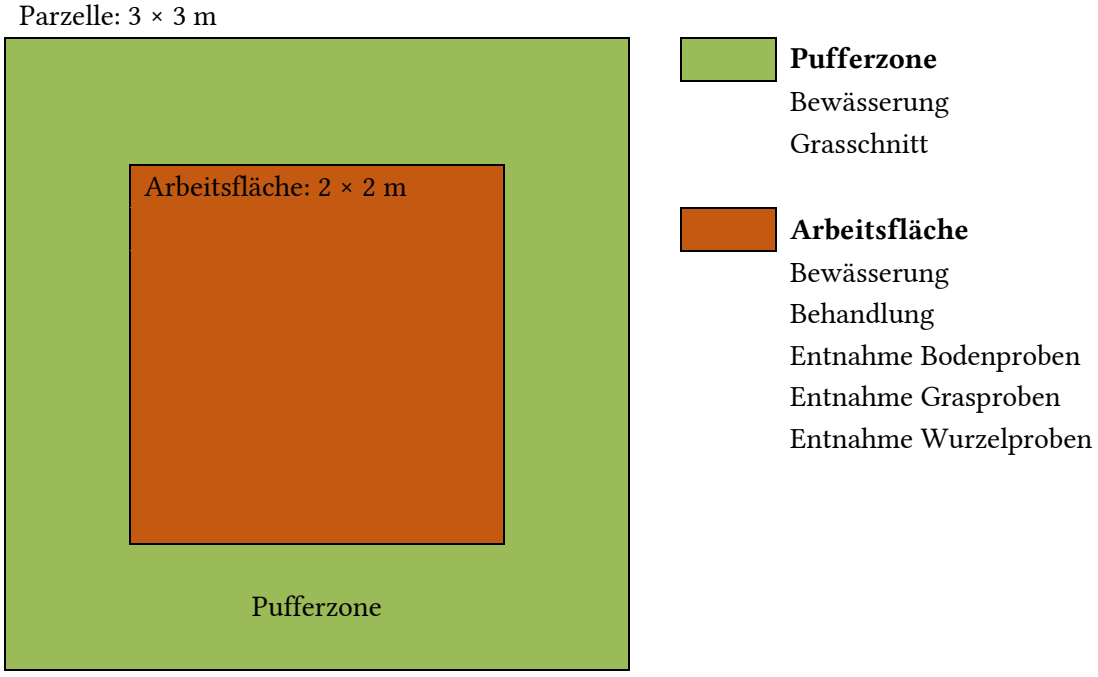


Abb. 5 – Aufbau einer Parzelle samt Legende mit auf den Flächenarten durchzuführenden Arbeiten.

In jeder Reihe wurden Kontroll- sowie Behandlungsflächen alterniert, sodass sich eine Anordnung einem Schachbrettmuster gleich ergab (s. Abb. 6 auf S. 16). Beide Arten von Parzellen wurden über den Versuchszeitraum hinweg bei Bedarf bewässert. Die Behandlungsflächen wurden in einem Abstand von 2–4 Wochen mit der Erweiterung der Phytoremediation behandelt. Die Kontrollflächen wurden zum gleichen Zeitpunkt erneut bewässert. Die initiale Probenahme des Versuchszeitraums fand Ende Mai 2018 statt (t_1). An diesem Termin wurde der Boden jeder Parzelle mittels eines Pürckhauer-Bohrstocks als Mischprobe aus 4 Teilproben beprobt, sowie das Gras zum ersten Mal geschnitten. Bis Ende September 2018 (t_5) wurden so insgesamt 5 Grasschnitte produziert. Zum finalen Termin des Versuchs Ende Oktober 2018 (t_6) wurde der Boden erneut beprobt, sowie 3 Bodenansprachen bis in ca. 110 cm Tiefe durchgeführt. Danach wurde das Versuchsfeld nicht mehr weiter betreut und sich selbst überlassen. Ende April (t_7) sowie Ende November (t_8) des darauf-

folgenden Jahres 2019 – ca. ½ bzw. ca. 1 Jahr später – wurden jeweils erneut Bodenmischproben aus jeder Parzelle entnommen. Dabei wurden 6 durch die Bodenansprachen gestörte Parzellen ausgelassen.

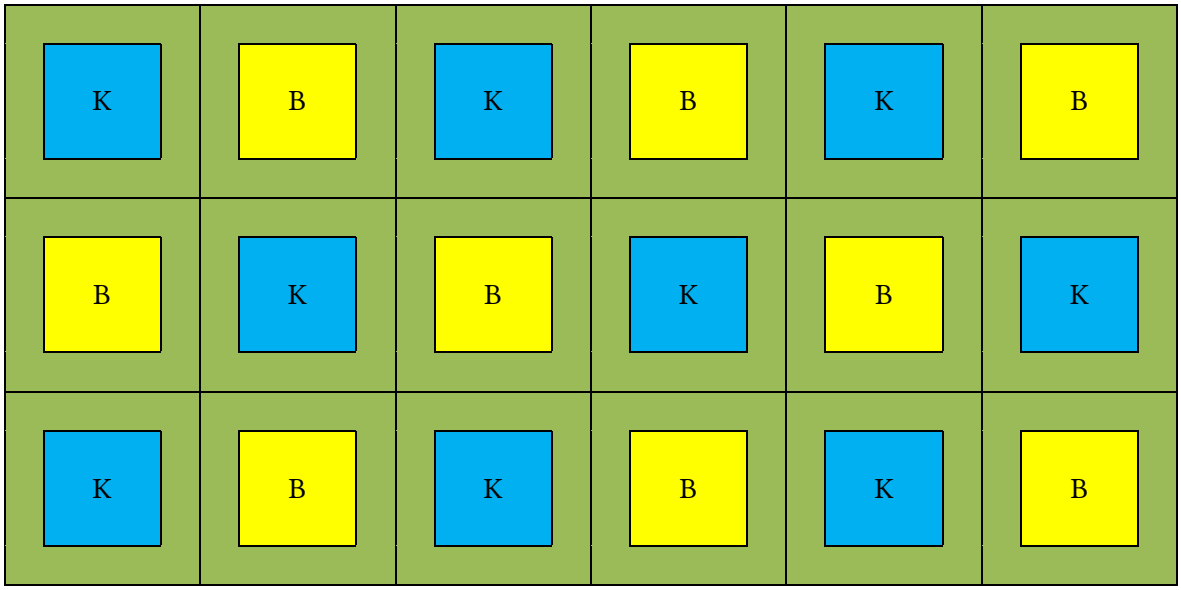


Abb. 6 – Anordnung der Versuchsparzellen. Blaue und gelbe Arbeitsbereiche stehen für Kontroll- (K) bzw. Behandlungsflächen (B). Grüne Flächen zeigen die Pufferzonen.

Die Bodenproben wurden im Institut für Geografie der Universität Tiflis, einem Projektpartner, gekühlt gelagert, die Grasschnittproben luftgetrocknet. Nach Transport wurden sie an der Justus-Liebig-Universität Gießen (JLU), Institut für Bodenkunde und Bodenerhaltung, extrahiert und auf ihre Konzentrationen an HCH, DDX und Trifluralin mittels MISOLEX (s. Kap. 2, AP 1) analysiert. Zusätzlich wurden die zum ersten Zeitpunkt genommenen Bodenproben genutzt, um den Boden jeder einzelnen Parzelle zu charakterisieren. Dazu wurden der pH-Wert, der Carbonatgehalt ($\%CaCO_3$), der Gesamtstickstoffgehalt ($\%N_{tot}$), der Gesamtkohlenstoffgehalt ($\%C_{tot}$), der Gehalt an organischem Kohlenstoff ($\%C_{org}$) sowie die Körnung des Bodens (Grob-, Mittel- und Feinsand, Grob-, Mittel- und Feinschluff sowie Ton) bestimmt. Die Pflanzenproben wurden entsprechend der in Woldetsadik et al. (2021) beschriebenen, auf QuEChERS basierenden, Methode extrahiert und analysiert.

1.5 Zusammenfassung der Ergebnisse und Diskussionen

1.5.1 Analytische Leistung der verglichenen Extraktionsmethoden

Die ermittelten Qualitätsparameter LOD und LOQ, die anhand der definiert dotierten Bodenproben ermittelt wurden, sind für die beiden untersuchten Methoden in Tabelle 2 dargestellt.

Tabelle 2 – Mediane der LODs, LOQs in µg·kg^{-1} und WFR in % beider Methoden (n = 15)

Analyt	MISOLEX			QuEChERS		
	LOD	LOQ	WFR	LOD	LOQ	WFR
Trifluralin	0,005	0,02	101,2	0,001	0,004	78,5
α-HCH	0,27	0,90	86,9	0,31	1,05	82,5
β-HCH	1,16	3,85	90,4	1,31	4,36	100,3
ɣ-HCH	0,90	3,00	90,5	0,39	1,29	83,2
δ-HCH	0,91	3,02	112,2	1,48	4,93	127,6
2,4′-DDD	0,32	1,05	92,2	0,32	1,08	118,1
4,4′-DDD	0,14	0,47	103,4	0,20	0,66	90,0
2,4′-DDE	0,04	0,12	111,0	0,06	0,19	109,4
4,4′-DDE	0,13	0,43	99,7	0,03	0,10	93,8
2,4′-DDT	0,25	0,82	107,6	0,47	1,57	94,2
4,4′-DDT	0,05	0,17	94,4	0,14	0,47	94,9

Die Methode MISOLEX liefert folgende Ergebnisse: Die LODs der DDX-Kongenere liegen zwischen 0,04 und 0,32 µg·kg^{-1}, die LOQs zwischen 0,12 und 1,05 µg·kg^{-1}. Der LOD und der LOQ von Trifluralin liegt bei 0,005 µg·kg^{-1} bzw. 0,02 µg·kg^{-1}. Die LODs der HCH-Isomere reichen von 0,27 bis 1,16 µg·kg^{-1} und die LOQs von 0,90 bis 3,85 µg·kg^{-1}. Damit liegen die LOQs gesamtheitlich weit unterhalb des von der Europäischen Kommission empfohlenen Grenzwertes für Pestizidanalysen in Böden von 50 µg·kg^{-1} (EC 2021). Die WFRs liegen zwischen 65,8 und 172,6 % für die meisten DDX-Kongenere und zwischen 70,2 und 126,1 % für Trifluralin und die meisten HCH-Isomere (s. Abb. 7 auf S. 18). ɣ-HCH und 2,4′-DDD werden mit Werten von 180,9 % bzw. 167,3 % überschätzt. Durch Interpolation der IS-Korrektur wird der angestrebte Wertebereich von 80 bis 120 % WFR erreicht. Die VarKs liegen zwischen 1,3 und 22,4 %, und damit meist unterhalb des Zielwertes von 20 %. Auch hier liefert ɣ-HCH mit 22,4 % einen erhöhten Wert, der durch die Interpolation verbessert wird. Insgesamt lässt sich mit der erreichten Sensitivität nicht nur die Eignung für Screening, sondern auch für Spurenanalytik attestieren.

Im Hinblick auf Sensitivität und Wiederfindung liefert MISOLEX vergleichbare Werte wie die modifizierte QuEChERS-Methode. Die Methode MISOLEX ist schneller, da es nicht nötig ist, Salzmixturen vorzubereiten und in Extraktionsgefäße zu wiegen. Die Varianz von MISOLEX ist im Allgemeinen höher als jene der QuEChERS-Methode. Dies liegt möglicherweise an dem geringeren Probenvolumen (0,5 g im Vergleich zu 1 g). Im Vergleich mit der klassischen ISO-Methode bietet MISOLEX einige Vorteile: (1) Es werden weniger Arbeitsschritte benötigt, was Aufwand, Zeit sowie das Risiko für Fehler und Analytverluste reduziert. (2) Die benötigte Menge an Lösungsmitteln ist weitaus geringer (ca. 200 mL gegenüber 15 mL). (3) In der ISO-Methode müssen aus jedem Extrakt Acetonrückstände mit Wasser ausgewaschen werden, wodurch jedes Mal ca. 1 L

kontaminierten Wassers entsteht. (4) MISOLEX benötigt ein viel geringeres Probenvolumen von 0,5 g im Vergleich zu 200 g. (5) Wegfall diverser Transfer- und Aufreinigungsschritte, die wie bereits erwähnt zu Analytverlusten führen können. Mit diesen Merkmalen erfüllt MISOLEX folgende Prinzipien der sog. Grünen Chemie (Gałuszka et al. 2013): (1) So wenig wie möglich Abfall zu generieren, (2) Derivatisierungen zu vermeiden, (3) mehrere Parameter oder Analyten auf einmal zu analysieren, (4) zu automatisieren, und vor allem (5) zu miniaturisieren.

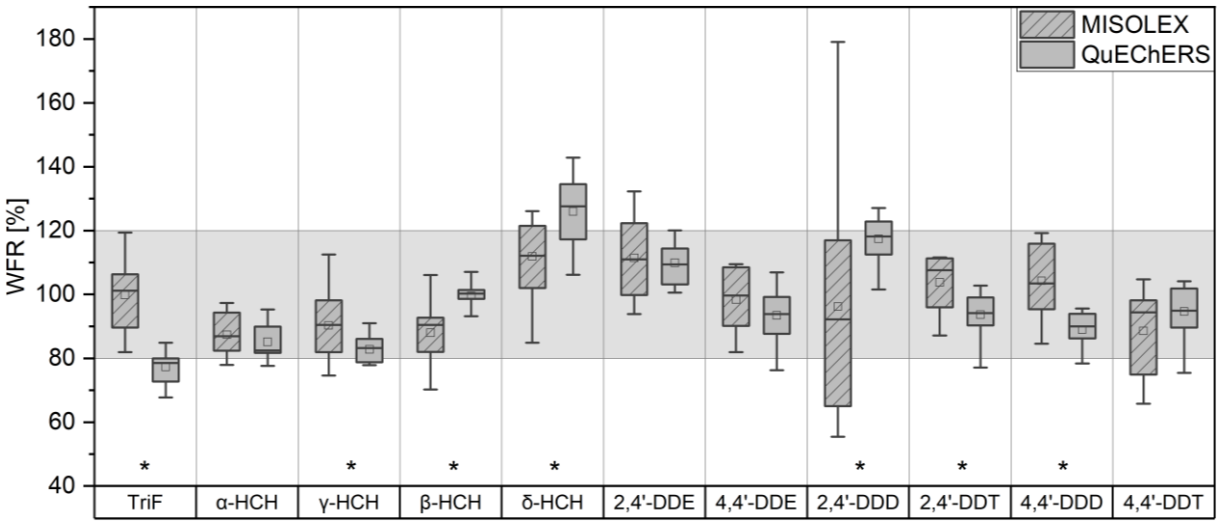


Abb. 7 – Boxplots der Wiederfindungsraten (WFRs) von 11 verschiedenen Analyten aus 3 dotierten Böden, gemessen mit den 2 verglichenen Methoden und 5 Replikaten pro Boden und Methode (n = 15). TriF: Trifluralin. Die Reihenfolge entspricht der Elutionssequenz. Die WFRs für γ-HCH, 2,4´-DDE und 2,4´-DDD wurden mittels interpolierter Interner-Standard-Korrektur ermittelt. Der graue Bereich zeigt den angestrebten Wertebereich zwischen 80 und 120 %. Sternchen markieren statistisch signifikante Unterschiede zwischen den beiden Methoden (p < 0,05). Abbildung ursprünglich publiziert in Simon et al. (2022), angepasst und übersetzt ins Deutsche.

Ein gravierender Nachteil von MISOLEX ist die Einschränkung, jeden Extrakt nur genau ein einziges Mal analysieren zu können, da durch die SPME die Analytkonzentrationen der Probe verändert werden. Möchte man dies umgehen, und z. B. eine Probe als Triplikat analysieren, gibt es mehrere Herangehensweisen: Zum Beispiel könnte man die Probe mehrfach extrahieren oder man könnte die Methode mit größeren Gefäßen hochskalieren und das dreifache an Probe sowie Lösungsmittel nutzen. Ein weiterer Nachteil ist der Einsatz einer relativ großen Anzahl isotopenmarkierter Standards. Zwar erhöhen sie die Sicherheit der WFR, sind aber recht kostspielig. Sie könnten durch alternative, unmarkierte und damit günstigere Standards ersetzt werden, sofern man deren Tauglichkeit im Vorfeld getestet hat. Ein Vorteil der Methode – das geringe Probenvolumen von 0,5 g – kann gleichzeitig ein Nachteil sein, sofern bei Probenahme und Homogenisierung nicht mit großer Sorgfalt vorgegangen wird. Falls SPME im Labor noch nicht etabliert ist, müsste anfangs ein höherer Aufwand aufgebracht werden, um die Nutzung des Systems zu routinieren und die Methode zu etablieren.

1.5.2 Zeitreihen der Elemente und organischen Verbindungen aus Seesedimenten

Die datierten Schichten decken den Zielversuchszeitraum 2015–1900 adäquat ab. Dabei reichen die Sedimentkerne der Seen AR, CR und PL bis in die 1800er Jahre, die der Seen ST und WM bis in die 1600er Jahre und der Kern von See SL bis in die Mitte der 1500er Jahre. Sie ermöglichen somit Aussagen über die Zeit vor dem Zielzeitraum.

Elemente

Die Verläufe der Elementkonzentrationen verhalten sich über alle Elemente und Seen hinweg relativ ähnlich, was an dem relativ kleinen Konfidenzintervall zu erkennen ist (s. Abb. 8).

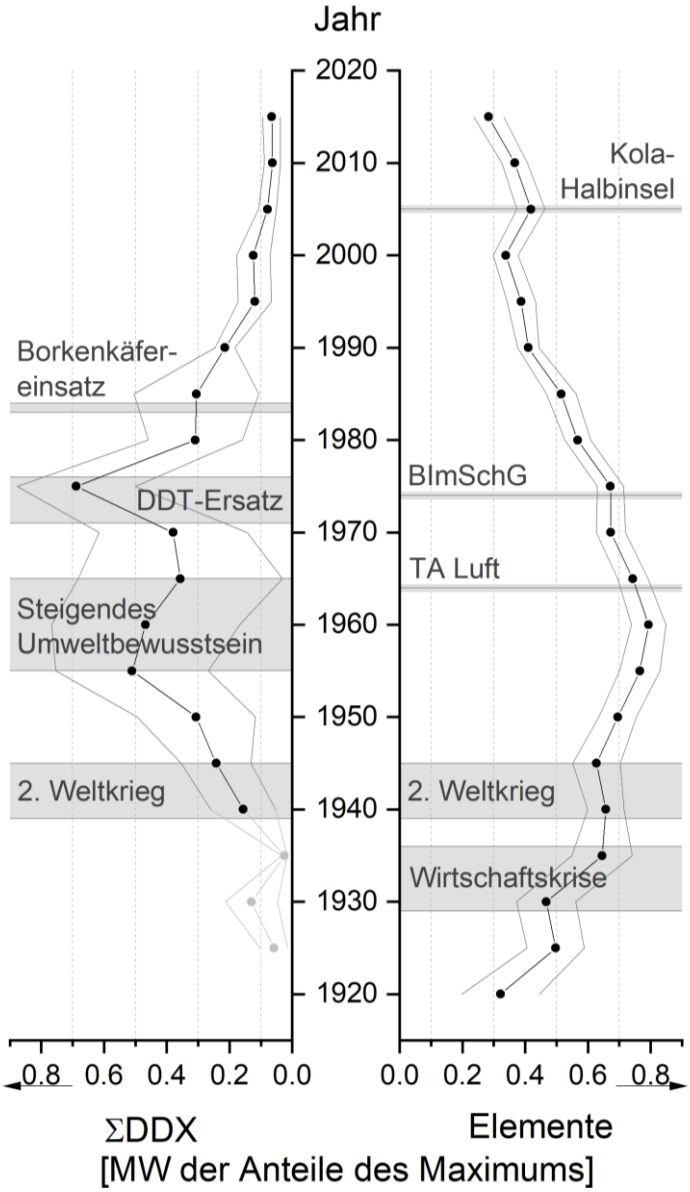


Abb. 8 – 5-Jahresmittelwerte (MW) der Konzentrationen von ΣDDX (links) und Elementen (rechts) aller 10 Seen von 1920 bis 2015, dargestellt als schwarze Punkte. Die Linien zwischen den Punkten sollen den Blick der Lesenden führen. Graue Linien zeigen das 95 %-Konfidenzintervall. Jeder Parameter wurde auf sein jeweiliges Maximum pro See normalisiert. Dabei wurde der See WM aufgrund ungenügender Daten bei ΣDDX ausgenommen. Für eine detaillierte Erklärung sei auf den Anhang des Ursprungsartikels verwiesen (s. Kap 3.2). Hellgraue Punkte und Führungslinien weisen fragwürdige Messwerte aus, die wahrscheinlich aufgrund Verschleppung bei der Probenahme eines Kerns entstanden. TA Luft (1964) und BImSchG (1974) waren die erste bzw. zweite politische Verordnung zur Emissionskontrolle in Westdeutschland. Abbildung ursprünglich publiziert in Simon et al. (2023), erweitert und übersetzt ins Deutsche.

Ab dem Betrachtungszeitraum um ca. 1920 sind die Konzentrationen im Anstieg begriffen. Sie starten von Werten oberhalb von geogenen Hintergrundkonzentrationen der Regionen (ca. 2–15-fach erhöht; LABO 2003). Mitte der 1960er Jahre gibt es einen Wendepunkt, ab dem sie wieder

sinken, allerdings nur bis zum Jahr 2000. Bis ca. zum Jahr 2005 steigen sie erneut an, sinken nach diesem zweiten Maximum wieder, erreichen ca. 2010 die Anfangswerte des Betrachtungszeitraumes und sinken bis zu den obersten Schichten weiter ab.

Dieses gleichförmige Verhalten legt den Schluss nahe, dass die Elemente über denselben Mechanismus in die Seen eingebracht wurden: diffuse atmosphärische Deposition. Gestützt wird diese These durch Ergebnisse von Pacyna (1984), welcher die atmosphärischen Emissionen europäischer Staaten für das Jahr 1979 approximierte. Die Reihenfolge der von ihm gemessenen Elemente mit der höchsten Konzentration zur niedrigsten ist jenen in dieser Arbeit gemessenen sehr ähnlich. Demnach wird, neben dem geogenen Hintergrund, die Atmosphäre – oder besser gesagt anthropogene industrielle Aktivität – als primäre Quelle identifiziert.

Die weiter in die Vergangenheit reichenden Kerne der Seen AR, CR, PL, SL, ST und WM zeigen den Beginn des in allen Seen beobachteten, generellen Konzentrationsanstiegs. Dieser liegt dort ungefähr in der Mitte des 19. Jahrhunderts und ist wahrscheinlich auf die in diesem Zeitraum in Deutschland einsetzende Industrialisierung zurückzuführen. Vergleichbares wurde auch von anderen Arbeiten berichtet (Thevenon et al. 2011; Elbaz-Poulichet et al. 2020).

Für die historischen Ereignisse größeren Ausmaßes in der ersten Hälfte des 20. Jahrhunderts, wie z. B. Erster und Zweiter Weltkrieg oder Weltwirtschaftskrise, gibt es keine offensichtlichen Anzeichen. Stattdessen steigen die Konzentrationen, möglicherweise aufgrund Kriegsanstrengungen und anschließender ökonomischer Rekonstitution. Der Wendepunkt des Konzentrationsverlaufs ab den 1960er Jahren passt mit den politischen und gesellschaftlichen Entwicklungen in Westdeutschland zusammen. Diese Periode ist durch ein wachsendes Umweltbewusstsein in der Bevölkerung charakterisiert, was auf politischer Ebene u. a. zum Erlass der ersten gesetzlichen Maßnahmen zum Schutz der Luft in Westdeutschland führte (TA Luft 1964; BImSchG 1974; BImSchV No. 1 1974). Dies legt den Schluss nahe, dass die beobachteten Konzentrationen einen Indikator für die industrielle Aktivität Westdeutschlands – anstelle jener der DDR – darstellen. Diese These stützend wurden die Beneluxländer einschließlich Westdeutschland als größte Emittenten Europas jener Zeit identifiziert (Pacyna 1984). Die Emissionen lagen weit über denen der DDR (Faktor ca. 3–26). Alle untersuchten Seen sind in der Nordhälfte der Ostdeutschlands angesiedelt, wo zu DDR-Zeiten keine größeren industriellen oder energieerzeugenden Anlagen existierten, die als lokale Quellen hätten dienen können (Buck 1996; Hornych und Schwartz 2009). Zudem ist die vorherrschende Windrichtung der Region nach Nordosten gerichtet (Westwindzone), wodurch Luftmassen von Südwesten (z. B. aus dem Gebiet Westdeutschlands) zu den Seen transportiert werden (Buck 1996; Traup und Kruse 1996; Bürger 2003). Die Elementgehalte sind demnach indikativ für die industrielle Aktivität Westdeutschlands auf überregionaler Ebene.

Dass auch lokale Gegebenheiten zu deutlichen Effekten führen können, zeigt sich z. B. in den vier Seen der Feldberger Seenlandschaft: FH, BL, SL und CR. Deren Profile ähneln sich relativ stark, was wahrscheinlich der großen räumlichen Nähe sowie der hydraulischen Verbindung der Seen untereinander geschuldet ist. Ein anderes Beispiel für lokale Einflüsse sind die Seen ST und WM, welche die höchsten Konzentrationen aller betrachteten Seen aufweisen. Möglicherweise liegt dies am hohen Anteil von Waldfläche in deren Einzugsgebieten. Eine Auskämmung von Partikeln und Schadstoffen aus der Luft im Kronendach der Wälder ist denkbar. Die nachfolgende Abwaschung

bei Niederschlag könnte den Eintrag in den darunterliegenden Boden und damit schlussendlich die Seen erhöhen (sog. Waldfiltereffekt; Horstmann und McLachlan 1998; Nizzetto et al. 2006).

Organochlorpestizide

Von allen untersuchten OCPs wurden lediglich die Transformationsprodukte von DDT gefunden: 4,4′-DDD, 2,4′-DDD, 4,4′-DDE und 2,4′-DDE (s. Abb. 9 auf S. 22). Entsprechend gibt ∑DDX die Summe dieser vier Analyten an (vgl. Abb. 8 auf S. 19). In dieser Arbeit wird von zwei Szenarien ausgegangen, die erklären, wieso anstatt DDT lediglich DDD- und DDE-Kongenere gefunden wurden. Diese hängen mit der Art und Weise zusammen, wie das ausgebrachte DDT zu den Sedimenten gelangte:

1. DDT-Formulierung erreicht das Seesediment direkt nach Ausbringung auf z. B. Feld oder Forst (z. B. durch Winddrift; Frank et al. 1994; Craig et al. 1998; Matthews 2014). Dabei wird hauptsächlich DDT abgelagert. Zwar könnten geringe Anteile während der Deposition aerob zu DDE abgebaut worden sein, jedoch wird der Hauptanteil nach erfolgter Deposition anaerob zu DDD abgebaut.
2. DDT erreicht das Sediment indirekt über die Erosion von Oberboden irgendwann nach erfolgter Applikation auf z. B. Feld oder Forst. Der Anteil an DDT im erodierten Material wird anfangs höher sein, aber je länger die Verweilzeit und damit der Abbau in aerobem Oberboden ist, desto höher werden die DDE-Anteile werden, bis sie schließlich jene von DDT überschreiten, dessen Anteil entsprechend sinkt (Seen CR, OR und SL; Dimond und Owen 1996). Je nach vorhandenen Kapazitäten in den die Seen umgebenden Reservoiren, wäre eine mehr oder weniger starke Leckage an DDE möglich, welche zu einem stetigen, niedrigkonzentrierten Eintrag führen würde (See TF; Bergknut et al. 2011). Es ist anzunehmen, dass beide Szenarien in der Praxis simultan, aber in unterschiedlichen Intensitäten auftreten.

Die Periode mit den stärksten Anstiegen und Maxima der ∑DDX-Konzentration liegt ungefähr zwischen den Jahren 1945 und 1975. Die einzige Ausnahme bildet der See TF mit einem Maximum um ca. 1985. Die Maxima liegen zwischen 30 und 380 $\mu g \cdot kg^{-1}$ (Median 225 $\mu g \cdot kg^{-1}$) und sind damit vergleichbar mit 4 von 5 in Kanada untersuchten Seen (Kurek et al. 2019), in welche in den 1950er bis 1970er Jahren direkte Lufteinträge von DDT stattfanden (Maxima ca. 130–575 $\mu g \cdot kg^{-1}$). Die Maximalkonzentrationen der einzelnen Kongenere nehmen in dieser Reihenfolge ab: 4,4′-DDD > 4,4′-DDE > 2,4′-DDD >> 2,4′-DDE. Für die erwähnte Periode überschreiten die Summen der gemessenen DDD- sowie jene der DDE-Konzentrationen den von MacDonald et al. (2000) entwickelten Sedimentqualitätsparameter PEC (Wahrscheinliche Wirkkonzentration, von engl. probable effect concentration) um das ca. 2–10-fache bzw. fast das 3-fache. Dementsprechend ist es sehr wahrscheinlich, dass sich die DDT-Konzentrationen auf der Sedimentoberfläche zur Zeit der Ausbringung negativ auf die benthische Fauna ausgewirkt haben.

Der Verlauf der 4,4′-DDD-Konzentrationen spiegelt den Einsatz von DDT in der DDR wider. Die insektizide Wirkung von DDT wurde 1939 entdeckt und nach dem zweiten Weltkrieg weithin eingesetzt (Mellanby 1992 ex Jürgens et al. 2016) – zu sehen in allen Seen, welche diesen Zeitraum abdecken. Ab den 1950er Jahren nahm der Einsatz drastisch zu, was besonders in den Profilen der Seen FH, BL, SL, OR und ST deutlich wird. Das wachsende Umweltbewusstsein in den 1960er

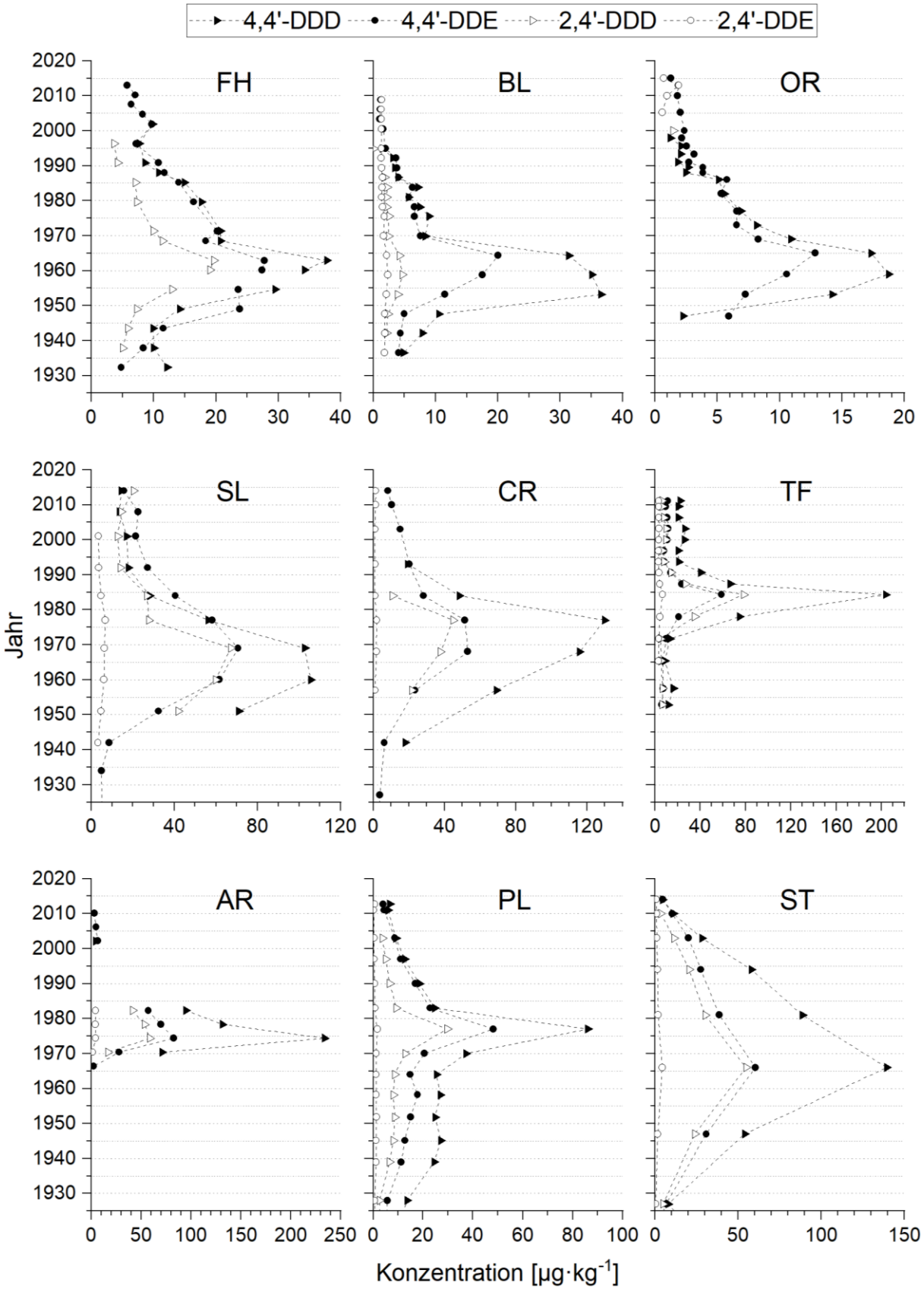


Abb. 9 – Konzentrationen der 4,4´- und 2,4´-Kongenere von DDD und DDE in µg·kg^{-1} in den untersuchten Seeprofilen (ausgen. Wummsee) zwischen den Jahren 1925 und 2015. AR: Arendsee, BL: Breiter Luzin, CR: Carwitzer See, FH: Feldberger Haussee, OR: Oberuckersee, PL: Scharmützelsee, SL: Schmaler Luzin, ST: Stechlinsee, TF: Tiefwarensee. Die gestrichelten Linien zwischen den Punkten sollen den Blick der Lesenden führen. Man beachte die unterschiedlichen x-Achsen. Abbildung ursprünglich publiziert in Simon et al. (2023), angepasst und übersetzt ins Deutsche.

Jahren beeinflusste den Agrarsektor ebenso wie die Industrie: Erkenntnisse über die negativen Effekte von DDT auf die Umwelt führten zu abnehmender Popularität des Insektizids (Mellanby 1992 ex Jürgens et al. 2016). Nachdem weltweit mehr und mehr DDT-Verbote erlassen wurden, sah sich die DDR-Führung Ende der 1960er Jahre dazu gezwungen, ihrerseits zu reagieren, um ihre Lebensmittelexporte nicht zu gefährden. Das Ergebnis war ein stufenweiser DDT-Ersetzungsplan, der von 1971 bis 1976 nach und nach den DDT-Einsatz bei den ausbringungsintensivsten Feldfrüchten verbot (Heinisch et al. 1993). Entsprechend sind die DDD-Konzentrationen Anfang der 1970er Jahre in den Seen FH, BL und OR niedriger. In den Profilen der Seen CR, PL und AR kommt es hingegen zu erhöhten Konzentrationen in den 1970er Jahren. Möglicherweise brachten Landwirte in diesen Regionen höhere Mengen an DDT-Formulierung als gewöhnlich auf die Felder aus, um sich dem bald verbotenen Pestizid zu entledigen. Die Mengen vertriebener wie auch ausgebrachter Mengen blieben nach dem Ersetzungsplan auf niedrigem Niveau, bis ca. 1983/1984 die Massenausbreitung des Falters *Lymantria monacha* (sog. Nonne) und weiteren Schädlingen (Riek et al. 2021) in Wäldern der DDR die Regierung zwang, von ihrem Plan auszuscheren. So wurden inoffiziell 260.000 ha der bis dahin 600.000 ha befallenen Waldfläche per Flugzeug mit einem DDT-Lindan-Gemisch behandelt. Besonders deutlich ist dies im Profil des Sees TF zu sehen. In den Seen BL und OR ist dies lediglich angedeutet (ca. 1985 bzw. ca. 1986). Danach fiel die Ausgabe von DDT wieder auf das vorherige Niveau und sank weiter, bis sie kurz vor dem Ende der DDR eingestellt wurde (Heinisch et al. 1993).

1.5.3 Vorläufige Ergebnisse der Phytoremediationsstudie

Zum Zeitpunkt des Verfassens dieser Arbeit liegen nicht alle Ergebnisse dieses Arbeitspakets ausgewertet vor. Aufgrund der Heterogenität und der benötigten hohen Probenzahl sind weitere Untersuchungen und Auswertungen erforderlich. Daher sind an dieser Stelle lediglich Vorergebnisse von den Kontrollflächen demonstriert.

In den Boden- und Pflanzenproben wurden die von MISOLEX umfassten DDX-Analyten detektiert. Daher steht in diesem Kapitel der Parameter ΣDDX, im Gegensatz zum vorherigen Kapitel, für die Summe der Kongenere von DDD, DDE *und* DDT. ΣHCH steht für die Summe der mit MISOLEX untersuchten HCH-Isomere, d. h. α-, β-, γ- und δ-HCH. Aus Gründen der Übersichtlichkeit wird sich auf diese Summenparameter beschränkt.

In Abb. 10 auf S. 24 sind die Konzentrationen von ΣDDX und ΣHCH zu Beginn (t_1) und zu Ende (t_6) des Versuchszeitraums, gemessen auf den Kontrollparzellen der Versuchsfläche, dargestellt. Es wurden alle untersuchten DDX-Analyten detektiert. Auffällig ist die große Spannweite der gemessenen Werte, die sich über mehrere Größenordnungen erstrecken. So liegen die Konzentrationen von ΣDDX zwischen 2 und ca. 2.700 $\mu g \cdot kg^{-1}$ und die von ΣHCH zwischen ca. 220 und ca. 3.070.000 $\mu g \cdot kg^{-1}$. Dies zeigt die hohe Heterogenität der Versuchsfläche. Der Median der prozentualen Abweichung vom Median (MPA) der ΣDDX- und ΣHCH-Konzentrationen liegt bei 100 bzw. ca. 12 %. Generell hat sich die Verteilung der Konzentrationen durch die Phytoremediation von t_1 zu t_6, d. h. innerhalb von 156 Tagen, zu niedrigeren Konzentrationen entwickelt. Es liegen weiterhin Maximalkonzentrationen in der Größenordnung wie zu Beginn des Versuchs vor. Über die Dauer der Phytoremediation haben die Konzentrationen auf den Kontrollflächen im Median abgenommen: ΣDDX sinkt von 196,25 auf 19,02 $\mu g \cdot kg^{-1}$ und ΣHCH von 11.122,32 auf 4.188,88 $\mu g \cdot kg^{-1}$. Dies sind Rückgänge um 90,3 bzw. 62,3 %. Die Unterschiede sind allerdings in beiden Fällen statistisch nicht signifikant (*t*-Test für verbundene Stichproben: $p = 0{,}14221$ bzw.

p = 0,41289. Signifikanz bei p < 0,05). Gleichzeitig verbleibt der MPA von ∑DDX bei 100 %, während jener von ∑HCH minimal von 13 auf 11,6 % sinkt.

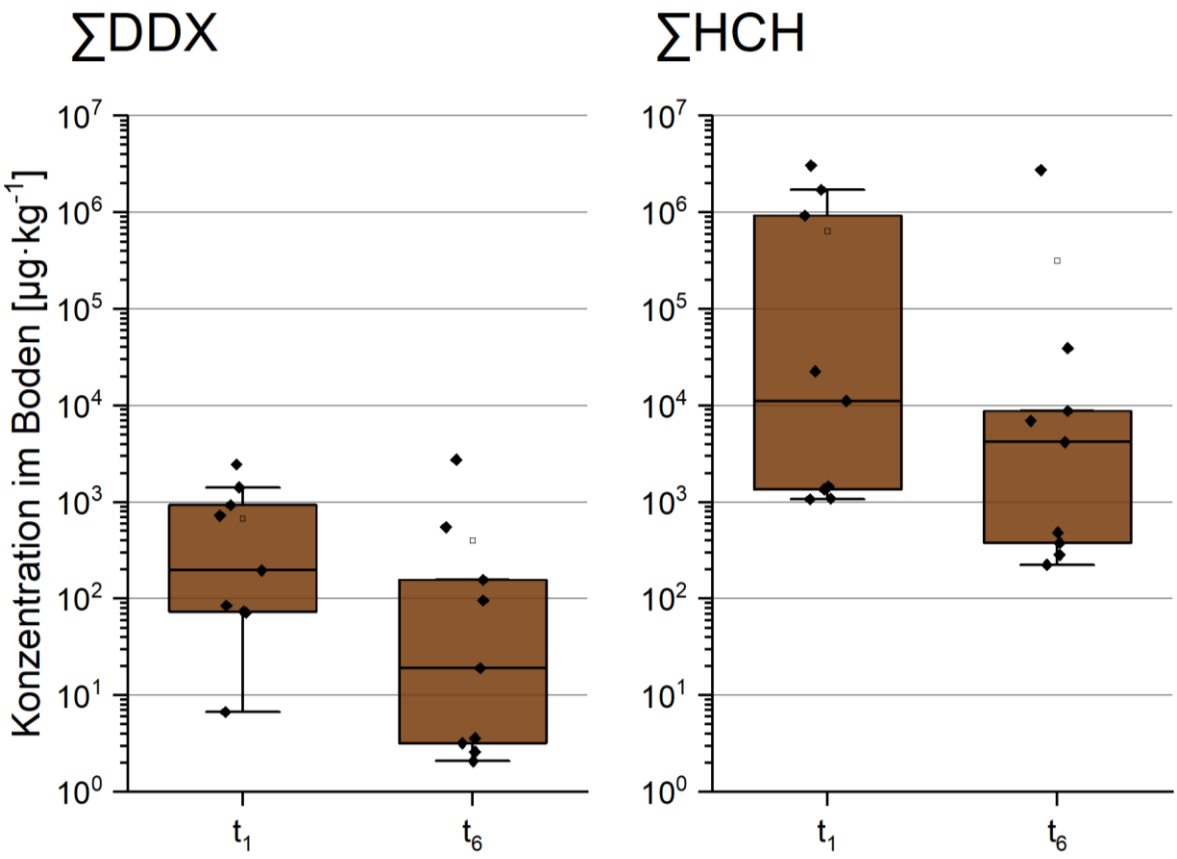


Abb. 10 – Boxplots der Konzentrationen der Summenparameter ∑DDX und ∑HCH im Boden der Kontrollparzellen zu Beginn (t_1) und Ende (t_6) des Versuchszeitraums (t_1–t_6 = 156 d) in µg·kg^{-1} (n = 9). Die y-Achse ist zur besseren Vergleichbarkeit der Wertebereiche logarithmiert.

In Abb. 11 auf S. 25 sind die Konzentrationen des geernteten Grasschnitts von einem Teil der Kontrollparzellen zu den Zeitpunkten t_1 und t_5 dargestellt. Aufgrund Unverfügbarkeit von Probenmaterial wurden 3 Parzellen von der Betrachtung ausgeschlossen. Die Analyten wurden im Grasschnitt detektiert. Die hohe Heterogenität der Kontamination auf der Versuchsfläche spiegelt sich auch in der Streuung der Konzentrationen in der Pflanze wider. ∑DDX liegt im Bereich von ca. 5–60 µg·kg^{-1}, ∑HCH im Bereich von ca. 0,5–15 µg·kg^{-1}. Der MPA von ∑DDX liegt zu t_1 bei 46,5 % und steigt auf 64,4 % zu t_5. Der von ∑HCH hingegen sinkt in dieser Zeit von 64,7 auf 60,3 %. Bemerkenswert sind die im Vergleich zum Boden umgekehrten Verhältnisse der beiden Stoffgruppen: Im Boden liegen die Konzentrationen von ∑HCH eine Größenordnung über jenen von ∑DDX, wohingegen es sich in der Pflanze entgegengesetzt verhält. Zudem ist die Streuung der Werte von ∑DDX zu t_1 niedriger als von ∑HCH, was ebenfalls im Gegensatz zu den Verhältnissen im Boden steht.

Einen Monat vor Ende des Versuchszeitraums wurden auch im Grasschnitt niedrigere Werte als zu Beginn gemessen: So sinkt innerhalb der 128 d der Median von ∑DDX um 73,1 % von 37,40 auf 10,05 µg·kg^{-1} und von ∑HCH um 51 % von 5,63 auf 2,76 µg·kg^{-1}. Der Unterschied ist für ∑DDX statistisch nicht signifikant (p = 0,07011). Die Abnahme der ∑HCH-Konzentrationen über den Versuchszeitraum hingegen ist signifikant (p = 0,00909).

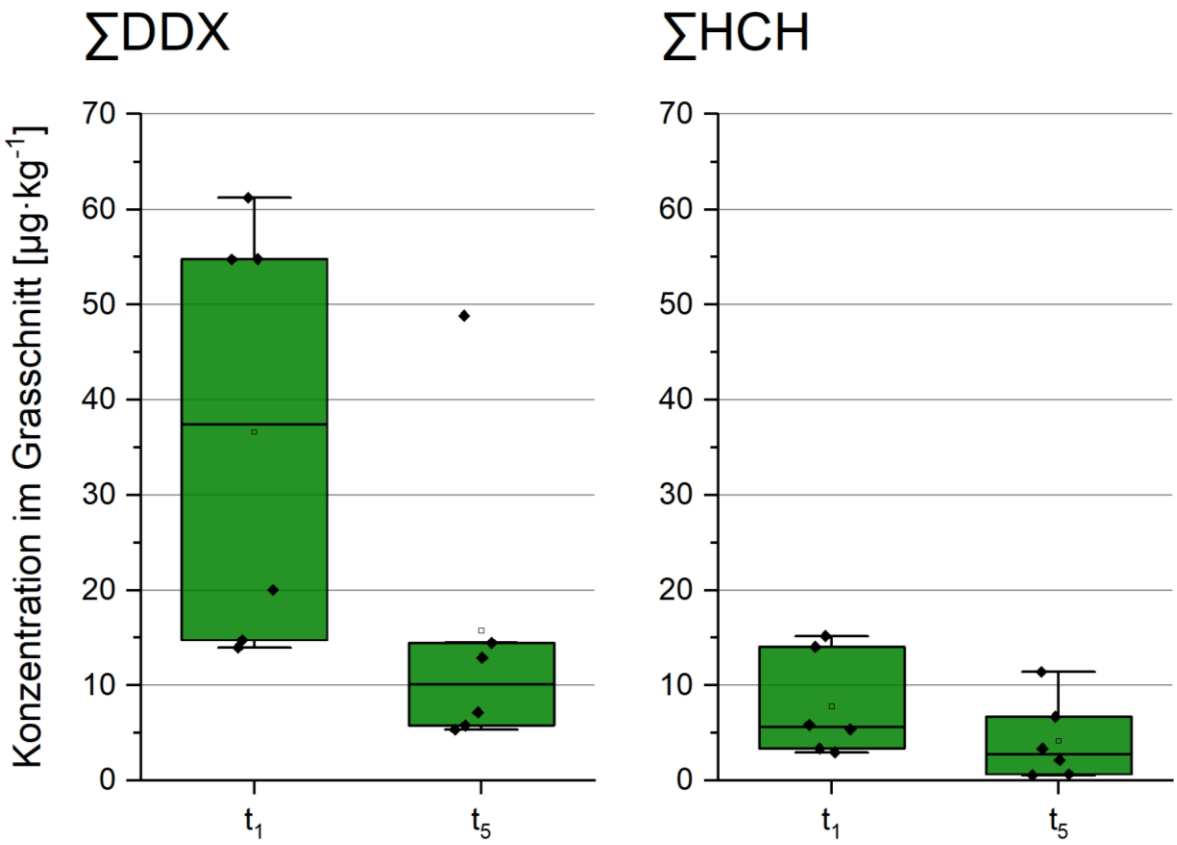


Abb. 11 – Boxplots der Konzentrationen der Summenparameter ΣDDX und ΣHCH im Grasschnitt zu Beginn (t_1) und einen Monat vor Ende (t_5) des Versuchszeitraums (t_1–t_5 = 128 d) in µg·kg^{-1} (n = 6).

Mit diesen hier gezeigten, vorläufigen Teilergebnissen soll ein erster Eindruck vom Effekt der Phytoremediation auf der Versuchsfläche vermittelt werden. Die vollständige und abschließende Auswertung sowie Veröffentlichung der Daten dieses Arbeitspakets wird im Anschluss an die Promotion stattfinden. Dabei sollen weitere bisher nicht berücksichtigte Aspekte in Betracht gezogen werden, u. a.

- der Unterschied zwischen gewöhnlicher und erweiterter Phytoremediation, um den Erfolg der Behandlungsmethode zu beurteilen und zu quantifizieren,
- die Berücksichtigung zusätzlicher Untersuchungszeitpunkte während sowie im Nachgang des Versuchszeitraums (t_2–t_4 bzw. t_7 und t_8),
- die Miteinbeziehung der ermittelten, den Boden charakterisierenden Parameter,
- die Konzentrationen der einzelnen Kongenere und Isomere, deren Verältnisse sowie deren Veränderung über die Zeit
- und eine Bilanzierung der Stoffströme, indem die Abnahme der absoluten Stoffmengen im Boden den durch die Pflanzenernten entfernten Stoffmengen gegenübergestellt werden.

1.6 Schlussfolgerung

In dieser Promotion wird der Verbleib von OCPs in der Umwelt untersucht. Dabei werden Regionen betrachtet, die vormals selbst Teil der SU waren oder zumindest in deren Einflussgebiet lagen. Dazu wurde im ersten Schritt eine Methode validiert, mit der alle weiteren Untersuchungen vorgenommen wurden. Die Methode liefert valide Ergebnisse und ermöglicht es, schnell und einfach OCPs in Boden- und Sedimentproben zu analysieren. Sie erfüllt mehrere Prinzipien der Grünen Chemie und ist nicht nur für großflächige Bodenscreeningkampagnen geeignet, sondern auch für Spurenanalytik. Die Leistung der Methode könnte mit hochauflösenderen Instrumenten, wie z. B. einem Tripel-quadrupol-MS, erhöht werden. Durch den Einsatz von SPME verfügt die Methode über einen vollautomatisierten Reinigungsschritt. Demnach wird Hypothese 1 angenommen: MISOLEX erfüllt die Qualitäts- und Leistungsanforderungen an analytische Methoden und liefert ein ähnliches Ergebnis wie die Vergleichsmethode. Und so stellt sie in der Arbeit von Woldetsadik et al. (Eingereicht 2024) die grundlegende Methode zur Extraktion und Analyse der Bodenproben.

MISOLEX kommt ebenfalls erfolgreich bei der Analyse von Seesedimenten zum Einsatz. Zehn Seen Nordostdeutschlands wurden auf Konzentrationen von OCPs untersucht. Die dadurch erhaltenen Zeitreihen sind die ersten ihrer Art dieser Region. Sie lieferten Hinweise auf den menschlichen Einfluss auf das die Seen umgebende Gebiet. So wurden Indikatoren für die industrielle Revolution, die wirtschaftlich-gesellschaftliche Erholung der Nachkriegszeit und die einsetzenden Umweltschutzbestrebungen auf politischer Ebene der 1960er und 1970er Jahre gefunden. Die Ergebnisse decken sich mit dem lokalen und regionalen Pestizidgebrauch in Forst- und Landwirtschaft. Sie zeigen Einzelereignisse und Perioden des Pestizideinsatzes sowie deren Intensität und damit Effekte mit kurzer Reichweite. In den Daten finden sich auch Hinweise auf Regierungsaktivitäten, die im Verborgenen stattfanden. Die Konzentrationen weisen darauf hin, dass zum Zeitpunkt des Einsatzes und der Deposition der Schadstoffe auf der Sedimentoberfläche, die Grenzwerte zur Toxizität überschritten wurden. Die zusätzlich gemessenen Elementkonzentrationen spiegeln die Luftemissionen anorganischer Schadstoffe aus den hochindustriellen Zentren in Westdeutschland und der EU wieder. Sie dienen demnach als Indikator für industrielle Aktivität und politische Maßnahmen mit großer geographischer Reichweite. Die generierten Elementprofile decken sich mit anderen Arten des Langzeitmonitorings – wie z. B. dem deutschen Moosmonitoring – und können zu diesen beitragen oder sie validieren. Zudem können sedimentäre Elementprofile als relativ kostengünstige Referenzdatensätze zur Datierung zukünftiger paläolimnologischer Untersuchungen der Region dienen. Somit wird auch Hypothese 2 angenommen: Aus den Schadstoffkonzentrationen lassen sich Rückschlüsse auf die menschliche Aktivität und ihren Einfluss auf die Umwelt ziehen. In weiterführenden Arbeiten sollte die vorhandene Datenbasis mit Daten aus weiteren Regionen Deutschlands (Südosten und Westen allgemein) erweitert werden. Dies würde einen direkten Vergleich zwischen industriellen und landwirtschaftlichen Regionen erlauben. Ebenso könnte das analytische Portfolio um Abbau-produkte von DDX und HCH, sowie um weitere Stoffgruppen von OCPs erweitert werden. Dann könnten Schlussfolgerungen zum Zustand des Abbaus mit höherer Sicherheit getroffen werden.

Im dritten und letzten Arbeitspaket sollte eine bestehende Kontaminationssituation durch ein erweitertes natürliches Abbauverfahren verbessert werden. Aufgrund der Datenlage zum Zeitpunkt des Verfassens dieser Arbeit konnten keine Aussagen zur Sanierungsleistung der

erprobten Methode getroffen werden. Die vorläufigen Ergebnisse lassen Tendenzen erkennen, dass die Aktivitäten der Phytoremediationsstudie die Konzentrationen der Schadstoffe in Boden und Pflanzen der Kontrollfläche reduziert haben könnten, doch sind weitergehende, umfangreichere Auswertungen notwendig, um dies einzuschätzen. Damit bleibt Hypothese 3 offen und wird im Nachgang Beantwortung finden.

Aus der Durchführung der Arbeiten um AP 3 ergaben sich dennoch Punkte für weiterführende Projekte. So blieb die Frage offen, was mit dem kontaminierten Pflanzenmaterial geschehen sollte. Zwar wäre eine Deponierung oder Trocknung mit anschließender Verbrennung im Rahmen des Möglichen, doch ist eine nachhaltigere Lösung angebracht, die nicht zu einer weiteren Kontamination der Umwelt führt. Hier wurde der Abbau durch Braun- oder Weißfäulepilze (Purnomo et al. 2011; Fan et al. 2013) in Bioreaktoren als vielversprechend gesehen, da diese Pilze imstande sind, OCPs abzubauen. Eine Promotion, um diese Folgefrage zu klären, ist zum Zeitpunkt des Verfassens der vorliegenden Arbeit bereits im Gange. Ein zweiter Aspekt für weiterführende Forschung ist der mögliche Transport der Schadstoffe in tiefere Bodenschichten, welcher durch eventuelle Mobilisierung der Stoffe denkbar ist. Die Gefahr der Kontamination des Grundwassers und weiterer Verbreitung ist ein Risiko, dass minimiert werden muss. Zu guter Letzt gibt es eine Vielzahl von Möglichkeiten, die Phytoremediation an sich zu verbessern: zum Beispiel durch (1) Optimierung des Wasser-Luft-Haushaltes des Bodens, (2) Anpassung des Mikrobioms durch Zugabe von Bakterienkulturen entweder zur cometabolischen Transformation oder Verbesserung des Pflanzenwachstums und Stoffaufnahme, (3) Zugabe von lösungsvermittelnden Stoffen zur verbesserten Aufnahme in die Pflanze oder (4) die Zugabe von Biokohle zur Steigerung der mikrobiellen Aktivität (Zhu et al. 2024).

Mit dieser Arbeit wird erneut gezeigt, dass POPs ihrem Namen gerecht werden und auf lange Zeit in der Umwelt überdauern. Je nach Expositionsmöglichkeit stellen sie eine Gefahr für Umwelt und Mensch dar. Entsprechend ist es angebracht, dass ihnen eine ebenso dauerhafte Aufmerksamkeit zuteilwird. Dies gilt nicht nur in der Forschung, sondern auch in der öffentlichen Wahrnehmung – insbesondere in den Ländern der ehem. SU. Die vorliegende Arbeit soll dazu beitragen.

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2 Artikel 1: Eine miniaturisierte Methode zur schnellen, einfachen und empfindlichen Pestizidanalyse in Böden

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Anhang zu Artikel 1 ab S. 53.

2.1 Haupttextteil von Artikel 1

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SOILS, SEC 3 • REMEDIATION AND MANAGEMENT OF CONTAMINATED OR DEGRADED LANDS • RESEARCH ARTICLE

A miniaturized method for fast, simple, and sensitive pesticide analysis in soils

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Abstract

Purpose Organochlorine pesticides (OCPs) like lindane and DDT have been used extensively after World War II until the 1990s. Still, residues of these pesticides can be found in agricultural soils all over the world, especially in developing countries. Often, they occur in extensive areas and elevated concentrations so that food safety is jeopardized. Hence, simple, cheap, and fast analytical methods are needed for a straight-forward assessment of risks. A miniaturized solid–liquid extraction combined with solid-phase microextraction (SPME) based on a proven ISO method is presented.

Methods The performance of the method is evaluated by extracting three different soils which were spiked with HCH and DDT congeners, and trifluralin, and aged for 35 days. The results are compared with those of a modified quick, easy, cheap, efficient, rugged, and safe (QuEChERS) method. For further validation, both methods are applied to three environmental soil samples.

Results Validation results show limits of detection and quantification as well as recovery rates in good agreement with standard requirements. The new method was found to be quicker than QuEChERS, which requires time-consuming preparation of reagents.

Conclusion Merits include low time and sample volume requirements (0.5 g) and the possibility to extract many samples simultaneously, which allows the screening of large sample sizes to determine the pollution status of whole landscape regions. However, access to an automated SPME apparatus is assumed. The authors can recommend this method as a cheap and fast alternative where SPME is available.

Keywords Organochlorine pesticides (OCPs) · Dichlorodiphenyltrichloroethane (DDT) · Hexachlorocyclohexane (HCH) · Trifluralin · Solid-phase microextraction (SPME) · Gas chromatography mass spectrometry (GC–MS)

1 Introduction

Soils are the foundation for human life. Among many services, they hold water and nutrients, are habitat for myriads of organisms, are the platform onto which structures are built, and most importantly, soils are the compartment where human food is grown. As such, keeping them in good condition is of utmost importance. All over the world, agricultural production systems are forced to develop in a more sustainable direction: simultaneously securing health and food safety for a growing population, minimizing detrimental environmental effects, preserving natural resources, and ensuring a sufficient yield and income especially in structurally weak, rural areas (subsistence farming) are only some of the associated challenges. However, soils are threatened by a multitude of factors, one of which is contamination with xenobiotics. To secure high crop yields, large quantities of pesticides are applied in agriculture each year, a great amount of which remains in the soil for a long time (Silva et al. 2019). While modern pesticides are required to be readily biodegradable and to minimize their impact on non-target organisms,

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historically applied compounds did not have these prerequisites. A recognized group of legacy compounds are organochlorine pesticides (OCPs), of which DDT (dichlorodiphenyltrichloroethane) and lindane (γ-hexachlorocyclohexane, γ-HCH) are well-known representatives. They were produced and used excessively after World War II until their toxicity, bioaccumulation, and persistence came to attention and led to various national restrictions and subsequent international ban on account of the Stockholm Convention 2001 (United Nations 2001). Yet, they are still found in occasionally large concentrations in agricultural soils all over the world, e.g., in Europe (Camenzuli et al. 2016), in states of the former Soviet Union (Aliyeva et al. 2012; Sharov et al. 2016; Tepanosyan et al. 2020), Africa (Olisah et al. 2020), or China (Li et al. 2014).

During HCH production, five main isomers are formed: 55–80% α-HCH, 5–14% β-HCH, 8–15% γ-HCH, 2–16% δ-HCH, and, 3–5% ε-HCH (Kutz et al. 1991). Of these, only γ-HCH has the desired insecticidal property, leading to approx. 85% of unwanted by-products. This technical mixture was either applied as is, or after purification to a formulation with a γ-HCH content of > 90% known as lindane. Apart from the contamination of agricultural land through intended application, many sites around the world were contaminated by the mainly uncontrolled dumping of the by-products (Vijgen et al. 2011).

During production of DDT, the two main congeners 4,4′-DDT and 2,4′-DDT make up 65–80% and 15–20% of the technical mixture, respectively (Haller et al. 1945). Only the first has insecticidal properties. When degraded in the soil, congeners retain their 2,4′ or 4,4′ conformation (Ricking and Schwarzbauer 2012). Under aerobic conditions, the primary transformation product (TP) of DDT is DDE (dichlorodiphenyldichloroethylene), and when anaerobic conditions prevail, it is DDD (dichlorodiphenyldichloroethane). In a study by Silva et al. (2019), in which the authors surveyed agricultural soils of 11 member states of the European Union, 4,4′-DDE was the fourth most found pesticide with median and maximum concentrations of 20 and 310 $\mu g \cdot kg^{-1}$, respectively.

Both analyte groups are stable, lipophilic, and semi-volatile, and, as such, are distributed widely from their points of origin by water, air, and soil (Garrison et al. 2014; Al Mahmud et al. 2015; Chen et al. 2017; Nežiková et al. 2019), leading to further contaminations of, e.g., ground and surface waters. They can enter the food chain, which leads to their bioaccumulation in fat cells of several types of organisms (Kutz et al. 1991; Nolan et al. 2012) also posing a threat to human health. From fat tissue they can be mobilized into the blood stream and further into breast milk among others (Longnecker et al. 1997; Smith 1999; Stuetz 2006).

HCH isomers as well as DDT and its TPs have been classified as carcinogenic and endocrine disruptors with genotoxic, mutagenic, and teratogenic effects (Kojima et al. 2004; Muñiz et al. 2017; Vandenberg et al. 2020). The latter is also assumed to be linked to obesity-related diseases like type 2 diabetes, and Alzheimer's disease (Lee et al. 2011; Richardson et al. 2014; Loomis et al. 2015; Evangelou et al. 2016; Elmore and La Merrill 2019).

This endangers food supply, as crops grown on these soils can be contaminated in turn (Lunney et al. 2004; Namiki et al. 2013). Apart from the challenges mentioned above, this might also jeopardize a country's export of foodstuff, if the contamination exceeds international regulations. Particularly affected groups are subsistence farmers, who rely solely on food grown on their own land to feed themselves. Quite often, this coincides with a lack of knowledge on correct and safe handling, storage, application or disposal of pesticides or even the general hazards associated with these substances (Oesterlund et al. 2014; Jallow et al. 2017; Sapbamrer 2018; Ndayambaje et al. 2019; Mubushar et al. 2019; Deng et al. 2019; Olisah et al. 2020).

In 2015, the nations of the UN defined and adopted 17 goals as calls to action for a more sustainable development on economic, social, and ecological scale in all member states (SDG, Social Development Goal; United Nations 2015). In order to support developing countries to screen and monitor large areas to determine pollution status (SDGs 2, 3, 6 and 15), simple, time, and cost-efficient methods are needed. Better yet, if these methods can be implemented in the framework of capacity building measures (SDG 17).

Generally proven methods to extract pesticides from environmental samples include solvent extraction, Soxhlet, ultrasound-assisted, microwave-assisted, or pressurized liquid extraction (Ayala-Cabrera et al. 2021). Nowadays, new developments in extraction and pre-extraction adhere to the principals of green chemistry and are therefore often miniaturized methods with little solvent consumption and small sample volumes (Ali et al. 2019; Prosen 2019). This includes QuEChERS (quick, easy, cheap, efficient, rugged, and safe; Anastassiades et al. 2003) extraction, originally intended for extraction of pesticide residues in food that has been adapted to other matrices, even soil (Vera et al. 2013). New methods on the basis of QuEChERS or dSPE (dispersive solid-phase extraction) continue to emerge (Eyring et al. 2021; Park et al. 2021). A lot of effort is directed into the development of new sorbents — e.g., on the basis of graphene (Li et al. 2021) or natural materials (Huang et al. 2020) — and new extraction materials like ionic liquids (Llaver et al. 2021) or deep eutectic solvents (Lee et al. 2020) among many others. Still, microextraction techniques both with solvent (e.g., liquid-phase microextraction, LPME; Prosen 2019; Rutkowska et al. 2019) and solventless (e.g., solid-phase microextraction, SPME; Liang et al. 2019; Naccarato and Tagarelli 2019) have been popular choices in extraction or clean-up of samples since their

invention in the 1990s, and have seen new developments as well (Da Soares Silva Burato et al. 2020). Among the latter group, SPME is an extraction and preconcentration method (Arthur and Pawliszyn 1990) in which a reusable sorbent-coated fiber is exposed to the sample either directly (immersed) or in the sample's headspace. During exposure, the fiber accumulates possible analytes which are subsequently thermally desorbed in the injector of a gas chromatograph, without the need of an additional clean-up step. Compared to conventional liquid injection where, usually, only a small portion of the sample extract is injected, everything the fiber extracted is injected with SPME. Especially when performed in headspace, co-extraction of interfering matrix compounds is reduced substantially and longevity of the fiber is increased (Zhang and Pawliszyn 1993; Zhang et al. 1994). SPME can also be used as a clean-up of extracts from solid samples if they have been extracted beforehand by a suitable solvent (Hernandez et al. 2000; Fidalgo-Used et al. 2003).

With the present study, a *mi*niaturized *so*lid–*li*quid *ex*traction technique is validated (hereinafter referred to as MISOLEX) that combines a modified standard method (ISO 10382 2002) with SPME as simple clean-up and preconcentration to sensitively and selectively analyze pesticides in a large number of soil samples with little effort. Among the method's merits are low solvent consumption, only one evaporation step, no laborious clean-up steps, and a sample requirement of only 0.5 g. Apart from SPME equipment and the requirement of internal standards (ISs) with appropriate physicochemical properties, it can be done with standard lab equipment and could be an affordable alternative. Larger sets of samples can be managed by this approach allowing for extensive area soil screening for OCPs to assess food security. With small adaptions, suitability of this method for further matrices (e.g., sediment or plant material) is conceivable. A preliminary version of this approach was used by Mukaj et al. (2016) on agricultural soils in Albania.

To prove the adequacy of MISOLEX, quality parameters such as recovery rate, limits of quantitation and detection (LOQ and LOD, respectively), and reproducibility were determined. As QuEChERS has long since been used to analyze soil samples for halogenated pesticides and other contaminants (Vera et al. 2013), the quality parameters were compared to a modified QuEChERS approach by Woldetsadik et al. (2021) that applies SPME as clean-up and preconcentration step as well. In addition, both methods were applied to analyze environmental samples from a contaminated site in Tamarissi municipality, Georgia. The results were used to further validate the performance of the two methods by demonstrating the applicability of the method to environmental samples.

2 Materials and methods

2.1 Chemicals

Organic solvents acetone, methanol, and acetonitrile (all gradient grade for HPLC) were purchased from VWR International (Radnor, PA, USA), petroleum ether (40–60 °C, p.a.) was purchased from Merck GmbH & Co. KG (Darmstadt, Germany), and *n*-pentane was purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Standards (purity) of trifluralin (TriF; 99.6%) 2,4′-dichlorodiphenyldichloroethane (DDD, 97.5%), 2,4′-dichlorodiphenyldichloroethylene (DDE, 99%), 2,4′-DDT (99.5%), 4,4′-DDD (99.5%), 4,4′-DDE (98%), 4,4′-DDT (99.5%), ^{13}C-2,4′-DDT (100%), γ-HCH (98.6%), and δ-HCH-D_6 (98%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). α-HCH (≥ 98%) and δ-HCH (≥ 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). β-HCH (99.5%) was obtained from Institute of Industrial Organic Chemistry (Warsaw, Poland). TriF-D_{14} (98%), 4,4′-DDD-D_8 (99.7%), 4,4′-DDE-D_8 (99.4%), and α-HCH-D_6 (99.2%) were purchased from CDN Isotopes (Pointe Claire, Canada). ^{13}C-4,4′-DDT (99%) was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Purity was considered when preparing stock solutions of standards. QuEChERS extraction salts magnesium sulfate ($MgSO_4$) and sodium citrate dibasic sesquihydrate (≥ 99%) were purchased from VWR International and Sigma-Aldrich, respectively. Trisodium citrate dihydrate (≥ 99.5%) was obtained from Th. Geyer GmbH & Co. KG (Renningen, Germany) and primary-secondary amine (PSA) from Supelco (Bellefonte, PA, USA). Sodium chloride (NaCl, ≥ 99.5%) for preparation of SPME salt solution was purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). All salts were of analytical grade or better. Ultra-pure water was produced with Milli-Q A10 water purification system (Merck KGaA).

2.2 Preparation of spiked soil samples

Three soil samples were chosen according to their soil organic carbon (SOC) content, to cover representative SOC contents for arable soils in temperate climates: 1.25, 2.27, and 2.74%. An overview of these samples' features is given in Table 1, while the full characterization is available in the Online Resource (Table S1). These samples were spiked with DDX (2,4′-DDD, 2,4′-DDE, 2,4′-DDT, 4,4′-DDD, 4,4′-DDE, 4,4′-DDT), HCHs (α-, β-, γ-, and δ-HCH), and TriF to a concentration of 50 $\mu g \cdot kg^{-1}$ per analyte. For that, *n*-pentane was added to 120 g of each

Table 1 Characteristics of the spiked soil samples used in the comparisons. For a full list of parameters, please refer to the electronic supplementary material (Table S1). N_{tot} total nitrogen, *SOC* soil organic carbon

Soil	Usage	Depth [cm]	Sand [%]	Silt [%]	Clay [%]	N_{tot} [%]	SOC [%]
Soil 1	Arable land	0–30	19.2	62.4	18.4	0.15	1.25
Soil 2	Arable land	0–30	33.5	47.5	19.0	0.26	2.27
Soil 3	Grassland	0–30	43.2	43.1	13.7	0.23	2.74

soil until a supernatant of ca. 1 cm occurred, and standard mixes containing DDX, HCHs, and TriF were injected into the supernatant. After thorough stirring, samples were placed on a horizontal shaker (Swip KS-10, Edmund Bühler GmbH, Bodelshausen, Germany) at 200 rpm and shaken until the solvent had evaporated completely. Then, samples were stored at 8 °C in a refrigerator for 35 days, to simulate aging for generation of field-like samples as suggested by Škulcová et al. (2017).

2.3 QuEChERS extraction

As comparative method, the QuEChERS extraction for plant material as described in Woldetsadik et al. (2021) was used. Extraction was done in quintuplet. In brief, 1 g of air-dried (30 °C, 24 h), homogenized sample was weighed into a 50 mL glass centrifuge tube, to which 10 mL of ultrapure water was added and vortexed for 10 s. After letting the samples rehydrate for 10 min, 15 mL acetonitrile was added and samples were shaken on a horizontal shaker for 15 min at 200 rpm (Swip KS-10, Edmund Bühler GmbH). Thereafter, 4 g $MgSO_4$, 1 g NaCl, 1 g sodium citrate (tribasic) dihydrate, and 0.5 g sodium citrate (dibasic) sesquihydrate were added and vortexed for another 10 s. Then, samples were centrifuged for 10 min at 1,000 rpm (207.2 g; Rotanta 460 R, Hettich AG, Bäch, Switzerland). Afterwards, 8 mL of supernatant was transferred into a centrifuge tube containing 1.2 g $MgSO_4$ and 0.2 g PSA. It was again vortexed for 10 s and centrifuged at 2,500 rpm (1,295 g) for 10 min. Of the supernatant, a 4 mL aliquot was transferred into a 20 mL brown glass head space vial; 2 µL of IS mix (see Table S2) was added and vortexed. Under a gentle stream of nitrogen at ambient temperature, the extract was evaporated to dryness and immediately resolubilized with 100 µL of methanol after which it was vortexed for 5 s, and 10 mL of salt solution (200 g NaCl in 1 L ultrapure water) was added. The glass vial was firmly closed with a septum screw cap for subsequent measurement by HS–SPME–GC–MS.

2.4 Miniaturized solid–liquid extraction (MISOLEX)

Extraction was done in quintuplet. 0.5 g of air-dried (30 °C, 24 h), homogenized soil sample was weighed in a 20 mL clear glass head space vial. 5 mL acetone and 5 mL petroleum ether were added and the vial was closed tightly with a screw cap. The sample was shaken on a horizontal shaker for 30 min at 200 rpm (Swip KS-10, Edmund Bühler GmbH) and then centrifuged for 10 min at 1000 rpm (207.2 g; Rotanta 460 R, Hettich AG). The supernatant was transferred into a 20 mL brown glass head space vial. Another 5 mL of petroleum ether was added to the sample, and the process was repeated. The supernatant was added to the one taken before, resulting in approx. 12 mL of extract. An aliquot of 10 mL was transferred to a fresh 20 mL brown glass head space vial, and 2 µL of an IS mix as well as 200 µL of acetonitrile acting as keeper was added. The extract was evaporated to keeper under a gentle stream of nitrogen at ambient temperature. Immediately thereafter, 10 mL of salt solution (200 g NaCl in 1 L ultrapure water) was added. The glass vial was firmly closed with a septum screw cap for subsequent measurement by HS–SPME–GC–MS.

2.5 Note on environmental samples

Even though only 1 g or 0.5 g of sample material is needed for QuEChERS and MISOLEX, respectively, standard protocols concerning representative sampling in the field do apply. That is, it is not correct to assume that only 0.5 g is supposed to be collected from a soil intended as representative sample. Rather, we recommend to collect adequately large (composite) samples to depict the in situ situation, to homogenize them sufficiently and only then to take the subsample of 1 g or 0.5 g intended for extraction from it. Although a larger sample amount has to be taken in the field, the small sample amount intended for pesticide extraction is still beneficial because the remaining soil sample can be used for further characterization (e.g., SOC, particle size analysis, pH).

2.6 Environmental sampling

The study area (108 m^2) from which environmental samples were taken was located near Tamarissi municipality, Georgia (N41.444311° E44.76041°) next to an abandoned, ruinous pesticide storage house. Three composite samples (A, B, and C) were collected in 2018, each consisting of five 10-cm cores, sampled with a soil corer (inner diameter 20 mm) in a subplot of 4

m^2. Detailed soil characteristics for these samples are available in the Online Resource (Table S1). The soil in the study area can be characterized as Vertic Kastanozem according to the World Reference Base for Soil Resources (IUSS Working Group WRB 2015). After transport to Germany, samples were air-dried (30 °C) for 24 h, homogenized, and sieved (2 mm) to gain the fine earth fraction. Samples were stored at −30 °C until extraction.

2.7 SPME and GC–MS analysis

OCP analysis in soil samples was carried out with a Trace 1310 gas chromatograph (Thermo Fisher Scientific, San Jose, CA, USA), a CombiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland) equipped with a SPME fiber assembly, and an ISQ 7000 mass spectrometer (Thermo Fisher Scientific). For all measurements, a SPME fiber coated with PDMS/DVB (65 µm StableFlex fiber) was used (Sigma-Aldrich, St. Louis, MO, USA). SPME of prepared samples started with a heat-up phase of 5 min to 80 °C in the agitator, followed by headspace extraction at the same temperature for 60 min. After extraction, the fiber was thermally desorbed in splitless mode in the GC injector for 3 min at 260 °C, after which it switched back to a split flow of 30 $mL \cdot min^{-1}$. At the start and end of each SPME sample cycle, the fiber was desorbed in a needle heater for 7.5 min at 270 °C to prevent potential carry-over of analytes between samples. Chromatographic separation was conducted on a fused silica capillary column (TG-XLBMS: 60 m, 0.25 mm inner diameter, 0.25 µm coating thickness; Thermo Fisher Scientific). Helium (≥ 99.999%, Praxair Inc., Danbury, CT, USA) was used as carrier gas at a constant flow of 1.0 $mL \cdot min^{-1}$. The initial oven temperature was set to 90 °C and held for 3 min. The temperature was ramped to 150 °C at a rate of 15 $°C \cdot min^{-1}$. Then, it was ramped to 280 °C at a rate of 5 $°C \cdot min^{-1}$ and held for 3 min. Quantification was done in selected ion monitoring (SIM) mode based on one target and one qualifier ion. The list of utilized ions and retention times (RTs) is available in the Online Resource (Table S3). The peak areas of analytes in sediment samples were corrected with their respective ISs (Online Resource, Table S2). The according concentration was determined by interpolation of the relative peak areas for each pesticide to standard peak areas of the calibration curve (compare section "Method Validation").

2.8 Method validation

Linearity, precision, and recovery rate were evaluated using a seven-level calibration curve at working solution concentrations of 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, and 2.0 $µg \cdot L^{-1}$ for DDX and TriF, and 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 $µg \cdot L^{-1}$ for HCHs. Calibrations were extended with concentrations of 12.5 and 25 $µg \cdot L^{-1}$ when analyzing environmental samples to assess linearity in very high concentration ranges. Recoveries of the analytes were calculated per soil as percentage of the expected concentration of 50 $µg \cdot kg^{-1}$. For determination of LODs and LOQs, the concentration result of each analyte in each (matrix) sample was divided by the corresponding signal to noise ratio of its peak as approximation to noise present at the analyte's RT. The resulting noise concentrations were multiplied by 3 and 10 to obtain LOD and LOQ, respectively.

Both applied methods make use of a large number of isotopically labeled ISs. For four analytes (2,4′-DDD, 2,4′-DDE, β-HCH, and γ-HCH), instead of isotopologues the IS of a similar congener (4,4′-DDD-D_8, 4,4′-DDE-D_8, δ-HCH-D_6, and α-HCH-D_6, respectively) was used. Incidentally, these four analytes demonstrated implausibly high recovery rates. As the IS correction was deemed the cause for this overestimation, an alternative approach for this step was applied. In principle, the RT of an analyte was used as indicator for its physicochemical properties. The closer the RTs of two analytes (or an analyte and IS) are, the closer these two compounds may also be in terms of their physicochemical properties. Because of this assumption, correction factors for each of the four mentioned analytes were calculated proportionally between the nearest two ISs that surrounded each of them. In the case of 2,4′-DDD and 2,4′-DDE, this meant using other ISs as before (4,4′-DDE-D_8 and ^{13}C-2,4′-DDT for the first, and δ-HCH-D_6 and 4,4′-DDE-D_8 for the latter). Further explanations can be found in the Online Resource (Table S3 and Figure S1).

2.9 Statistics and figures

Statistical calculations to check assumptions and determine likeliness between methods were carried out with the computational software R, version 4.0.4 (R Core Team 2020). Shapiro–Wilk test was used to test for assumption of normality. Statistical significance was set at $p < 0.05$ level. Single pairwise comparisons were done with Welch's *t*-test or ANOVA-type rank test by Brunner and Munzel (2013), if assumptions were not met, as it does require neither normal distribution nor homoscedasticity of data. Multiple pairwise comparisons to test for significant difference between three soils were computed with *t*-tests with Holm correction to correct for inflated familywise error rates. In those cases, where the assumptions were violated, the robust trimmed means bootstrap post hoc test (mcppb20) described by Wilcox (2016) was applied, which is available in the package WRS2 (Mair and Wilcox 2020). Figures were created with OriginPro 2020 (OriginLabs Corp., Northampton, MA, USA).

Table 2 Overview of the analytes' LODs and LOQs as median ($n = 15$) in µg·kg^{-1} for the two compared methods

Analyte	MISOLEX		QuEChERS	
	LOD	**LOQ**	**LOD**	**LOQ**
TriF	0.005	0.02	0.001	0.004
α-HCH	0.27	0.90	0.31	1.05
γ-HCH	0.90	3.00	0.39	1.29
β-HCH	1.16	3.85	1.31	4.36
δ-HCH	0.91	3.02	1.48	4.93
2,4′-DDE	0.04	0.12	0.06	0.19
4,4′-DDE	0.13	0.43	0.03	0.10
2,4′-DDD	0.32	1.05	0.32	1.08
4,4′-DDD	0.14	0.47	0.20	0.66
2,4′-DDT	0.25	0.82	0.47	1.57
4,4′-DDT	0.05	0.17	0.14	0.47

3 Results

For MISOLEX, LODs and LOQs of DDX congeners were 0.04–0.32 and 0.12–1.05 µg·kg^{-1}, respectively. LOD of TriF was 0.005 µg·kg^{-1}, and LODs of HCHs ranged from 0.27 to 1.16 µg·kg^{-1}. LOQs were 0.02 and between 0.90 and 3.85 µg·kg^{-1}, respectively. Recovery rates were between 65.8 and 172.6% for most DDX, and between 70.2 and 126.1% for TriF and most HCH isomers (Online Resource Fig. S2 and Table S4). Here, γ-HCH and 2,4′-DDD were overestimated with values up to 180.9% and 167.3%, respectively. The average recovery rate for the whole method was 110%. Repeatability expressed as relative standard deviation (RSD) was 23.7%. On a per soil basis, it ranged from 1.3 to 22.4%, and between 6.7 and 20.6% if soils were taken together. γ-HCH, again, demonstrated elevated values between 12.9 and 22.4%.

For the modified QuEChERS method, LODs and LOQs of DDX congeners were between 0.03 and 0.47 µg·kg^{-1}, and between 0.10 and 1.57 µg·kg^{-1}, respectively (Table 2). For TriF and HCHs, LODs were 0.001 and between 0.31 and 1.48 µg·kg^{-1}, respectively, and LOQs were 0.004 and between 1.05 and 4.93 µg·kg^{-1}, respectively. Recovery rates were satisfactory, ranging from 67.8 to 127.0% for most analytes (Online Resource Fig. S2 and Table S5). The rates for 2,4′-DDE and δ-HCH were above 120%, with values up to 169.3% and 140.7%, respectively. The overall average for all analytes was 102.4%. Repeatability (RSD) was 21.8% for the whole method. Separated into analytes, it ranged between 1.2 and 9.4% on a per soil basis and between 3.6 and 8.8% if calculated for all three soils together.

On average, the interpolated IS correction resulted in the preferred range of 80 to 120% for all analytes of both methods (Fig. 1 and Online Resource Tables S6 and S7), the exception being δ-HCH and 2,4′-DDD in the QuEChERS method. The former was not significantly altered and still remained mostly outside of range whereas the latter was slightly worsened. The most drastic effects in terms of recovery rate adjustment (all significant) were shown by 2,4′-DDE of the QuEChERS method and by γ-HCH, β-HCH, and 2,4'-DDD of the MISOLEX method. In terms of repeatability, the RSD of γ-HCH was reduced from 20.6 to 12.8%, while that of 2,4′-DDD was increased from 11.2 to 40.9%. Figures showing means and standard deviations (SDs) of the results discriminated by soil are included in the Online Resource (Figs. S2 and S3).

Comparing the results of regularly and interpolated IS-corrected environmental samples shows a very similar pattern (Fig. 2). Interpolation results in considerable reduction in concentration (mean of all three samples) of γ-HCH (−30%), 2,4′-DDE (−60%), and 2,4′-DDD (−74%)

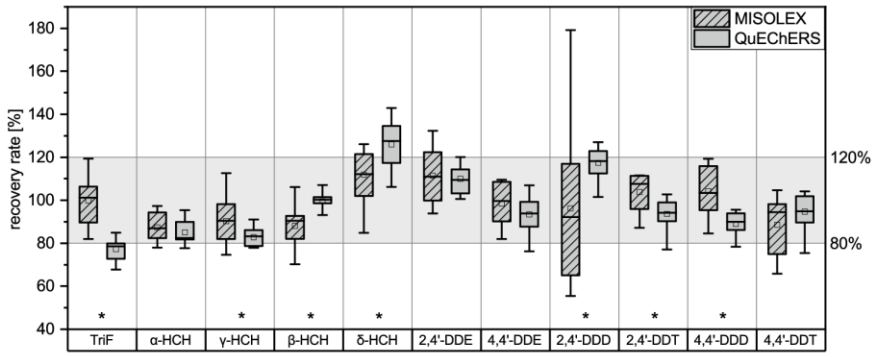


Fig. 1 Boxplots of recovery rates of 11 different analytes in three spiked soils for the two examined methods with five replicates per soil and method ($n = 15$ per boxplot). Order follows elution sequence. γ-HCH, 2,4′-DDE, and 2,4′-DDD are derived from interpolated internal standard correction. Gray area depicts the targeted recovery rate range between 80 and 120%. Asterisks denote statistically significant difference between the two methods ($p < 0.05$). Figures discriminating between the three soils are available in the Online Resource (Figs. S2 and S3)

for MISOLEX as well as QuEChERS (−39%, −30%, and −40%, respectively). Consequently, the three mentioned analytes were corrected by the interpolation approach in the environmental samples.

Repeatability of the two methods is assessed by the RSD of the five replicates: averaged across all analytes, RSDs for MISOLEX extraction were 23%, 19%, and 16% for samples A, B, and C, respectively. For QuEChERS, averaged RSDs were 11%, 13%, and 15%, respectively.

Both methods yielded similar results in the same orders of magnitude on a per analyte basis but with significant differences in some cases. TriF was not detected in any sample, regardless of the method. In general, QuEChERS seemed to yield higher values for HCH isomers.

In samples A and B, values of HCHs were higher than those of DDX by at least one order of magnitude. In sample C, differences were not as pronounced between compound groups. Concentrations in the three samples ranged from 0.33 to 849.0 $\mu g \cdot kg^{-1}$, or from 0.39 to 1,006.9 $\mu g \cdot kg^{-1}$ if analyzed by MISOLEX or QuEChERS, respectively. For detailed concentration values, the reader is referred to the Online Resource (Tables S8 to S11).

4 Discussion

The miniaturized method showed good LODs, LOQs, recovery rates, and repeatability for the three tested soils, with only few exceptions. LOQs were far below the limit of 50 $\mu g \cdot kg^{-1}$ recommended by the European Commission (2021) for pesticide analyses in soil. Means of recovery rates and RSDs were mostly between 80 and 120% and below 20%, respectively. The parameters are comparable with previous results reported in other studies for samples from, e.g., a SOC rich garden soil and a clay rich soil from Spain (LOD 0.15–2.2 $\mu g \cdot kg^{-1}$, recovery rates 62–92%, SD 0.1–3.4 percentage points (pp); Pinto et al. 2010), two Portuguese strawberry farm soils (LOD 1.7–7.6 $\mu g \cdot kg^{-1}$, recovery rates 70–151%, relative SD 1–14 pp; Fernandes et al. 2013), field soils in China (LOD 0.1–0.8 $\mu g \cdot kg^{-1}$, recovery rates 80.6–118.3%, SD 2.4–8.4 pp; Ma et al. 2020), mineral and peat soils from vegetable farms in Malaysia (LOD 1 $\mu g \cdot kg^{-1}$, LOQ 3.33 $\mu g \cdot kg^{-1}$, recovery rates 82–104%; Chai et al. 2013), and an agricultural soil from Gran Canaria (LOD 0.024–6.25 $\mu g \cdot kg^{-1}$, LOQ 0.5–20 $\mu g \cdot kg^{-1}$, recovery rates 63.7–122.8%; Acosta-Dacal et al. 2021). In fact, the low LODs and LOQs make the presented MISOLEX method not only applicable in screening cases, but constate suitability for use in trace analyses as well.

Differences of recovery rates between the three soils — while being significant in several cases — were mostly relatively small, attesting good reproducibility for each separate case. Preliminary experiments with soils of lower and higher SOC content (between 0.13 and 5.86%) showed similar reproducibility, although these results were not further validated and are therefore not considered here (Online Resource Fig. S4).

The performance of MISOLEX is comparable to that of the modified QuEChERS method, both in terms of sensitivity and recovery. In terms of quickness, however, MISOLEX was found to be faster, as there was no necessity to prepare salt mixtures and subsequently weigh them into each vessel separately. In general, the variability of MISOLEX was higher than that of QuEChERS, both in spiked and environmental samples, which might be due to the lower sample volume that is extracted (0.5 g vs. 1 g).

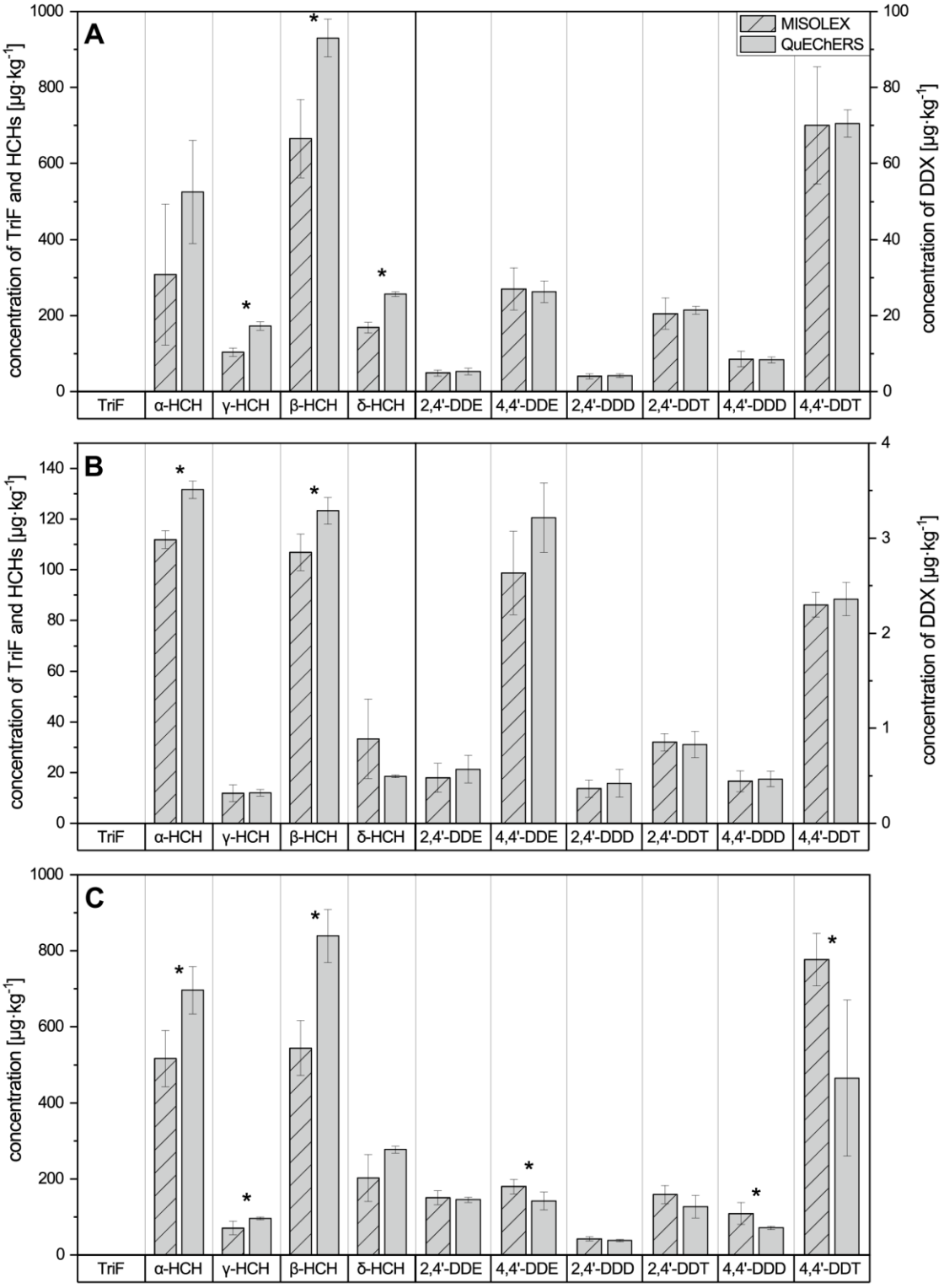
The overestimation of γ-HCH, 2,4′-DDE and 2,4′-DDD could be alleviated with the interpolated IS correction for these analytes. The recovery rates of γ-HCH showed even less variability than before. In the case of 2,4′-DDD, however, the correction led to an increasing variability. This was less pronounced when regarding the results for each soil separately (Online Resource Fig. S3). The large standard deviation of 2,4′-DDD in Fig. 1 is mainly due to the large differences between the soils.

Recovery rates differed significantly, which was confirmed by the results of the environmental samples. Based on this, the authors can recommend to apply the interpolated IS correction to 2,4′-DDD, 2,4′-DDE, and especially γ-HCH when using MISOLEX and to 2,4′-DDE when using the modified QuEChERS method.

Additionally, several other interpolation approaches of an increasing range between the applied ISs were calculated that would even further reduce the number of ISs needed. But as these did not yield consistent results especially between the two different methods, and would therefore require further experiments, they are not discussed here. Still, this interpolation approach should serve as incentive for other researchers. It could be adapted and made suitable for other applications or ISs and by this help reduce effort and costs.

To the best of the authors' knowledge, this approach has not been published before. Although the combination of two IS was reported as an option in an analytics software (Thermo Electron PlasmaLab) for ICP-MS (inductively coupled plasma mass spectrometry) as "interpolation technique between masses when multiple ISs" a detailed description of this combination was not given (Niemelä et al. 2005). In the recent past, other studies in analytics of organic contaminants have rather focused on determining the most suitable IS for larger groups of analytes in multiresidue methods. This was done on the basis of, e.g., shared variation, similar chemical properties, and matrix effect (Ueno et al. 2004; Cervera et al. 2010; Tsuchiyama et al. 2017).

ISs are intended to parallel as much as possible the physico-chemical properties of the analytes they are


A
B
C
MISOLEX
QuEChERS
concentration of TriF and HCHs [µg·kg⁻¹]
concentration of DDX [µg·kg⁻¹]
concentration [µg·kg⁻¹]
TriF
α-HCH
γ-HCH
β-HCH
δ-HCH
2,4'-DDE
4,4'-DDE
2,4'-DDD
2,4'-DDT
4,4'-DDD
4,4'-DDT

◂**Fig. 2** Means of concentrations of 11 different analytes determined in three environmental soil samples A, B, and C from Tamarissi municipality, Georgia ($n=5$ per bar). Note the different y-axes. Error bars depict standard deviation. Asterisks denote statistically significant difference between the two methods ($p<0.05$)

supposed to correct (Poerschmann et al. 1997; Stokvis et al. 2005). Ideally, there would be one IS for each analyte and this — in case of mass spectrometric detection — would be an isotope-labeled version of its analyte counterpart. Such standards are usually quite expensive or even not available at all, which was one reason why interpolation of ISs was examined here. The other fact was the overestimation of those analytes that did not have a very close IS counterpart. As the RT is a function of the substance's properties, it serves as an indication of similar behavior. Therefore, it could be assumed that greater distances in RT between two substances imply less similarity and less similar behavior. If this applies to the pair of a substance and its IS, the latter is not as representative of losses of the former that may occur during execution of an analysis, possibly resulting in overestimation or underestimation of the substance when corrected. In terms of losses, the most critical part in the methods presented here is the evaporation step, for which vapor pressure and lipophilicity are very important: two properties that are of high influence for RT as well. Another important factor could be the presence of organic residues in the extract, which could serve as sorbent for analytes and ISs that prevents their evaporation or drift with the nitrogen stream when the supernatant level decreases. This is corroborated by results from Woldetsadik et al. (2021) who used the modified QuEChERS method for plant material, where overestimation did not occur. This factor would be very much dependent on hydrophobicity.

Compared to the classic ISO method, MISOLEX features several advantages. The standard method relies on a great number of different steps that increase labor and necessary time per sample, and with that the risks for errors and losses of analyte. As well, the required amount of solvent per sample (ca. 200 mL compared to ca. 15 mL) is by far higher than with MISOLEX. Additionally, each extract has to be washed with water to remove acetone, resulting in 1 L of contaminated washing water per sample. The relatively high sample amount of 20 g compared to 0.5 g renders it unsuitable for all cases, where sample volume is scarce or is impractical to collect, e.g., when a large number of samples need to be shipped. In the ISO method, apart from the washing step, multiple evaporations and transfers are necessary. Process standards that are added before these critical steps could serve as indicator if analyte losses occurred. With the utilization of mere injection standards as it is required in the ISO method, however, only deviations of measurement performance are considered. Taken together, the features of MISOLEX are in accordance with several principles of green analytical chemistry (Gałuszka et al. 2013), e.g., to generate as little waste as possible, to avoid derivatization, to analyze multiple parameters or analytes at once, and to automate and miniaturize.

But MISOLEX is not without disadvantages: The most prominent is the limitation that each extract can only be measured once, as the SPME alters the concentration of analytes in a sample. If a sample is to be analyzed in, e.g., a triplet, there are two options. (1) It could be solvent-extracted the same number of times, at the cost of the maximum number of samples that could be simultaneously extracted. Or (2) the method could be upscaled with larger vessels that can contain thrice as much sample as well as solvent to generate the necessary extract volume for three aliquots in one step. Of course, if analyte concentrations are sufficiently high, the extract could be divided in as many aliquots as adequate before evaporation and SPME extraction without upscaling, also allowing for retention samples. Another point which is just as much an advantage as it is a disadvantage is the use of a large number of isotope-labeled standards. While they greatly enhance the certainty of recovery rates of the analytes, they are also quite costly. They could be exchanged for alternative, unlabeled, and thus cheaper standards, whose suitability needs to be validated beforehand. When using such a low sample amount as presented here, particular care has to be given to the homogenization of samples. The main sample from which the 0.5 g is taken has to be of adequate size and be homogenized sufficiently beforehand to ensure representative results for depiction of a real pollution situation in situ. And finally, as is the case with every new system, the implementation of SPME into existing routines initially requires additional method development after installment. It should be noted, however, that it is possible to use SPME manually if no autosampler is available, but for that, great care to timing needs to be exercised. The implementation of SPME in general enables the adoption of certain other standard methods for analysis of, e.g., water samples (ISO 27108 2010; ISO 17943 2016). It is of course possible to adapt this method to include more OCPs like aldrin, dieldrin, or endosulfan, but also pollutants in general like polychlorinated biphenyls (PCBs) or polycyclic aromatic hydrocarbons (PAHs).

5 Conclusion

The presented miniaturized method allows to quickly and simply determine OCPs in soil samples. With its low sample amount and solvent requirements, it fulfills several principles of green analytical chemistry and is well suited for large area soil screenings or even trace amount analytics. It applies SPME and a single-quadrupole GC–MS, the latter of which

is considered standard in terms of mass spectrometry. With more sophisticated instrumentation, e.g., a triple-quadrupole or high-resolution MS, the method's performance could likely be improved. SPME adds the advantage of a fully automized clean-up procedure. The authors are aware that the appropriate equipment is not available in every laboratory. In such cases, SPME could be operated manually, which would save instrument costs but at the same time remove the advantage of automation.

In our laboratory, the extraction of 40 samples per day was very well manageable. So, for 80 samples, including evaporation and subsequent measurement with calibrations, it took 7 days in total. With more samples to be measured, the next set could be extracted during evaporation and measurement, so that a continuous routine with considerable throughput of samples would be established.

The reproducibility of the MISOLEX method in this case leaves room for improvement, especially in comparison with the very well performing modified QuEChERS method, but is more than sufficient for screening purposes. This could be demonstrated with the application on environmental samples that cover a broad concentration range. MISOLEX might be improved by higher sample amounts, e.g., 1 g instead of 0.5 g, to decrease the impact of the samples' homogeneity, but this requires further experiments.

In addition, a first test of a new approach to interpolate different ISs was introduced. It uses the analytes' RTs as indication for likeliness of physical properties. In the present study, it performed well for two out of four analytes and improved their recovery rates. Future studies should evaluate additional samples with differing properties, different combinations of ISs between which interpolation is applied, and should expand the method to more substance groups.

The described approach of a highly efficient analytical method meets the urgent need to further identify the widespread contamination of soils and sediments with OCPs, especially in developing countries.

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Availability of data and material Detailed data together with additional information and figures is supplied alongside the text in the Online Resource on the article's webpage.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

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2.2 Anhang zu Artikel 1

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Table S1.1 – Comprehensive characterization of the three soil samples for recovery rate determination. gS = coarse sand, mS = medium sand, fS = fine sand, gU = coarse silt, mU = medium silt, fU = fine silt, H2O = reverse osmosis water, CEC = cation exchange capacity, Mn_{ox} = manganese from oxalate extraction, n.d. = not determined.

a) Texture

No	Use	Depth	gS	mS	fS	gU	mU	fU	Clay
	-	cm	%						
1	arable land	0-30	0.6	3.7	14.8	40.3	17.5	4.7	18.4
2	arable land	0-30	7.2	9.3	17.0	28.0	13.7	5.8	19.0
3	pasture	0-30	0.2	3.8	39.2	29.3	10.6	3.3	13.7

(determined after DIN EN ISO 17892-4: https://dx.doi.org/10.31030/2362539)

b) pH and CEC

No	pH_{CaCl2}	pH_{H2O}	pH_{KCl}	Ca	K	Mg	Na	CEC_{pot}
	-			$cmolc \cdot kg^{-1}$				
1	5.74	6.15	5.47	9.10	0.47	1.51	0.08	11.17
2	5.54	5.85	5.25	15.94	1.41	7.14	0.21	24.70
3	6.78	7.18	6.78	22.61	0.13	1.21	0.04	23.99

c) Nutrient and trace elements

No	N_{tot}	SOC	S_{tot}	$CaCO_3$	Mn_{OX}	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu
	%				$mg \cdot g^{-1}$	$mg \cdot kg^{-1}$								
1	0.15	1.25	0.04	n.d.	1.27	24,895	5.76	239	1.27	3,280	0.43	12	22	24
2	0.27	2.27	0.06	n.d.	0.59	52,020	2.79	292	1.68	8,238	0.35	49	554	46
3	0.23	2.74	0.07	0.26	0.36	22,048	8.59	339	2.27	6,984	0.69	9.09	20	32

No	Fe	Hg	K	Mg	Mn	Mo	Na	Ni	P	Pb	Sb	Sn	V	Zn
	$mg \cdot kg^{-1}$													
1	24,714	0.10	4,078	4,537	1,822	n.d.	178	28	2,072	32	0.81	1.99	74	106
2	66,928	0.09	2,025	54,334	1,738	n.d.	425	347	2,883	23	0.51	1.91	149	140
3	19,165	0.36	2,349	3,924	547	n.d.	168	22	1,482	44	2.78	2.80	56	144

(elements Al till Zn determined by aqua regia microwave-assisted extraction followed by ICP-OES analysis)

Table S1.2 – Characterization of the three environmental soil samples. gS = coarse sand, mS = medium sand, fS = fine sand, gU = coarse silt, mU = medium silt, fU = fine silt, H2O = reverse osmosis water, CEC = cation exchange capacity, Mn_{ox} = manganese from oxalate extraction, n.d. = not determined.

a) Texture

No	Use	Depth	gS	mS	fS	gU	mU	fU	Clay
	-	cm	%						
A	pasture	0-10	4.7	7.5	5.9	5.5	9.7	8.5	58.2
B	pasture	0-10	2.0	4.3	5.0	5.8	12.4	8.0	62.4
C	pasture	0-10	2.6	5.7	6.2	6.5	12.1	8.8	58.0

(determined after DIN EN ISO 17892-4: https://dx.doi.org/10.31030/2362539)

b) pH and CEC

No	pH_{CaCl2}	pH_{H2O}	pH_{KCl}	Ca	K	Mg	Na	CEC_{pot}
	-			$cmolc \cdot kg^{-1}$				
A	6,0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
B	6,1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C	6,2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

c) Nutrient and trace elements

No	N_{tot}	SOC	S_{tot}	$CaCO_3$	Mn_{OX}	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu
	%				$mg \cdot g^{-1}$	$mg \cdot kg^{-1}$								
A	0.3	3.1	0.06	0.04	n.d.	55,854	5.56	n.d.	n.d.	12,026	0.15	19	55	358
B	0.3	2.7	0.06	0.09	n.d.	55,854	5.56	n.d.	n.d.	12,026	0.15	19	55	358
C	0.3	2.7	0.08	0.10	n.d.	53,589	6.95	n.d.	n.d.	10,167	0.23	22	53	247

No	Fe	Hg	K	Mg	Mn	Mo	Na	Ni	P	Pb	Sb	Sn	V	Zn
	$mg \cdot kg^{-1}$													
A	40,665	n.d.	10,482	12,283	773	0.61	950	41	674	14	n.d.	n.d.	135	130
B	40,665	n.d.	10,482	12,283	773	0.61	950	41	674	14	n.d.	n.d.	135	130
C	40,264	n.d.	10,342	11,287	862	0.74	734	41	931	15	n.d.	n.d.	135	298

(elements Al till Zn determined by aqua regia microwave-assisted extraction followed by ICP-OES analysis)

Table S2 – Composition of the internal standard mix. Sorted by concentration.

Component	Concentration [µg·mL^{-1}]
TriF-D_{14}	5
4,4'-DDE-D_8	5
4,4'-DDD-D_8	10
^{13}C-2,4'-DDT	15
^{13}C-4,4'-DDT	15
α-HCH-D_6	15
δ-HCH-D_6	45

Table S3 – Retention times (RT) and ions used for identification and quantification of analytes and internal standards (IS). TriF-D_{14} corrected TriF, α-HCH-D_6 corrected α- and γ-HCH, δ-HCH-D_6 corrected β- and δ-HCH, 4,4'-DDE-D_8 corrected both DDE congeners, 4,4'-DDD-D_8 corrected both DDD congeners, and the ^{13}C substituted IS were used to correct their respective unmarked counterparts.

Name	Purpose	RT [min]	Quantifier [m·z^{-1}]	Qualifier [m·z^{-1}]
TriF-D_{14}	IS	18.99	315	207
TriF	Analyte	19.18	306	264
α-HCH-D_6	IS	20.95	224	185
α-HCH	Analyte	21.12	219	181
γ-HCH	Analyte	22.52	219	181
β-HCH	Analyte	23.77	219	181
δ-HCH-D_6	IS	24.67	224	185
δ-HCH	Analyte	24.80	219	181
2,4'-DDE	Analyte	28.83	246	318
4,4'-DDE-D_8	IS	30.18	254	326
4,4'-DDE	Analyte	30.27	246	318
2,4'-DDD	Analyte	30.63	235	165
^{13}C-2,4'-DDT	IS	31.80	247	177
2,4'-DDT	Analyte	31.82	235	165
4,4'-DDD-D_8	IS	32.19	243	173
4,4'-DDD	Analyte	32.28	235	165
^{13}C-4,4'-DDT	IS	33,44	247	177
4,4'-DDT	Analyte	33,44	235	165

Example for interpolated internal standard correction: **γ-HCH**

The two IS surrounding γ-HCH are **α-HCH-D_6** at RT 20.95 min and **δ-HCH-D_6** at RT 24.67 min. The time span between these two IS is 3.72 min. γ-HCH elutes at RT 22.52 min, which is a1.57 min distance from α-HCH-D_6 and2.15 min from δ-HCH-D_6. This is 42.2% and 57.8% of the span between the two IS, respectively. Now, the peak area of γ-HCH is corrected with each of the two IS separately, and each of the two values is converted into a concentration with a separate linear regression. Then, they are multiplied with their corresponding inverted percentage of the span. Finally, these two values are added, giving the interpolated corrected value.

$$c_{interp.} = c_{a1} * \left(1 - \frac{t_a - t_1}{t_2 - t_1}\right) + c_{a2} * \left(1 - \frac{t_2 - t_a}{t_2 - t_1}\right)$$

$c_{interp.}$: concentration of analyte corrected by IS interpolation,
$c_{a1,\,a2}$: concentration of analyte corrected with IS 1 or 2,
t_a : retention time of analyte *a* [min],
$t_{1,\,2}$: retention time of IS 1 or 2 [min].

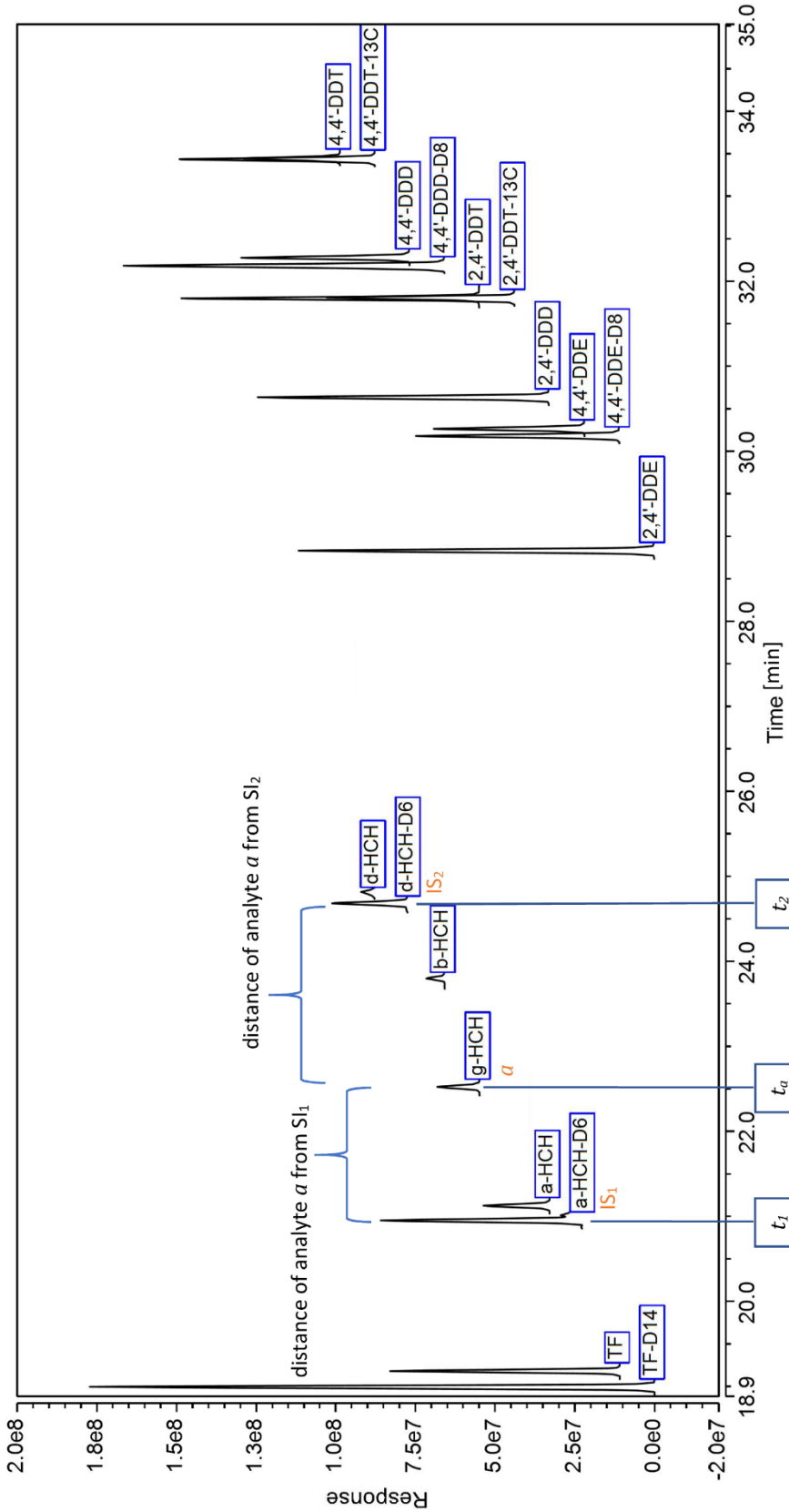


Figure S1 – Exemplary SIM chromatogram of a sample (2.1). Annotations visualize the principle of interpolated IS correction explained above (Table S3, page 4).

Table S4: Concentrations [µg·kg^{-1}] in **spiked soil samples** for recovery rate determination by **MISOLEX** method with **regular** internal standard correction. Target concentration was 50 µg·kg^{-1}. First and second digit in sample number denote soil number and iteration, respectively. TriF = Trifluralin, RSD = relative standard deviation.

Sample	TriF	HCH				DDE		DDD		DDT	
		α	γ	β	δ	2,4’	4,4’	2,4’	4,4’	2,4’	4,4’
1.1	46.82	44.35	92.27	40.70	52.02	60.16	42.10	82.09	44.10	45.80	34.21
1.2	43.86	39.76	70.36	35.81	43.27	52.17	40.97	68.87	42.29	43.59	32.88
1.3	52.14	44.98	96.10	44.21	49.24	60.27	46.38	85.89	47.98	50.24	37.47
1.4	53.15	49.62	92.86	46.51	61.96	63.13	49.83	85.96	51.34	52.47	37.95
1.5	50.58	46.53	65.67	41.83	57.20	65.71	45.07	79.24	46.62	50.56	37.25
Mean	49.31	45.05	83.45	41.81	52.74	60.29	44.87	80.41	46.46	48.53	35.95
RSD	5.2%	6.6%	12.9%	6.5%	2.0%	3.8%	1.6%	1.9%	1.8%	1.3%	1.5%
2.1	44.82	42.72	55.76	46.19	56.47	65.76	50.20	71.04	53.36	53.78	49.62
2.2	45.48	42.02	53.91	45.26	55.63	62.73	48.77	65.87	51.72	54.05	49.60
2.3	41.89	40.12	55.56	41.90	53.09	59.33	45.49	60.42	48.37	47.81	45.85
2.4	40.95	40.10	56.69	39.67	51.99	58.59	44.88	68.37	47.67	47.98	44.88
2.5	49.94	48.11	86.28	48.24	64.14	68.46	54.23	85.32	57.95	55.77	52.36
Mean	44.62	42.61	61.64	44.25	56.26	62.97	48.71	70.20	51.81	51.88	48.46
RSD	7.9%	8.0%	17.1%	9.7%	13.7%	8.4%	7.9%	8.8%	7.5%	7.6%	6.3%
3.1	57.29	42.97	72.63	47.28	61.43	66.44	54.71	82.10	56.97	55.71	48.65
3.2	56.10	43.47	69.00	48.18	62.39	65.20	53.61	86.31	58.15	55.68	48.66
3.3	59.69	48.94	95.08	54.12	61.62	60.94	54.48	83.10	59.63	55.36	48.47
3.4	52.98	45.29	77.08	46.11	61.28	66.92	52.70	84.81	57.34	54.07	47.19
3.5	52.98	49.51	76.68	47.30	64.30	63.42	54.74	83.66	58.52	55.64	49.09
Mean	55.81	46.04	78.09	48.60	62.20	64.59	54.05	84.00	58.12	55.29	48.41
RSD	7.9%	7.7%	22.4%	7.8%	8.5%	6.7%	7.8%	13.3%	8.0%	7.2%	6.3%
All soils											
Mean	49.91	44.57	74.39	44.89	57.07	62.61	49.21	78.20	52.13	51.90	44.28
RSD	11.5%	7.7%	20.6%	9.8%	10.8%	6.7%	9.8%	11.2%	11.0%	7.7%	14.5%

Table S5: Concentrations [µg·kg^{-1}] in **spiked soil samples** for recovery rate determination by modified **QuEChERS** method with **regular** internal standard correction. Targeted concentration was 50 µg·kg^{-1}. First and second digit in sample number denote soil number and iteration, respectively. TriF = Trifluralin, RSD = relative standard deviation.

Sample	TriF	HCH				DDE		DDD		DDT	
		α	γ	β	δ	2,4'	4,4'	2,4'	4,4'	2,4'	4,4'
1.1	41.48	45.22	54.88	51.15	58.65	89.41	52.82	63.52	45.36	49.34	51.59
1.2	39.52	44.21	45.55	46.59	60.78	83.27	49.64	58.10	45.03	47.50	48.61
1.3	39.96	45.43	47.55	50.69	57.43	81.26	49.56	60.65	43.28	45.89	47.28
1.4	42.45	47.65	50.91	49.29	64.70	84.65	53.45	62.34	47.54	49.74	52.05
1.5	39.97	44.96	48.36	49.85	59.64	84.47	50.12	60.28	44.07	46.57	47.51
Mean	40.68	45.49	49.45	49.51	60.24	84.61	51.12	60.98	45.05	47.81	49.41
RSD	2.0%	1.2%	7.1%	3.1%	3.6%	4.5%	4.9%	7.5%	4.9%	5.0%	6.4%
2.1	36.37	40.96	43.20	49.40	56.50	75.84	45.10	59.07	44.09	45.41	46.25
2.2	33.88	40.86	45.84	47.32	53.09	70.42	38.14	50.78	39.18	38.55	37.70
2.3	36.22	40.58	45.14	50.88	63.78	72.20	43.84	58.64	43.11	45.15	44.82
2.4	38.34	43.03	47.24	50.23	67.29	74.36	45.89	59.62	45.33	47.09	47.29
2.5	34.51	38.83	40.58	46.78	60.82	72.93	42.21	56.26	41.08	42.93	43.84
Mean	35.87	40.85	44.40	48.92	60.30	73.15	43.04	56.87	42.55	43.82	43.98
RSD	3.0%	2.8%	7.3%	3.6%	4.6%	3.5%	3.6%	3.4%	3.6%	3.5%	4.6%
3.1	40.20	42.20	51.61	50.59	70.37	79.64	47.70	61.41	46.96	50.37	50.93
3.2	39.88	41.17	47.25	53.52	67.99	73.48	47.64	63.31	47.79	51.39	51.47
3.3	39.27	41.17	55.03	50.13	71.42	72.84	46.92	58.35	47.22	49.51	49.22
3.4	38.14	41.23	46.71	50.72	66.64	71.76	42.32	52.19	42.25	45.14	43.73
3.5	39.25	40.84	47.91	49.29	65.70	71.77	45.34	56.10	45.00	47.93	47.44
Mean	39.35	41.32	49.70	50.85	68.42	73.90	45.98	58.27	45.85	48.87	48.56
RSD	4.9%	3.7%	5.8%	3.7%	9.4%	2.8%	7.1%	6.4%	5.7%	7.5%	8.5%
All soils											
Mean	38.63	42.56	47.85	49.76	62.99	77.22	46.71	58.71	44.48	46.83	47.31
RSD	6.3%	5.7%	8.2%	3.6%	8.5%	7.8%	8.8%	6.3%	5.5%	7.0%	8.0%

Table S6 – Concentrations [µg·kg^{-1}] in **spiked soil samples** for recovery rate determination by **MISOLEX** method with **interpolated** internal standard correction. As 2,4'-DDT and 4,4'-DDT were corrected with ^{13}C-labelled internal standards that elute exactly at the same time as their respective analyte, no interpolation was calculated for them. Their regularly corrected concentrations are shown here for comparison. TriF = Trifluralin, RSD = relative standard deviation.

Sample	TriF	HCH				DDE		DDD		*DDT*	
		α	γ	β	δ	2,4'	4,4'	2,4'	4,4'	*2,4'*	*4,4'*
1.1	47.05	41.08	46.73	70.88	47.26	49.90	43.56	30.99	46.83	*45.80*	*34.21*
1.2	42.77	37.19	39.85	50.04	41.15	50.37	42.10	27.74	43.26	*43.59*	*32.88*
1.3	51.42	41.70	49.09	75.30	44.96	53.08	46.75	28.76	51.60	*50.24*	*37.47*
1.4	54.81	43.81	56.27	57.11	54.68	59.94	50.17	32.51	54.90	*52.47*	*37.95*
1.5	49.82	41.24	41.36	49.72	50.73	55.74	46.28	58.47	50.25	*50.56*	*37.25*
Mean	49.18	41.00	46.66	60.61	47.76	53.81	45.77	35.69	49.37	*48.53*	*35.95*
RSD	5,4%	6,2%	6,8%	16,6%	2,6%	6,6%	1,6%	15,4%	1,5%	*1.3%*	*1.5%*
2.1	43.32	38.56	41.41	49.70	50.81	51.50	51.37	82.73	57.53	*53.78*	*49.62*
2.2	44.12	38.02	40.96	48.21	50.12	48.21	49.87	89.55	55.87	*54.05*	*49.60*
2.3	40.81	35.88	38.10	47.00	47.49	46.90	46.51	72.22	51.52	*47.81*	*45.85*
2.4	40.86	35.70	37.30	45.67	46.33	49.93	45.92	49.52	49.53	*47.98*	*44.88*
2.5	49.84	42.68	54.81	56.95	56.95	60.26	55.55	48.64	59.84	*55.77*	*52.36*
Mean	43.79	38.17	42.52	49.51	50.34	51.36	49.84	68.53	54.86	*51.88*	*48.46*
RSD	9,2%	5,8%	14,1%	19,6%	10,9%	7,7%	6,8%	36,0%	9,1%	*7.6%*	*6.3%*
3.1	56.65	40.57	45.47	58.96	59.55	62.62	55.96	47.20	58.34	*55.71*	*48.65*
3.2	54.88	40.95	42.21	61.43	60.27	64.66	54.94	36.74	59.17	*55.68*	*48.66*
3.3	58.88	45.52	50.58	84.04	57.41	55.50	55.90	33.78	60.74	*55.36*	*48.47*
3.4	51.38	42.72	47.77	58.04	59.32	61.17	53.97	46.11	58.99	*54.07*	*47.19*
3.5	52.94	46.48	45.23	62.73	61.71	66.13	56.08	36.38	59.64	*55.64*	*49.09*
Mean	54.95	43.25	46.25	65.04	59.65	62.02	55.37	40.04	59.38	*55.29*	*48.41*
RSD	8,4%	7,4%	16,7%	8,9%	8,2%	10,3%	7,9%	27,4%	7,8%	*7.2%*	*6.3%*
All soils											
Mean	49.30	40.81	45.14	58.39	52.58	55.73	50.33	48.09	54.54	*51.90*	*44.28*
SD	11.9%	8.0%	12.8%	19.1%	12.2%	11.3%	9.7%	40.9%	9.9%	*7.7%*	*14.5%*

Table S7 – Concentrations [µg·kg^{-1}] in **spiked soil samples** for recovery rate determination by modified **QuEChERS** method with **interpolated** internal standard correction. As 2,4'-DDT and 4,4'-DDT were corrected with ^{13}C-labelled internal standards that elute exactly at the same time as their respective analyte, no interpolation was calculated for them. Their regularly corrected concentrations are shown here for comparison. TriF = Trifluralin, RSD = relative standard deviation.

Sample	TriF	HCH				DDE		DDD		*DDT*	
		α	γ	β	δ	2,4'	4,4'	2,4'	4,4'	*2,4'*	*4,4'*
1.1	44.80	43.66	45.49	51.15	58.46	53.56	52.64	69.26	46.72	*49.34*	*51.59*
1.2	42.10	43.48	41.85	46.59	60.70	51.59	49.44	63.24	45.93	*47.50*	*48.61*
1.3	43.31	42.52	43.21	51.78	56.79	56.81	49.49	60.88	44.37	*45.89*	*47.28*
1.4	46.37	43.87	42.24	50.34	63.89	59.56	53.34	62.59	48.39	*49.74*	*52.05*
1.5	43.57	41.86	42.74	50.93	58.95	57.19	50.04	64.15	45.34	*46.57*	*47.51*
Mean	44.03	43.08	43.11	50.16	59.76	55.74	50.99	64.02	46.15	*47.81*	*49.41*
RSD	2.5%	1.8%	3.6%	3.1%	3.5%	3.8%	4.9%	8.7%	5.1%	*5.0%*	*6.4%*
2.1	39.72	38.44	39.79	50.47	55.89	60.03	45.17	54.27	45.05	*45.41*	*46.25*
2.2	36.93	37.77	38.93	48.34	52.44	54.70	38.19	52.52	40.31	*38.55*	*37.70*
2.3	39.30	37.69	39.36	51.97	63.03	56.08	43.87	53.17	43.75	*45.15*	*44.82*
2.4	42.20	39.61	39.20	51.31	66.44	59.68	45.93	55.23	46.06	*47.09*	*47.29*
2.5	37.45	36.82	39.37	47.79	60.21	54.43	42.26	54.58	42.11	*42.93*	*43.84*
Mean	39.12	38.07	39.33	49.98	59.60	56.98	43.08	53.95	43.46	*43.82*	*43.98*
RSD	3.7%	2.0%	3.3%	4.1%	4.5%	5.7%	3.6%	4.9%	3.3%	*3.5%*	*4.6%*
3.1	43.62	40.79	43.04	50.59	70.16	51.49	47.65	72.23	48.86	*50.37*	*50.93*
3.2	42.83	40.48	43.32	53.53	67.90	50.55	47.62	61.22	48.66	*51.39*	*51.47*
3.3	43.66	39.10	41.27	50.14	71.04	50.30	46.83	64.60	48.20	*49.51*	*49.22*
3.4	41.16	40.32	41.60	50.72	66.51	53.59	42.26	59.83	43.30	*45.14*	*43.73*
3.5	43.51	39.41	39.57	49.29	65.49	54.86	45.26	58.49	45.71	*47.93*	*47.44*
Mean	42.95	40.02	41.76	50.85	68.22	52.16	45.92	63.27	46.94	*48.87*	*48.56*
RSD	5.3%	2.7%	0.8%	3.7%	9.3%	4.7%	7.1%	2.0%	5.3%	*7.5%*	*8.5%*
All soils											
Mean	42.04	40.39	41.40	50.33	62.53	54.96	46.66	60.42	45.52	*46.83*	*47.31*
RSD	6.3%	5.7%	4.8%	3.5%	8.7%	5.9%	8.7%	9.7%	5.5%	*7.0%*	*8.0%*

Figure S2 – Recovery rates for all analytes separately for each spiked soil as mean with standard deviation (error bars), **regular** internal standard correction. Grey area depicts targeted recovery rate range. Small letters above error bars indicate significant difference between soils. SOC = soil organic carbon.

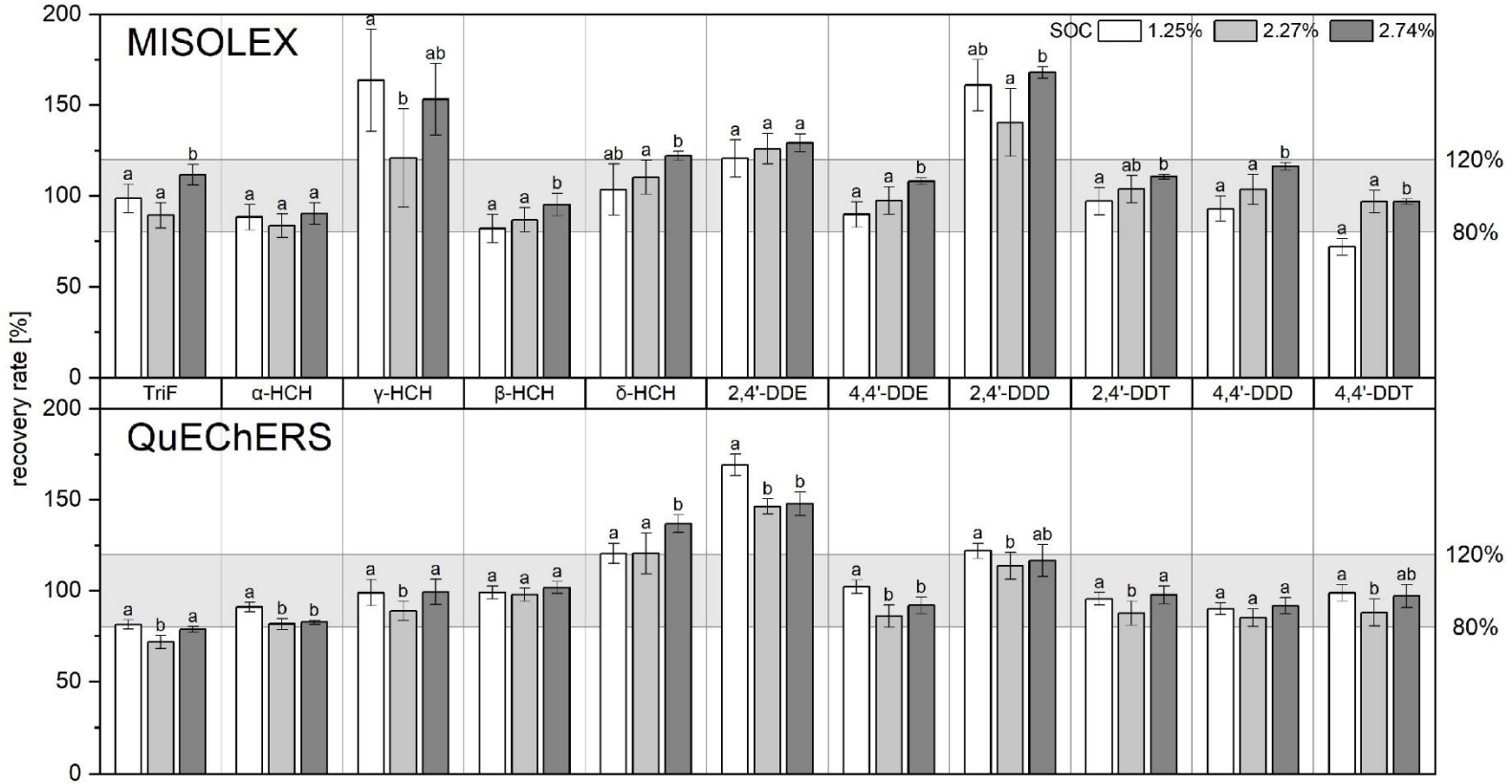


Figure S3 – Recovery rates for all analytes separately for each spiked soil as mean with standard deviation (error bars), **interpolated** internal standard correction. Grey area depicts targeted recovery rate range. As 2,4'-DDT and 4,4'-DDT were corrected with ^{13}C-labelled internal standards that elute exactly at the same time as their respective analyte, no interpolation was calculated for them. Their regularly corrected concentrations are shown here for comparison. Small letters above error bars indicate significant difference between soils. SOC = soil organic carbon.

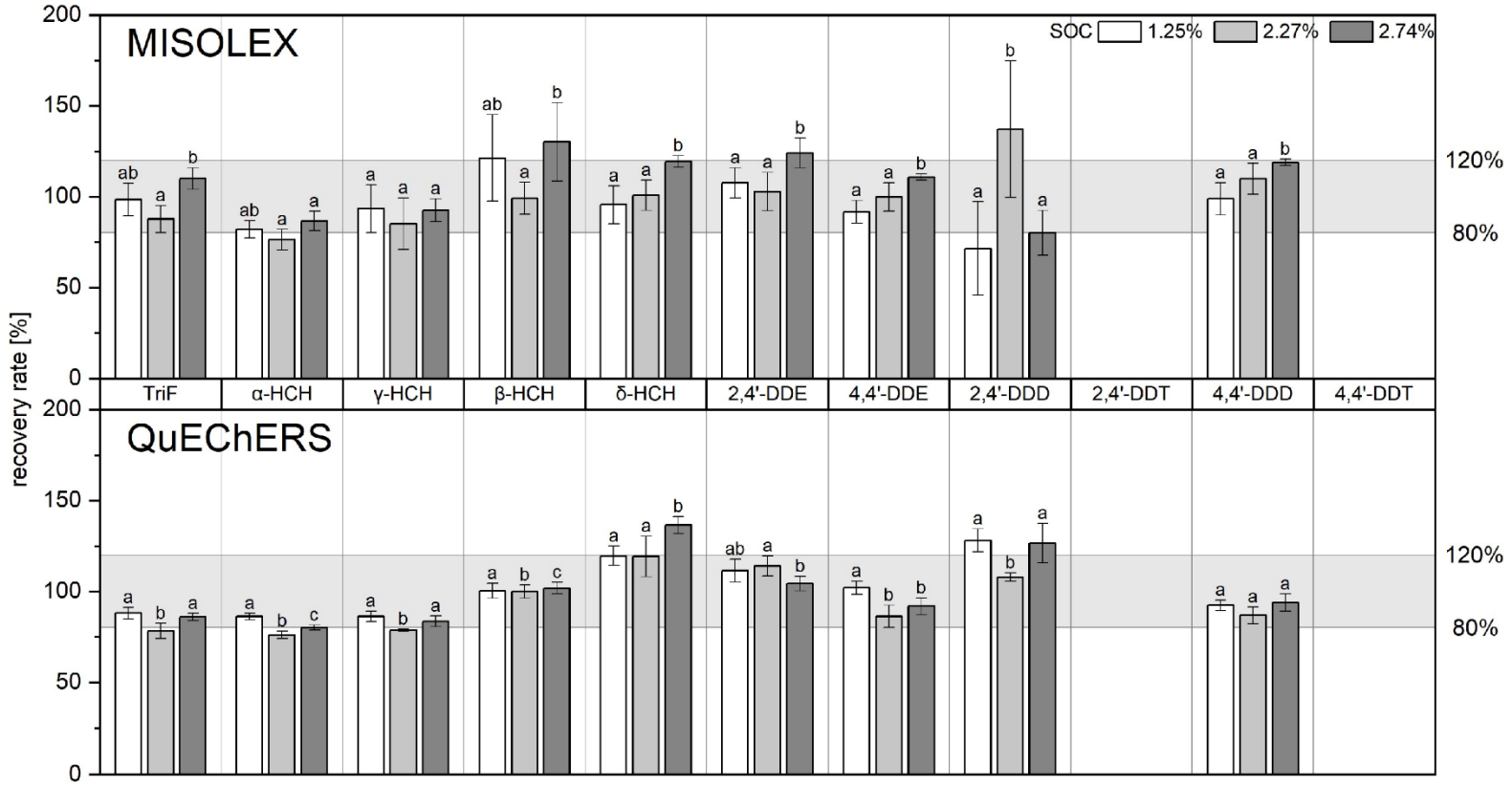


Table S8 – Concentrations [µg·kg^{-1}] in **environmental samples** A, B, and, C by **MISOLEX** method, obtained through **regular** internal standard correction. Digit in sample name denotes iteration. TriF = Trifluralin, n.d. = not detected, RSD = relative standard deviation.

Sample	TriF	HCH				DDE		DDD		DDT	
		α	γ	β	δ	2,4’	4,4’	2,4’	4,4’	2,4’	4,4’
A.1	n.d.	78.20	206.42	818.30	189.60	9.47	32.74	8.86	10.97	25.85	90.83
A.2	n.d.	404.58	119.67	628.43	152.09	7.62	25.95	6.22	7.81	18.36	60.97
A.3	n.d.	365.89	109.45	552.88	158.81	7.14	23.74	5.86	7.07	16.43	56.86
A.4	n.d.	158.71	171.88	714.66	167.87	10.31	32.61	8.21	10.53	23.93	82.31
A.5	n.d.	531.91	121.52	612.81	173.92	6.03	20.12	4.91	6.45	18.00	59.36
Mean	-	307,86	145,79	665,42	168,46	8,11	27,03	6,81	8,57	20,51	70,07
RSD	-	60,3%	28,6%	15,5%	8,6%	21,5%	20,6%	24,4%	24,0%	20,1%	22,0%
B.1	n.d.	107.72	11.02	115.04	21.58	1.13	3.21	0.85	0.57	0.97	2.30
B.2	n.d.	114.95	11.99	104.25	23.85	0.80	2.81	0.95	0.56	0.92	2.44
B.3	n.d.	113.98	19.12	111.37	49.18	0.71	2.54	0.56	0.40	0.78	2.13
B.4	n.d.	108.48	16.89	96.14	51.61	0.51	2.01	0.42	0.33	0.82	2.41
B.5	n.d.	114.41	12.62	107.82	19.94	0.64	2.59	0.46	0.37	0.77	2.23
Mean	-	111,91	14,33	106,93	33,23	0,76	2,63	0,65	0,44	0,85	2,30
RSD	-	3,1%	24,4%	6,8%	47,4%	30,9%	16,6%	36,8%	25,1%	10,5%	5,6%
C.1	n.d.	596.79	90.57	554.84	166.17	253.03	188.96	66.36	83.38	141.25	669.99
C.2	n.d.	592.36	126.06	623.29	299.08	205.57	162.46	69.44	104.15	149.35	848.98
C.3	n.d.	434.03	58.24	446.08	142.03	205.78	161.78	65.62	100.49	137.66	814.72
C.4	n.d.	492.47	90.49	596.17	225.15	294.72	207.04	76.82	97.07	168.15	796.12
C.5	n.d.	467.96	84.76	501.13	179.03	213.91	178.98	89.68	159.26	196.35	752.23
Mean	-	516,72	90,02	544,30	202,29	234,60	179,84	73,58	108,87	158,55	776,41
RSD	-	14,3%	26,8%	13,2%	30,6%	16,6%	10,6%	13,6%	26,9%	15,3%	8,9%

Table S9 – Concentrations [µg·kg^{-1}] in **environmental samples** A, B, and, C by modified **QuEChERS** method with **regular** internal standard correction. Digit in sample name denotes iteration. TriF = Trifluralin, n.d. = not detected, RSD = relative standard deviation.

Sample	TriF	HCH				DDE		DDD		DDT	
		α	γ	β	δ	2,4’	4,4’	2,4’	4,4’	2,4’	4,4’
A.1	n.d.	301,79	232,54	1006,89	258,92	7,89	27,64	5,99	8,19	20,09	64,57
A.2	n.d.	511,41	204,65	922,21	255,51	8,33	29,32	6,83	9,35	22,95	72,36
A.3	n.d.	565,00	200,38	921,48	246,76	7,65	27,89	6,45	9,02	21,54	70,19
A.4	n.d.	586,20	277,73	868,29	255,43	6,30	23,00	5,04	7,38	20,88	71,34
A.5	n.d.	661,55	256,71	931,40	264,70	6,10	23,54	5,15	7,79	21,62	73,95
Mean	-	525,19	234,40	930,05	256,27	7,25	26,28	5,89	8,35	21,42	70,48
RSD	-	25,9%	14,2%	5,3%	2,5%	13,7%	10,8%	13,4%	9,9%	4,9%	5,1%
B.1	n.d.	137,28	14,67	118,83	17,83	1,25	3,86	0,83	0,59	1,06	2,66
B.2	n.d.	128,10	17,50	118,84	18,35	0,75	3,02	0,44	0,39	0,78	2,20
B.3	n.d.	130,15	13,50	122,48	18,94	0,69	2,98	0,52	0,48	0,79	2,30
B.4	n.d.	130,97	16,56	124,97	19,02	0,71	3,05	0,42	0,40	0,81	2,34
B.5	n.d.	131,78	14,61	131,57	18,40	0,67	3,15	0,46	0,47	0,70	2,30
Mean	-	131,66	15,37	123,34	18,51	0,82	3,21	0,53	0,47	0,83	2,36
RSD	-	2,6%	10,6%	4,3%	2,6%	29,8%	11,4%	31,9%	17,6%	16,6%	7,4%
C.1	n.d.	655,65	147,09	835,21	271,31	181,73	152,94	53,33	70,70	142,55	557,20
C.2	n.d.	633,80	127,94	918,64	268,75	179,36	152,83	52,84	72,70	139,05	566,70
C.3	n.d.	712,08	147,26	780,85	274,55	165,09	139,98	47,74	65,76	126,45	507,51
C.4	n.d.	794,04	166,31	899,97	292,21	94,18	102,76	79,70	67,81	76,61	101,84
C.5	n.d.	686,15	147,26	761,29	278,36	189,97	160,38	57,48	77,67	149,80	593,38
Mean	-	696,34	147,17	839,19	277,04	162,07	141,78	58,22	70,93	126,89	465,33
RSD	-	8,9%	9,2%	8,3%	3,3%	24,1%	16,2%	21,5%	6,5%	23,1%	44,2%

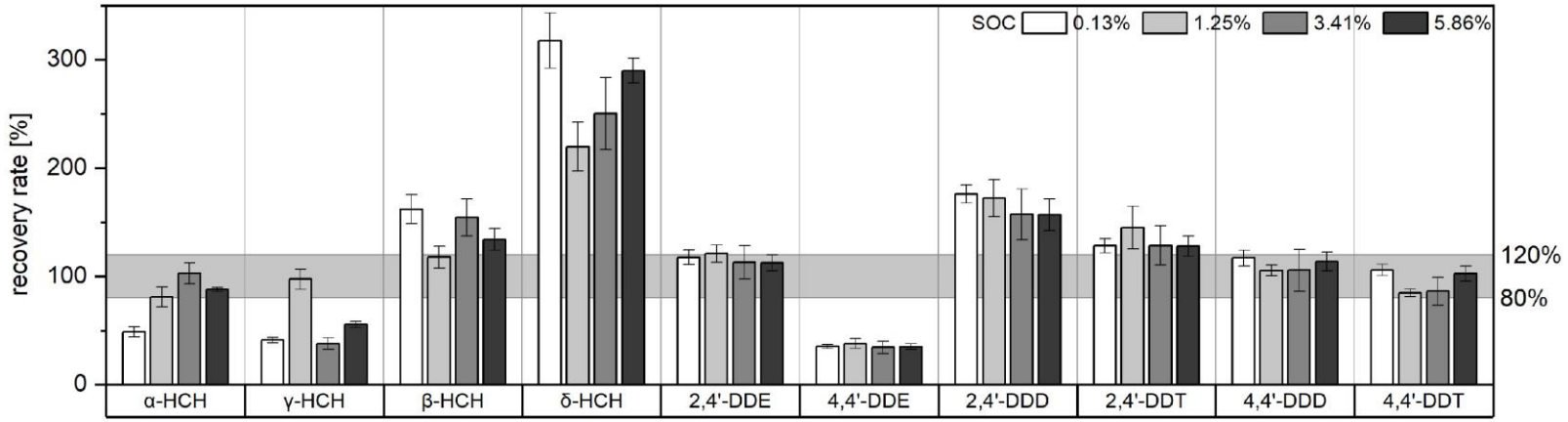
Table S10 – Concentrations [µg·kg^{-1}] in **environmental samples** A, B, and, C by **MISOLEX** method with **interpolated** internal standard correction. Digit in sample name denotes iteration. As 2,4'-DDT and 4,4'-DDT were corrected with ^{13}C-labelled internal standards that elute exactly at the same time as their respective analyte, no interpolation was calculated for them. Their regularly corrected concentrations are shown here for comparison. TriF = Trifluralin, n.d. = not detected, RSD = relative standard deviation.

Sample	TriF	HCH				DDE		DDD		*DDT*	
		α	γ	β	δ	2,4'	4,4'	2,4'	4,4'	*2,4'*	*4,4'*
A.1	n.d.	128,06	118,85	1018,05	184,52	5,84	33,40	4,87	11,50	*25.85*	*90.83*
A.2	n.d.	422,50	100,52	653,00	151,36	4,54	26,45	4,18	8,28	*18.36*	*60.97*
A.3	n.d.	387,93	88,54	581,38	157,82	4,76	24,10	3,40	7,35	*16.43*	*56.86*
A.4	n.d.	198,73	110,28	819,86	163,92	5,56	28,91	4,33	9,68	*23.93*	*82.31*
A.5	n.d.	553,63	99,57	646,73	172,92	3,80	20,61	3,29	6,78	*18.00*	*59.36*
Mean	-	338,17	103,55	743,80	166,11	4,90	26,69	4,01	8,72	*20,51*	*70,07*
RSD	-	51,1%	11,1%	23,8%	7,8%	16,7%	18,1%	16,6%	21,9%	*20,1%*	*22,0%*
B.1	n.d.	104,86	9,32	119,74	21,47	0,73	3,28	0,48	0,60	*0.97*	*2.30*
B.2	n.d.	111,56	9,94	109,13	23,72	0,49	2,88	0,43	0,59	*0.92*	*2.44*
B.3	n.d.	111,05	16,26	115,70	48,95	0,44	2,60	0,33	0,42	*0.78*	*2.13*
B.4	n.d.	106,47	14,55	100,20	51,71	0,33	2,38	0,29	0,41	*0.82*	*2.41*
B.5	n.d.	108,83	9,05	118,94	19,70	0,40	2,64	0,28	0,40	*0.77*	*2.23*
Mean	-	108,56	11,82	112,74	33,11	0,48	2,75	0,36	0,48	*0,85*	*2,30*
RSD	-	2,7%	28,3%	7,2%	47,8%	32,2%	12,4%	24,7%	21,2%	*10,5%*	*5,6%*
C.1	n.d.	552,10	65,57	617,76	164,28	150,52	191,91	43,59	84,49	*141.25*	*669.99*
C.2	n.d.	556,65	97,37	674,08	296,62	141,96	165,22	37,44	104,13	*149.35*	*848.98*
C.3	n.d.	417,73	47,93	469,08	141,23	136,36	164,53	36,57	100,82	*137.66*	*814.72*
C.4	n.d.	472,87	74,61	627,82	223,90	182,72	210,07	46,31	97,65	*168.15*	*796.12*
C.5	n.d.	446,95	67,67	533,26	177,81	141,03	181,99	48,39	159,02	*196.35*	*752.23*
Mean	-	489,26	70,63	584,40	200,77	150,52	182,75	42,46	109,22	*158,55*	*776,41*
RSD	-	12,8%	25,3%	14,0%	30,6%	12,4%	10,5%	12,4%	26,4%	*15,3%*	*8,9%*

Table S11 – Concentrations [µg·kg^{-1}] in **environmental samples** A, B, and, C by modified **QuEChERS** method with **interpolated** internal standard correction. Digit in sample name denotes iteration. As 2,4'-DDT and 4,4'-DDT were corrected with ^{13}C-labelled internal standards that elute exactly at the same time as their respective analyte, no interpolation was calculated for them. Their regularly corrected concentrations are shown here for comparison. TriF = Trifluralin, n.d. = not detected, RSD = relative standard deviation.

Sample	TriF	HCH				DDE		DDD		*DDT*	
		α	γ	β	δ	2,4'	4,4'	2,4'	4,4'	*2,4'*	*4,4'*
A.1	n.d.	834,35	192,16	748,24	247,26	5,69	28,01	4,53	8,37	*20,09*	*64,57*
A.2	n.d.	698,00	165,77	704,59	243,87	6,35	29,77	4,67	9,47	*22,95*	*72,36*
A.3	n.d.	678,97	164,73	705,71	236,04	5,67	28,28	4,54	9,20	*21,54*	*70,19*
A.4	n.d.	757,78	167,41	667,82	214,32	4,58	23,46	3,67	7,60	*20,88*	*71,34*
A.5	n.d.	725,60	172,92	706,25	223,20	4,28	24,02	3,67	7,99	*21,62*	*73,95*
Mean	-	738,94	172,60	706,52	232,94	5,31	26,71	4,22	8,53	*21,42*	*70,48*
RSD	-	8,3%	6,6%	4,0%	6,0%	16,2%	10,5%	11,9%	9,3%	*4,9%*	*5,1%*
B.1	n.d.	125,01	12,04	115,23	17,67	0,83	3,86	0,67	0,62	*1,06*	*2,66*
B.2	n.d.	116,15	13,46	115,25	18,13	0,52	3,01	0,36	0,40	*0,78*	*2,20*
B.3	n.d.	120,17	11,91	118,65	18,81	0,48	2,98	0,40	0,49	*0,79*	*2,30*
B.4	n.d.	118,58	12,72	121,02	18,79	0,50	3,05	0,32	0,41	*0,81*	*2,34*
B.5	n.d.	95,73	10,11	99,32	14,19	0,52	3,14	0,34	0,48	*0,70*	*2,30*
Mean	-	115,13	12,05	113,89	17,52	0,57	3,21	0,42	0,48	*0,83*	*2,36*
RSD	-	9,8%	10,3%	7,5%	11,0%	25,5%	11,4%	34,5%	18,1%	*16,6%*	*7,4%*
C.1	n.d.	428,33	96,13	645,77	228,23	141,49	170,45	38,46	72,86	*142,55*	*557,20*
C.2	n.d.	426,03	94,56	698,65	227,19	144,88	170,25	36,95	74,68	*139,05*	*566,70*
C.3	n.d.	450,18	90,50	611,35	230,21	136,64	154,02	32,93	67,15	*126,45*	*507,51*
C.4	n.d.	477,66	99,77	686,80	244,60	152,85	179,18	38,71	79,57	*76,61*	*101,84*
C.5	n.d.	443,94	99,34	597,70	234,46	150,96	174,91	41,23	78,38	*149,80*	*593,38*
Mean	-	445,23	96,06	648,05	232,94	145,36	169,76	37,66	74,53	*126,89*	*465,33*
RSD	-	4,7%	4,0%	6,9%	3,0%	4,6%	5,6%	8,1%	6,6%	*23,1%*	*44,2%*

Figure S4 – Recovery rates for all analytes but TriF as mean with standard deviation (error bars) and **regular** internal standard correction from **preliminary tests** covering a broader soil organic carbon (SOC) range. Samples were spiked as well but aged for over a year at room temperature. Losses may have occurred. Further differences to the experiments in the present study include: four iterations instead of five, 100 µm PDMS SPME fiber instead of 65 µm PDMS/DVB, only one IS for all four HCH isomers (α-HCH-D_6). The extreme overestimation of δ-HCH (> 200%) is probably due to the use of only one IS for all HCH isomers, demonstrating the need for a further IS or an approach like IS interpolation.



3 Artikel 2: Dissens im Sediment? Seesedimente als Archive von Auswirkungen anthropogener Aktivitäten mit kurzer und langer Reichweite auf Nordostdeutschland

Erschienen auf Englisch in *Environmental Science and Pollution Research* 2023 als:
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Anhang zu Artikel 2 ab S. 92.

3.1 Haupttextteil von Artikel 2

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RESEARCH ARTICLE

Dissent in the sediment? Lake sediments as archives of short- and long-range impact of anthropogenic activities in northeastern Germany

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Abstract
The suitability of lake sediment cores to reconstruct past inputs, regional pollution, and usage patterns of pesticides has been shown previously. Until now, no such data exist for lakes in eastern Germany. Therefore, 10 sediment cores (length 1 m) of 10 lakes in eastern Germany, the territory of the former German Democratic Republic (GDR), were collected and cut into 5–10-mm layers. In each layer, concentrations of trace elements (TEs) As, Cd, Cr, Cu, Ni, Pb, S, and Zn, as well as of organochlorine pesticides (OCPs), i.e., dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH), were analyzed. A miniaturized solid–liquid extraction technique in conjunction with headspace solid-phase microextraction (HS-SPME) and gas chromatography–mass spectrometry (GC–MS) was used for the latter. The progression of TE concentrations over time is uniform. It follows a trans-regional pattern and is indicative of activity and policy making in West Germany before 1990 instead of those in the GDR. Of OCPs, only transformation products of DDT were found. Congener ratios indicate a mainly aerial input. In the lakes' profiles, several regional features and responses to national policies and measures are visible. Dichlorodiphenyldichloroethane (DDD) concentrations reflect the history of DDT use in the GDR. Lake sediments proved to be suitable to archive short- and long-range impacts of anthropogenic activity. Our data can be used to complement and validate other forms of environmental pollution long-term monitoring and to check for the efficiency of pollution countermeasures in the past.

Keywords Organochlorine pesticide (OCP) · Dichlorodiphenyltrichloroethane (DDT) · Sediment core · Chronology · Trace elements · Mecklenburg-Brandenburg lake district · Landscape development · Transformation products

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Background

Over the last two centuries, the territory of eastern Germany was subject to a large number of fundamental changes in economic and institutional conditions, e.g., the Industrial Revolution (starting approx. 1815–1835), two World Wars (1914–1918 and 1939–1945), an economic depression (1929–1936), the separation from West Germany (1949), the rise and fall of the German Democratic Republic (GDR; 1949–1990) and the German reunification (1990) along with the integration into the European Union (EU).

These developments affected the population, their activity, and their growth (population size). Humans have always perhaps more than any other species shaped their surroundings to fit their needs, i.e., to assure their livelihood. Apart from urbanization and sealing of soils, the most severe effects on the landscape were due to agricultural activities that were later complemented by industrial activities and led to a general deterioration of the environment (Goudie 2019; Scheffer et al. 2019).

The first large-scale deterioration through agricultural intensification occurred in medieval times, when large areas of wood were systematically deforested (Sommer et al. 2008). After World War 2, intensification was accomplished through industrialization of agriculture. The 1950s were the decade of collectivization of agricultural property in the GDR, so that in 1960, about 85% of farmland was either collectivized or state owned. In the 1970s and 1980s, agriculture developed towards an industrial organized production system. The creation of very large field units (60–100 ha) was accompanied by habitat loss through removal of field boundaries and terraces (Sommer et al. 2008). Additionally, more powerful farm machinery enabled deeper soil tillage practices. All this led to oversized irrigation projects, intensive soil exploitation, and the large-scale use of pesticides and fertilizers among others (Bauerkämper 1993; Radkau 2012). In the late 1970s, a general discourse about ramifications of environmental exploitation started in West Germany and led to countermeasures there (Bauerkämper 2004). In the GDR, however, despite results of several scientific studies, only limited measures for the protection of the environment were taken (Reichelt 1992). It was only after Germany's reunification that the real extent of environmental damage became clear to the public and only then serious countermeasures were taken (Welford 1991).

In terms of industrial development, the highest priority for the economic lead of the GDR's regime was to the fulfillment of annual economic plans. Establishing records of production at almost any cost was seen as a guarantee for the regime to stay in power (Buck 2000). The environmental effects of this strategy became obvious at the end of the GDR. It had been leading the ranks of countries polluting the air with SO_2 and dust emissions for several years, supplemented with high emissions of NO_x and hydrocarbons (Buck 1996). Most of these remained inside of the territory and were deposited back to terrestrial and aquatic surfaces in the vicinity of the sources, of which the energy-producing sector was the main emitter. The most affected districts were in the center or south of the GDR, where most of the industry was situated. A significant proportion was exported to neighboring countries downwind (15% in 1988; Buck 1996). Apart from detrimental effects on the health of the population (e.g., respiratory diseases), effects on the environment were enormous. SO_2 and NO_x emissions led to acid rain and acidification of soils and vegetation. The ensuing forest dieback ("Waldsterben") diminished and deforested entire forest districts (Buck and Spindler 1982). Depositions of dust contaminated the soil with heavy metals. Regulatory limits in soils surrounding smelters and accumulator factories were continuously and considerably exceeded (AdW 1990).

The state of the water compartment was similarly disastrous. In particular, the combination of naturally low precipitation rates, very high water consumption, and usage (up to 4 times as much as neighboring countries; Melzer 1985) combined with insufficient to nonexistent wastewater treatment had worsened the situation in aquatic systems. In 1989, almost 50% of all categorized waterways in the GDR were biologically desolated or dead due to pollution. Almost a quarter of all standing waters were unsuited for drinking water generation, and in 54% pollution rendered it unprofitable. One-third of all lakes were incapable of self-cleaning, and this ability was hampered in another third. Only 1% of lakes were biologically intact (DBT 1994).

Understanding the environmental impacts of such agricultural practices and policy making is important. It can benefit the prediction of developments associated with similar practices nowadays. Environmental archives like peat cores, growth rings in trees, ice cores, or lacustrine sediments are used to reconstruct past developments (Waters and Turner 2022). They help understand pre-disturbed conditions and provide long-term monitoring data (Blais et al. 2015), which is especially valuable where other data is scarce or nonexistent (Bálint et al. 2018). An often used proxy indicator for human impacts in paleolimnology studies that utilize these archives is the concentration profile of trace elements (TEs) like As, Cd, Cr, Cu, Ni, Pb, S, and Zn (Krachler et al. 2003; Aliff et al. 2020; Shotyk 2022). They are generally harmful in higher concentrations to plants or animals including human beings (Tóth et al. 2016). Depending on the respective geogenic background, TEs occur naturally in soils and water. Through human (industrial) activity, they can be mobilized, leached and reallocated, and often accumulate

to concentrations that pose a threat to plant and animal life (Alloway 2013). Human activities include mining, refining, combustion of fossil fuel, and metallurgy, and they share the atmosphere among others as a common path of emission (Csavina et al. 2011). When emitted into the air, they are mostly adsorbed to particles and can thus be subject to dry and wet deposition following atmospheric transport over short and long distances (Johansson et al. 2001; Shevchenko et al. 2003; Marina-Montes et al. 2020). Telmer et al. (2004) reported that dry deposition contributes significantly within shorter distances of ca. 15 km from an anthropogenic source such as a smelter, whereas wet deposition is the dominant process controlling the deposition of TEs beyond 15 km of the source. Depending on weather, ca. 50% of all emissions are available for long-range atmospheric transport (LRAT) of hundreds to thousands of kilometers (ca. 5.000 km under average weather conditions).

Pesticide records in biological archives can serve as another proxy indicator for human impact. Such records can result from intensification in agricultural activity or—close to production sites—of industrial activity. In the past, organochlorine pesticides (OCPs) have been used intensively, beginning with World War 2. Two very well-known representatives, DDT (dichlorodiphenyltrichloroethane) and lindane (hexachlorocyclohexane (HCH)) were produced and used widely in the 1940s to 1980s (AMAP 1998; van den Berg et al. 2017). Because of their toxicity to non-target organisms and high persistence in the environment, their production and use were restricted and banned following the Stockholm Convention 2001 (UN 2001). Today, they are still found in multiple media all over the world (Li et al. 2014; Camenzuli et al. 2016; Tepanosyan et al. 2020; Olisah et al. 2020). As lipophilic and semi-volatile compounds, they tend to adsorb to organic matter, but can be volatilized and thus be transported and deposited in areas far away from their points of production or application via LRAT. Therefore, they tend to accumulate in colder areas, e.g., Arctic/Antarctic or in high altitudes, where they reach concentrations comparable to source regions (Wania and Mackay 1993; Lee et al. 1998).

The northern part of eastern Germany features a high density of water bodies in a landscape which has been subjected to over 80 years of intensive agriculture (Bauerkämper 2004; Sommer et al. 2008), providing a perfect opportunity for the examination of lacustrine sediment records for TEs and OCPs throughout the history of the GDR and beyond.

While such data was used to reconstruct pollution history in other industrialized countries, e.g., in Russia (Adams et al. 2018), Canada (Kurek et al. 2019), and Switzerland (Chiaia-Hernández et al. 2020), no such data exist for Germany. Therefore, the aim of this work is to find evidence of agricultural and industrial activity of East Germany in dated lacustrine sediment profiles. Ten lakes in northeastern Germany were sampled and dated, and their contents of As, Cd, Cr, Cu, Ni, Pb, S, Zn, DDT and its transformation products (TPs), and HCH determined. The results were intended to shed light on anthropogenic impacts on the environment throughout the last 100 years. Data was evaluated with regard to finding indicators for system changes and possibly cultural and socioeconomic transitions.

Methods

Study sites

Sediments in 10 freshwater lakes in the north of the former GDR's territory (Fig. 1) were sampled.

All lakes shared common characteristics. They were alkaline with a pH range of 7.5–9, their conductivity varied from 250 to 800 $\mu S \cdot cm^{-1}$, and they were formed during the last glacial period. Only Lake Arend (AR) is different as the present lake was formed more recently in a sinkhole after suberosion of a salt dome in the years 822 and 1685 (Halbfass 1896). A summary of the lakes' characteristics is displayed in Table 1.

Sediment core collection and sample preparation

Sediment cores were collected with a gravity corer (90-mm diameter; UWITEC, Mondsee, Austria) at the deepest points of the lakes, where sediment accumulation is strongest (Blais and Kalff 1995; Table 1). The core length of 1 m was deemed enough to cover a time span of at least 100 years starting from the year of sampling, i.e., the year 1915, which was on average located between 210-mm and 510-mm sediment depth, depending on the lake. Coring was performed in August 2015 (all but one lake) and December 2016 (Lake Stechlin, ST). Cores were transported to the lakeshore, and were immediately subsampled by slicing with a designated core slicer (UWITEC). Sediment slices were 5 mm (Lakes Feldberger Haussee, FH, and Breiter Luzin, BL), or 10 mm in thickness (all other lakes) to account for different sedimentation rates, which depend on lake trophy and biochemical processes (Ahn 2018). Samples were transported to the laboratory at 4 °C, weighed, and immediately frozen at – 20 °C until further processing.

Loss on ignition

Sediment weight loss on ignition (LOI) was analyzed according to the method of Nelson and Sommers (1996) described in Bensharada et al. (2022). Crucibles were weighed without sample (WC), and samples were dried in crucibles overnight at 105 °C. After cooling, crucibles with dry samples were re-weighed (WS). For

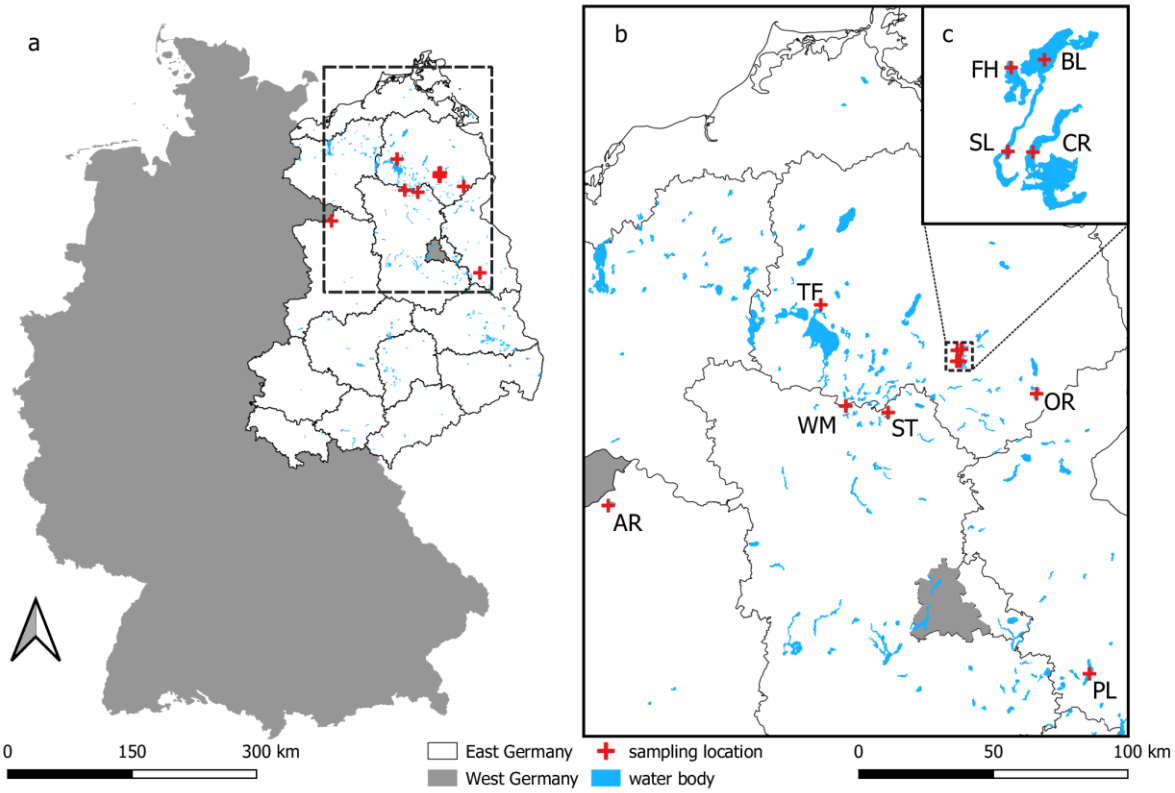

Fig. 1 Map of today's Germany (**a**) divided into West Germany (gray) and East Germany (white) with district borders of the GDR. Blue areas indicate water bodies. Red crosses show sampling locations in the lakes. Section **b** shows a closer view of the sampling locations. Section **c** shows a close-up of the four interconnected lakes FH, BL, SL, and CR. This figure was created with QGIS Desktop 3.16.16 (QGIS Development Team 2022) using open GIS data "vg-hist-001" of the German Federal Agency for Cartography and Geodesy (BKG 2020) and "Waterbodies" of the German Federal Institute of Hydrology (BfG 2021)

determination of the organic matter content, samples were combusted in an electric muffle furnace (SNOL 8,2/1100, Utena, Lithuania) at 500 °C for 4 h. After cooling in a desiccator, the samples were reweighed (WA). LOI was calculated as $\frac{WS-WA}{WS-WC} \times 100$.

Radioisotope dating and cross-correlation

Cores from Lakes BL, Schmaler Luzin (SL), Carwitzer (CR), Tiefwaren (TF), Oberucker (OR), Scharmützel (PL), ST, and Wumm (WM) were dated with ^{210}Pb and ^{137}Cs radioisotopes. Sediment horizons were freeze-dried before radioisotope dating. Dating was performed by direct gamma assay of the isotopes of 1 g of freeze-dried samples at the Department of Geosciences and Natural Resource Management of the University of Copenhagen. A constant rate of supply (CRS) dating model was applied to construct ^{210}Pb chronologies (Appleby and Oldfield 1978). These models were independently verified with ^{137}Cs.

Between the cores from lakes BL and FH, the concentrations of several elements were highly correlated (Online Resource: Fig. S1). These correlations were used to align the two cores, and the age model of BL was applied to establish the FH chronology.

For lake AR, the LOI values were aligned with the organic matter (OM) content of another core for which an age model was already published (Rothe et al. 2015). Both of these cores were taken close to the deepest point of lake AR. The chronology of the AR core was established based on this alignment (Online Resource: Fig. S2).

In lakes BL and TF, the initial age model suggested the presence of peaks of DDT derivatives in the nineteenth century. This is inconsistent with loads observed in all other lakes, and with the onset of DDT application in the twentieth century. In addition, lake TF received a hypolimnic treatment with aluminum between 2001 and 2005 as a restoration measure from eutrophic to mesotrophic states (Wauer et al. 2009; Rösel et al. 2012). The original age model would place

Table 1 List of sampled lakes and their characteristics (UBA 2004), sorted into the former GDR districts they belonged to. Coordinates are given as string expressions and show the sampling location within a lake. Proportions of catchment composition were determined by counting pixels per respective area in catchment maps provided by Geoportal.de the Open Data map service of the German Federal Agency for Cartography and Geodesy (BKG) on 13 May 2019. Meadows and fields were combined to agricultural area, as it was not possible to discern a difference between them with sufficient certainty in the map data. Waterbodies were excluded from the calculations

Lake	Abbrev	Latitude	Longitude	Surface area (km^2)	Maximum depth (m)	Catchment area (km^2)	Catchment composition		
							Forest	Agriculture	Settlement
Neubrandenburg district									
Feldberger Haussee	FH	+53.351516	+013.439390	1.31	12.5	5.3	59%	11%	31%
Breiter Luzin	BL	+53.354081	+013.463740	3.45	58.3	12	40%	58%	2%
Schmaler Luzin	SL	+53.315475	+013.433281	1.45	33.5	29.5	32%	61%	7%
Carwitzersee	CR	+53.314518	+013.451346	7.22	42.2	53.6	36%	59%	4%
Tiefwarensee	TF	+53.529629	+012.690718	1.41	23.6	21.9	28%	41%	31%
Oberückersee	OR	+53.189547	+013.864672	5.89	24.5	23	37%	53%	10%
Frankfurt (Oder) district									
Scharmützelsee	PL	+52.242076	+014.048144	12.1	29	112	56%	35%	10%
Magdeburg district									
Arendsee	AR	+52.888519	+011.460285	5.14	48.7	29.8	37%	56%	8%
Potsdam district									
Stechlin	ST	+53.157715	+013.034102	4.25	68	12.4	99%	0%	1%
Wummsee	WM	+53.187020	+012.800844	1.48	36	14	92%	7%	1%

the Al peak of the treatment in the 1970s. Fallout peaks of ^{137}Cs in 1986 (Chernobyl disaster) and 1962/1963 (peak of nuclear bomb tests in the high atmosphere) were re-evaluated, and adjusted the age model after considering these inconsistencies (Online Resource: Fig. S3).

Microwave-assisted aqua-regia extraction

Acids used for microwave-assisted aqua-regia extraction (MAE-AR) were of analytical-reagent grade. Nitric acid (HNO_3, 69% (w/v)) and hydrochloric acid (HCl, 35% (w/v)) were purchased from Merck KGaA (Darmstadt, Germany) and Carl Roth GmbH & Co. KG (Karlsruhe, Germany), respectively. Ultra-pure water (mQ) was obtained through filtering of deionized water with Milli-Q A10 water purification system (Merck KGaA) and was used for all experiments.

A StarT-1500 microwave (MLS GmbH, Leutkirch, Germany) was used to perform MAE-AR, which holds up to 10 polytetrafluorethylene (PTFE) digestion vessels with a volume of 100 mL each. A modified US EPA method (3051A (SW-846); US EPA 2007) as described by Öztan and Düring (2012) was applied. In brief, 0.3 g of freeze-dried sediment sample was weighed directly into the PTFE vessels, 6 mL HCl (35%) and 2 mL HNO_3 (69%) were added, and the microwave program as described in the Online Resource (Table S1) was run. Following extraction and cooling, extracts were transferred to 50-mL calibrated polypropylene flasks, pretreated with HNO_3. Extracts were made up to volume with deionized water, filtered (185 mm; Macherey–Nagel MN 280 1/4), and stored in polyethylene bottles at 4 °C until analysis. Blanks were subjected to the same extraction procedure as samples were. To avoid cross contamination of PTFE vessels with TEs from previous extractions, vessels were cleansed in between each sample extraction using 10 mL HNO_3 (69%) and the same MAE-AR program as used for samples.

Inductively coupled plasma–optical emission spectrometry analysis

Concentrations of elements in sediments were measured using an inductively coupled plasma–optical emission spectrometer (ICP–OES; Agilent 720ES, Darmstadt, Germany) with axial torch and echelle optic configuration, charge couple device (CCD) detection system, and full wavelength coverage from 167 to 785 nm. Operating parameters were as follows: Incident power was 1.20 kW, and plasma gas and auxiliary gas flow were 16.5 and 1.5 $L{\cdot}min^{-1}$, respectively. Sample uptake and test time per repetition were 45 and 30 s, respectively. Element calibration solutions were produced by dilution of ICP standards (Carl Roth GmbH & Co. KG). Although more elements were measured, the considerations in this work were limited to the elements As, Cd, Cr, Cu, Ni, Pb, S, and Zn, as these were deemed most suitable for evaluating industrial impact (Alloway 2013; Mills et al. 2017).

Miniaturized solid–liquid extraction of OCPs

Organic solvents acetone and methanol (both gradient grade for HPLC) were purchased from VWR International (Radnor, PA, USA), and petroleum ether (40–60 °C, p.a.) was purchased from Merck KGaA. Analytical standards (purity) were used for calibration or as internal standards if isotopically labeled: 2,4'-dichlorodiphenyldichloroethane (DDD, 97.5%), 2,4'-dichlorodiphenyldichloroethylene (DDE, 99%), 2,4'-DDT (99.5%), 4,4'-DDD (99.5%), 4,4'-DDE (98%), 4,4'-DDT (99.5%), ^{13}C-2,4'-DDT (100%), and γ-HCH (98.6%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). α-HCH (≥98%) and δ-HCH (≥98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). β-HCH (99.5%) was obtained from the Institute of Industrial Organic Chemistry (Warsaw, Poland). 4,4'-DDD-D_8 (99.7%), 4,4'-DDE-D_8 (99.4%), and α-HCH-D_6 (99.2%) were purchased from CDN Isotopes (Pointe Claire, Canada). ^{13}C-4,4'-DDT (99%) was purchased from the Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Purity was considered when preparing stock solutions of standards.

Samples were extracted based on a miniaturized solid–liquid extraction method (MISOLEX; Simon et al. 2021). In brief, 0.5 g of freeze-dried sediment sample was weighed in a 20-mL clear-glass head-space vial. Five milliliters of acetone and 5 mL of petroleum ether were added, and the vial was closed tightly with a screw cap. The sample was shaken in a horizontal shaker for 30 min at 200 rpm (Swip KS-10, Edmund Bühler GmbH, Bodelshausen, Germany) and then centrifuged for 10 min at 1000 rpm (207.2 g; Rotanta 460 R, Hettich AG, Bäch, Switzerland). The supernatant was transferred into a 20-mL brown-glass head-space vial. Another 10 mL of petroleum ether was added to the sample, and the process was repeated. The supernatant was added to the one taken before, resulting in approx. 12 mL of extract. An aliquot of 10 mL was transferred to a fresh 20-mL brown-glass head-space vial, and 2 µL of internal standard mix (Online Resource: Table S2) was added, equivalent to a concentration between 1 and 3 ng·mL^{-1} in the final sample. The extract was evaporated to dryness under a gentle stream of nitrogen. Immediately after evaporation, 100 µL of methanol, serving as solubilizer, and 10 mL of salt solution (200 g NaCl in 1 L ultrapure water) were added.

SPME and GC–MS analysis

Analysis of OCPs in sediment samples was carried out with a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, San Jose, CA, USA), a CombiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland) equipped with a SPME fiber assembly, and an ITQ 900 mass spectrometer (Thermo Fisher Scientific). For all measurements, a SPME fiber coated with PDMS (100 µm) was used (Sigma-Aldrich, St. Louis, MO, USA). Extraction by SMPE of prepared samples started with a heat up phase in the agitator for 5 min to 80 °C, followed by headspace extraction at the same temperature for 30 min. After extraction, the fiber was thermally desorbed in splitless mode in the GC injector for 3 min, after which it switched back to a split flow of 30 mL·min^{-1}. At the start and end of each SPME sample cycle, the fiber was desorbed in a needle heater for 5 min at 270 °C. Chromatographic separation was conducted on a fused silica capillary column (TG-XLBMS 60 m, 0.25-mm inner diameter, 0.25-µm coating thickness; Thermo Fisher Scientific). Helium (≥99.999%, Praxair, Danbury, CT, USA) was used as carrier gas at a constant flow of 1.0 mL·min^{-1}. The initial oven temperature was set at 90 °C and held for 3 min. The temperature was ramped to 150 °C at a rate of 15 °C·min^{-1}. Then, it was ramped to 280 °C at a rate of 5 °C·min^{-1} and held for 3 min. Quantification was done in selected ion monitoring (SIM) mode based on one target and one qualifier ion. A list of ions and retention times used is available in the Online Resource (Table S3). The peak areas of analytes in sediment samples were corrected with their respective internal standard (see caption of Table S3). The respective concentration was determined by interpolation of the relative peak areas for each pesticide to standard peak areas of the calibration curve.

Congener ratios

In this study, DDD was used as indicator for direct input of DDT formulation into the lake, followed by transformation to DDD in the mostly anaerobic sediment. In contrast, DDE was deemed indicative of erosive transport into the sediment following transformation in aerobic conditions in the topsoils outside the lake body. DDD/DDE ratios were calculated of 4,4' congeners only, as these were found in higher concentrations and thus more consistently throughout the length of the profiles. For the same reason, 4,4'/2,4' ratios were calculated only of DDD. The technical mixture of DDT contains about 63–80% 4,4'-DDT and 15–21% 2,4'-DDT, resulting in ratios between 3 and 5.1 (Braun et al. 1999; Ricking and Schwarzbauer 2012), while in higher quality mixtures, the 4,4'-DDT proportion is higher.

Data analysis

To generate mean values that span over several lakes and years, the following method was applied: For each analyte (TE or OCP) and lake separately, values were normalized to the maximum value, which was set to 1. Then, normalized values of a single element of all lakes were put together, ordered according to their date, and then, means covering all values in 5-year spans were calculated. Lakes with a higher sedimentation rate had thicker sediment layers per year than those

with lower rates. This means that for the given core length of 1 m, layers from lakes with higher sedimentation rate cover a smaller time period and also yield more data points per 5-year period than the latter. Consequently, for the 5-year periods, not always the same number of points or lakes was covered and sometimes lakes were covered twice. Tables S4 and S5 in the Online Resource provide an overview of data points per 5-year period and which lakes were included.

Land use area proportions in catchment areas of the lakes were analyzed graphically by pixel area counting of map excerpts using Paint.NET Version 4.1.6 (dotPDN LLC). Maps were taken from Geoportal.de, the Open Data map service of the Federal Agency for Cartography and Geodesy (BKG) on 13 May 2019. Meadows and fields were combined to agricultural area, as it was not possible to discern a difference between them with sufficient certainty in the map data. Waterbodies were excluded from the calculations.

Data storage

Data for this study were published open access (Simon et al. 2023). Additional figures and tables mentioned in the text are available as part of the Online Resource on the article's webpage (Supplementary file 1; PDF).

Results

Radioisotope dating

The dating reasonably covered the time period of interest (1915–2015). Well-resolved ^{137}Cs peaks were found in the profiles, indicating the nuclear weapon testing in 1963, which was used to correct the ^{210}Pb dating. Figures of age profiles for each lake showing activities of the isotopes per depth are available in the Online Resource (Fig. S4).

Trace element concentrations

Lakes in general

Normalized mean values covering all lakes and elements (As, Cd, Cr, Cu, Ni, Pb, S, Zn) are shown in Fig. 2. Elemental profiles of each lake are available in the Online Resource (Figs. S5–S14). A prominent general pattern is visible: Values are increasing from 1920 from higher than background concentrations until the 1960s, which demarks a turning point. Thereafter, values are decreasing until the year 2000, with a slightly stronger slope from 1975. Concentrations start to rise again until they reach a second maximum in 2005, after which values from before are reached in 2010 and continue to decline until the most recent layers of the cores (ca. 2015). Lakes SL, CR, PL, ST, and WM include data that precede 1900 (Fig. 3 and Online Resource: Figs. S15–S17). In their profiles, elemental concentrations show strong increases starting from assumed background concentrations at around 1850 and 1870 which reach a first peak or plateau at ca. 1900 and develop as described before. Profiles of elements Al, Cr, Ni, and Co show a remarkable resemblance throughout the sampled lakes.

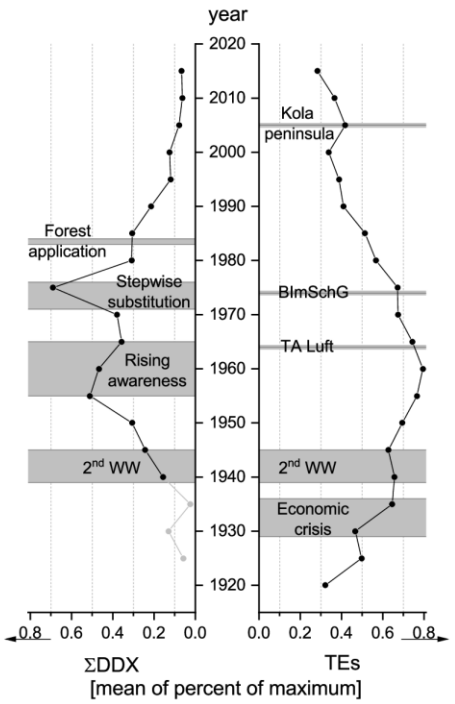

Fig. 2 Five-year means of concentrations of ΣDDX (left) as well as TEs (right) of all 10 lakes normalized to the respective maximum of each sum parameter in each lake (excluding lake WM for ΣDDX). A detailed explanation about the calculation is given in the text (Sect. Data analysis). Light gray points depict implausible measurement results that are probably caused by carry-over during sampling. TA Luft (1964) and BImSchG (1974) were the first and second implemented air emission control regulations in West Germany, respectively. This figure was created with OriginPro 2022b (OriginLab Corp., Northampton, MA, USA)

Traits of specific lakes

Table 2 shows minimum and maximum concentrations, and the year of the maximum for each lake and element between 1925 and 2015. Lakes ST and WM show the highest ranges of elemental concentrations, followed by lakes SL, CR, AR, and TF. Generally, the elemental concentrations of lakes FH, BL, PL, and OR are the lowest of all 10 lakes. Profiles from lake FH and its neighboring lake BL (Online Resource: Figs. S1, S5, and, S6) show a remarkable resemblance, not only in behavior but also in concentration. This holds true

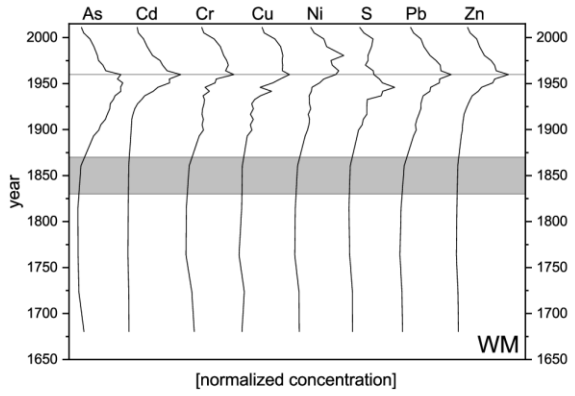

Fig. 3 Plot showing normalized concentrations of TEs As, Cd, Cr, Cu, Ni, S, Pb, and Zn in lake WM relative to the maximum concentration of each TE, which was set to 1. The gray area depicts the onset period of the Industrial Revolution in Germany. The gray line denotes the year 1964, when the first air pollution control regulation (TA Luft 1964) was implemented in West Germany. This figure was created with OriginPro 2022b (OriginLab Corp.)

for the pairs SL–CR and ST–WM, albeit with less similarity. Regarding single elements, noticeably high concentration peaks are present for As in lake TF in ca. 1965 (87 $mg \cdot kg^{-1}$) and for Cu in lake ST in ca. 1981 (313 $mg \cdot kg^{-1}$). Considering all profiles, the median of the maximum concentrations of TEs follows this order: S (27,150 $mg \cdot kg^{-1}$) > Zn (379 $mg \cdot kg^{-1}$) > Pb (170 $mg \cdot kg^{-1}$) > Cu (41 $mg \cdot kg^{-1}$) > As (33 $mg \cdot kg^{-1}$) > Cr (15 $mg \cdot kg^{-1}$) > Ni (15 $mg \cdot kg^{-1}$) > Cd (3 $mg \cdot kg^{-1}$).

Organochlorine pesticide concentrations

Lakes in general

As only the lower half of the lake WM core was analyzed for OCPs and thus covers a time frame from ca. 1680 to only ca. 1955, it was left out of all further calculations. Of the analyzed OCPs, only 2,4'-DDD, 4,4'-DDD, 2,4'-DDE, and 4,4'-DDE were found. Consequently, ΣDDX denotes the sum of these four congeners. Figure 2 shows 5-year normalized mean values of ΣDDX, calculated for all lakes and congeners. Disregarding implausible values from earlier dates, concentrations started to rise in 1935 and reached a first peak in the mid-1950s (ca. 50% of maximum). After a short decline until 1965, concentrations sharply rose until the main peak in 1975 (ca. 70% of maximum), before they dropped to concentrations before the second peak and, thereafter, continued to decline. Concentrations levelled off at ca. 10% of maximum in 2010.

Traits of specific lakes

Table 3 shows minimum and maximum concentrations, and the year of the maximum for each lake and congener between 1925 and 2015. Maximum concentrations of congeners follow this order: 4,4'-DDD > 4,4'-DDE > 2,4'-DDD ≫ 2,4'-DDE. 2,4'-DDE concentrations were by far the lowest of the four congeners, constantly staying below 10 $\mu g \cdot kg^{-1}$, and in the case of lakes FH and OR below the limit of detection (LOD).

Among the 10 studied lakes, highest concentrations of ΣDDX were found in lake AR (ca. 380 $\mu g \cdot kg^{-1}$, ca. 1974) and lake TF (ca. 350 $\mu g \cdot kg^{-1}$, ca. 1985). Lower concentrations (225–250 $\mu g \cdot kg^{-1}$) were present in lakes ST, SL, and CR (ca. 1966, 1969 and 1977, resp.). Whereas the lowest concentrations (30–165 $\mu g \cdot kg^{-1}$) were found in lakes FH, BL, OR, and PL (ca. 1963, 1959, 1965 and 1977, resp.).

In the single lake profiles (Fig. 4), three points in time of increased concentrations are visible, mirroring the averaged profile of the lakes of Fig. 2: The first is between 1955 and 1965, especially prominent in lakes FH, BL, OR, and PL, while in lake SL, it is 5 years later. The second event is in the 1970s and can be seen in lakes AR, CR, and PL. Lake TF is the only lake where the third event in ca. 1984 is clearly visible, as it constitutes the main peak. Much less distinct indications of this event are present in lakes BL and OR. Lakes ST and WM show a similar behavior compared to TEs (data of WM not shown), where concentrations slowly rose until maximum in the late 1960s followed by a likewise slow decrease to very low concentrations at the top in ca. 2015. However, the very coarse time resolution of these cores could have masked any short-term developments of OCP concentrations.

Congener ratios

Since only TPs of DDT were found, ratios were calculated between them to assess the quality of the used product (4,4'-DDD/2,4'-DDD), as well as to distinguish between direct and erosive input (4,4'-DDD/4,4'-DDE). Box plots summarizing the ratios of all studied lakes in the 5-year periods are depicted in Fig. 5. Light gray, hatched box plots show values that have to be considered with caution, either because only a limited number of lakes is represented, or the occurrence of values at that time is not considered historically sound (see "Data analysis" section).

4,4'-DDD/2,4'-DDD ratios stay mostly between values of 2 and 3 over the length of the observed period from ca. 1950 to ca. 1995 (Fig. 5a). Ratios of 4,4'-DDD/4,4'-DDE are mostly above 1 until ca. 1985. The median of ratios peaks in ca. 1955 after which it declines until ca. 1970. Then, it slowly increases, reaching a secondary peak in ca. 1980, and drops

Table 2 Minimum and maximum concentration in $mg \cdot kg^{-1}$ and year of maximum of each element and lake for the period from 1925 to 2015

	As			Cd			Cu			Cr			Ni			Pb			S			Zn		
Lake	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year
Neubrandenburg district																								
FH	0.15	14.5	1953	0.08	1.98	1953	5.74	39	1986	0.74	8.47	1953	1.23	7.16	1986	2.07	108	1953	1,274	15,603	1953	8.92	171	1953
BL	3.94	14.6	1953	0.21	1.96	1953	7.21	16.8	1976	2.59	7.97	1953	3.08	7.01	1953	12.5	102	1959	4,465	16,132	1953	33.6	169	1953
SL	8.95	32.8	1960	0.37	4.7	1960	25	39.8	1960	8.51	17.5	1960	6.26	14	1960	50	232	1960	10,000	566,689	1969	150	397	1960
CR	10.1	33.4	1942	1.25	5.39	1957	27.5	42	1957	14.3	37.4	1957	13.4	26.1	1957	81	279	1968	15,000	34,587	1968	180	403	1968
TF	6	88	1965	0.48	2.3	1971	25	53	1984	8	15.5	1984	7	15	1971	35	140	1971	10,500	21,500	1984	90	360	1984
OR	1.5	6	1965	0.1	0.8	1953	6	18	1982	3.5	10	1977	4	12.5	1959	6	37.5	1953	5,500	11,500	1965	25	85	1953
Frankfurt (Oder) district																								
PL	2.5	8.75	1958	0.2	1.4	1951	16.6	23	1964	3.5	8	1958	4.5	7	1983	22	92	1958	11,700	23,500	1970	60	150	1958
Magdeburg district																								
AR	*n.d.*	33	1954	*n.d.*	4	1974	9	50	1974	2	15	1974	5	22	1974	1	200	1974	6,300	30,800	1958	*n.d.*	500	1974
Potsdam district																								
ST	12	68	1966	1	9	1947	30	300	1981	4	25	1966	6	20	1966	50	550	1947	9,800	33,000	1927	140	1,400	1966
WM	15	66	1951	2.5	12.43	1960	25	54	1960	10	24.6	1960	7.5	21.7	1980	150	649	1960	16,500	47,270	1946	230	960	1960
Median	4.97	32.9	1956	0.29	3.15	1955	20.8	40.9	1975	3.75	15.3	1960	5.5	14.5	1969	28.5	170	1960	9,900	27,150	1962	75	379	1960

n.d. not detected

Table 3 Minimum and maximum concentration in $\mu g \cdot kg^{-1}$ and year of maximum of each DDT transformation product for the period from 1925 to 2015. Lake WM is excluded as its data only covers the time frame until ca. 1955

	4,4'-DDD			2,4'-DDD			4,4'-DDE			2,4'-DDE			ΣDDD			ΣDDE			ΣDDX		
Lake	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year	Min	Max	Year
Neubrandenburg district																					
FH	8	38	1963	3	19	1963	5	28	1963	*n.d.*	*n.d.*	*n.d.*	9.86	57.4	1963	4.79	27.8	1963	11.5	170	1963
BL	1.5	36.5	1953	0.1	5	1958	1.1	20	1964	1.3	2.4	1958	1.58	40.5	1953	2.40	22.2	1964	4.80	119	1959
SL	8.5	105	1960	13	67.5	1969	3	70.5	1969	3.3	6.8	1977	8.53	173	1969	10.9	78.3	1969	20.4	251	1969
CR	18	130	1977	11	45	1977	1.3	53	1968	1.0	2	1977	–*	175	1977	1.25	55	1968	1.25	228	1977
TF	8.5	204	1984	5	78	1984	6	59	1984	3.0	6.5	1984	13.6	282	1984	6	65.1	1984	24.2	346	1984
OR	1.5	19	1959	*n.d.*	*n.d.*	*n.d.*	1.3	13	1965	0.6	1.9	2013	1.46	18.8	1959	1.96	12.9	1965	1.96	30.2	1965
Frankfurt (Oder) district																					
PL	5.5	86	1977	2.5	30	1977	0.5	48	1977	0.25	1.6	1977	6.63	116	1977	4.64	49.8	1977	10.7	166	1977
Magdeburg district																					
AR	4	235	1974	17	58	1974	2.5	83	1974	1.6	4.4	1974	–*	350	1974	3.77	87.3	1974	3.77	437	1974
Potsdam district																					
ST	4.5	140	1966	3.4	55	1966	1.2	60	1966	0.1	4.3	1966	4.47	194	1966	5.42	64.6	1966	9.89	259	1966
WM	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Median	5.5	105	1966	5	50	1972	1.3	53	1969	1.15	3.35	1977	6.63	173	1969	4.64	55	1968	9.89	228	1969

n.d. not detected

*Because of limited data points, a plausible minimum is not present

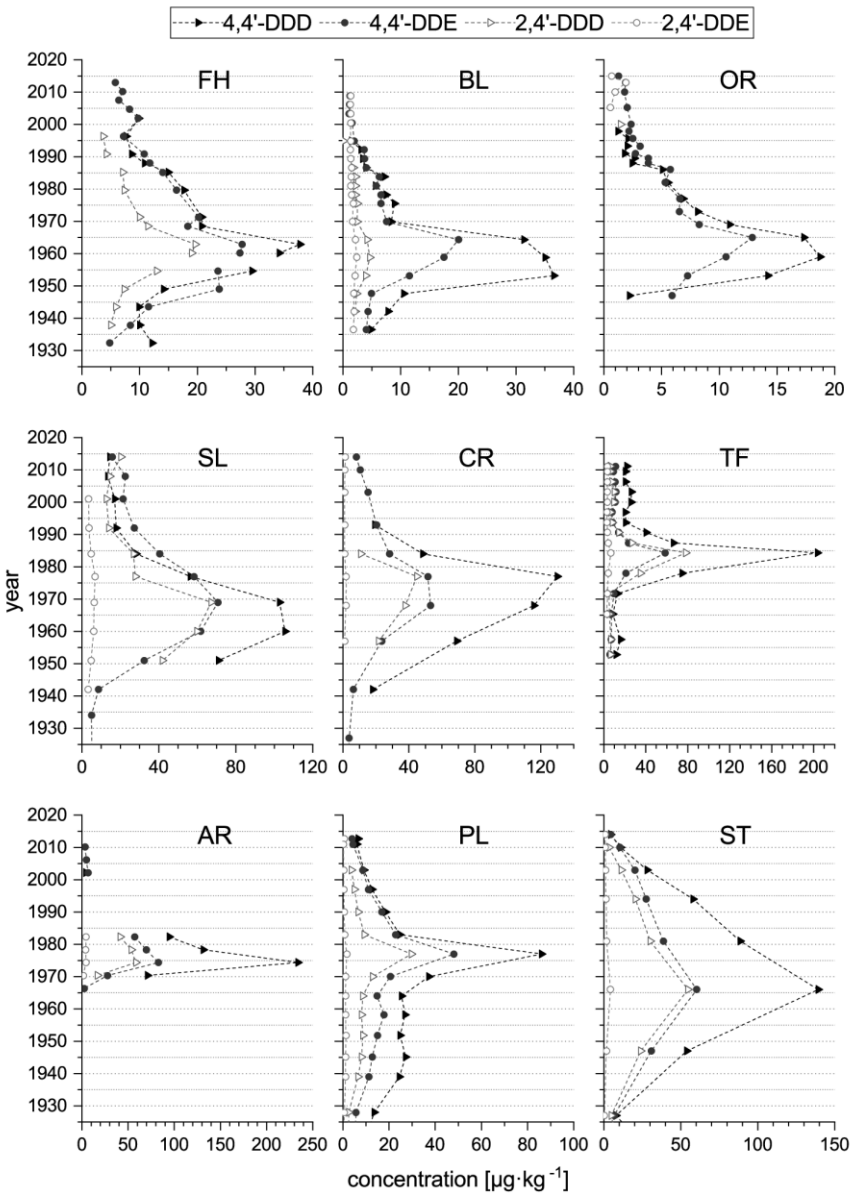

Fig. 4 Concentrations of transformation products of DDT in µg·kg^{-1} in each lake profile (excluding lake WM) between the years 1930 and 2015. Note the different *x*-axes. This figure was created with OriginPro 2022b (OriginLab Corp.)

beneath 1 in ca. 1990. In ca. 1995, it shortly peaks slightly above 1, and returns to almost the same value in ca. 2000.

Discussion

Trace elements

The fact that the TE concentrations in sediment cores of different lakes show a very similar behavior among each other leads to the conclusion that they were mainly introduced via diffuse atmospheric deposition. Pacyna (1984) estimated the atmospheric emission of TEs from anthropogenic sources in Europe per country for the year 1979. The order of emitted element concentrations from highest to lowest was Zn > Pb > Cu > As > Cr > Ni > Cd. This is similar to the order found throughout all lakes in this study, indicating that besides the geogenic background, the atmosphere or rather anthropogenic industrial activity is the primary source. Still, an influence of other anthropogenic activities in the vicinity of the lakes cannot be completely excluded. This includes direct run-off from settlements or input from treated or

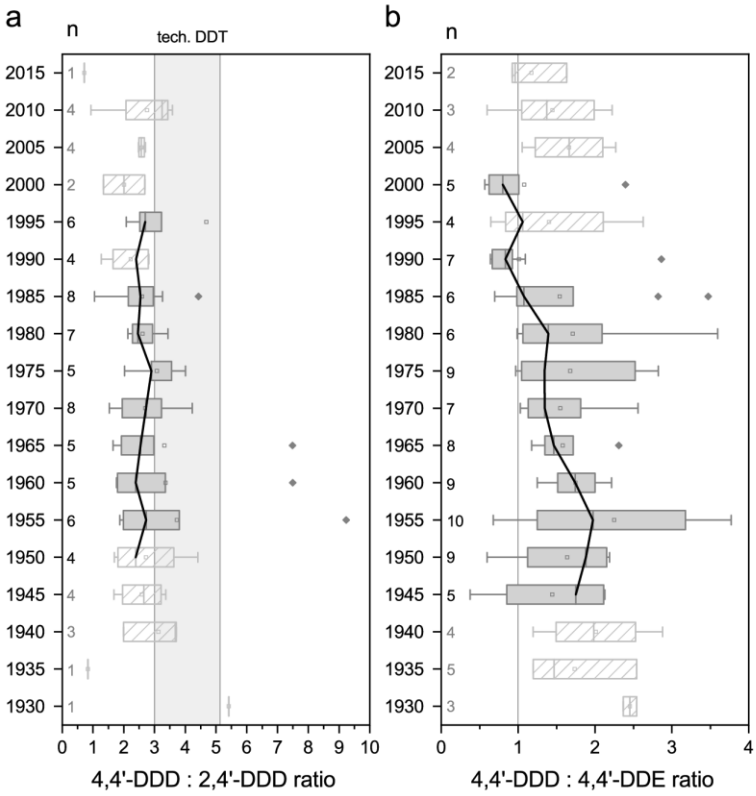

Fig. 5 Box plots of 4,4'-DDD/2,4'-DDD (**a**) and 4,4'-DDD/4,4'-DDE (**b**) congener ratios of 5-year periods. *n* is the number of different lakes that are included in a box plot. The gray area in **a** depicts the ratio range which is typical for technical DDT mixtures. High-quality formulations feature higher ratios. The gray line in **b** marks a ratio of 1. Values above 1 are indicative of a higher influence of direct DDT input, while those below 1 indicate a higher proportion of erosive input in the form of DDE. Light gray bordered and hatched unfilled box plots have to be considered with caution, either because only a limited number of lakes is represented, or because the occurrence of DDX at that time is not considered historically sound. This figure was created with OriginPro 2022b (OriginLab Corp.)

untreated wastewater and other surrounding waterbodies for example, although no clear indications were discernible for most lakes. The only exception is lake ST, which has been impacted by the nuclear power plant Rheinsberg (see below).

Compared to the average geogenic background of the respective federal state in which a lake is situated (LABO 2003), the concentrations of the elements found in the lake sediments were mostly higher (factors ca. 2–15), when taking the period of industrial activity into account. Where the concentrations are lower, at least a trend is visible. In lakes ST and WM, concentrations of Cd, Cr, Pb, and Zn rise above background levels starting from ca. 1893. For both lakes, there are reports of local glass-producing industry in the nineteenth century dumping substantial amounts of ash from wood burning into the lakes, which could be an explanation (Casper et al. 1985). Additionally, the visible increase starting in the second half of the nineteenth century is present for most of the elements in the extended profiles and is probably due to the onset of industrialization in general that has been reported in other studies from European lakes (e.g., Gunten et al. 1997; Shotyk et al. 2002; Thevenon et al. 2011; Elbaz-Poulichet et al. 2020), and which has been proposed as the beginning of the Anthropocene (Swindles et al. 2015; Waters and Turner 2022). A similar pattern can be assumed for the other lakes that were not dated as far back in time. Concentrations before that, i.e., in the deepest layers of these cores (Fig. 3 and Online Resource Figs. S15–S17), are rather constant over a longer period of time and may be considered local background concentrations.

The first half of the twentieth century is dominated by three major world crises: the First World War (1914–1918), the Great (economic) Depression (1929–1936), and the Second World War (1939–1945) that had substantial influence on production and, thus, pollutant emissions (Niedertscheider et al. 2014). However, no obvious indications of these events were found. TE concentrations started to increase anywhere between the 1940s to the 1970s. The earlier increases could be attributed to war efforts, while later ones could be because of post-war recovery. These periods coincide with the "Great Acceleration," a time of rapidly increasing, global anthropogenic impacts on the whole planet that is set to approx. 1950 (Swindles et al. 2015). It is marked by a rapid increase of spheroidal carbonaceous particles (SCPs) in stratigraphic records around the globe which are distinctly formed during burning of fossil fuels in energy production and heavy industry.

Starting from the 1960s, there is a remarkable general decline of TE concentrations. One would be inclined to accredit these reductions to policies and measures undertaken in the GDR to improve air quality. But the

government failed to implement any substantial measures up to its demise in 1989, except for a reduction in fly ash of about 16% in the last 9 years (Buck 1996). Contrary to this, West Germany established its first legislation to control air pollution in 1964 (TA Luft 1964), followed 10 years later by 2 further novel legislature measures (BImSchG 1974; BImSchV No. 1 1974) regulating emissions of firing systems among others. A growing sense for the environment and its necessary protection essentially characterized this time period. These developments coincide nicely with the turning point in TE concentrations in the 1960s and the slightly stronger decrease in the 1970s, suggesting that the patterns in the cores are indicative of the atmospheric burden coming from West Germany instead of that from the GDR. In support of this theory, Pacyna (1984) identifies the Benelux countries and the western part of West Germany as a major emission area in Europe for that time, with emitted amounts of TEs that are approx. 3–26 times higher than those from the GDR. Additionally, the northern half of the former GDR, where the lakes are situated, harbored no greater industry or energy plants which could have served as local sources (Hornych and Schwartz 2009). Accordingly, the districts with the highest recorded dust emissions are in the south: Berlin (East), Cottbus, Halle, and Leipzig (Buck 1996). And finally, prevailing winds in the territory of the northern GDR are directed to the northeast (i.e., Westerlies), transporting air masses predominantly from the southwest to the lakes (Buck 1996; Traup and Kruse 1996; Bürger 2003). In this way, LRAT of air emissions from the southern GDR are rather directed to, e.g., Poland (Buck 1996), than to the lakes in the north of the GDR. Gunten et al. (1997) experienced the same sharp decline in lake sediment cores from Lake Zurich and ascribed this to environmental protection measures in Switzerland as the major cause as well.

The years afterwards (1980–2015) are characterized by a steady decline in TE concentrations to levels slowly approaching those before 1925 (Fig. 2). For the years 1990 until present, this is supported by national monitoring data of air emissions in Germany (UBA 2020), as well as bioaccumulation data of the national moss surveys (Schröder and Nickel 2019), and is accredited mostly to ash and SO_2 reduction measures which are part of the legislative and technology measures to reduce air pollutants on an European level since the 1970s (Turnock et al. 2016). It remains to be seen, however, if those pre-industrial levels are reached in the future. Soils have been accumulating TEs for a very long time and are slowly releasing them, as several studies have shown (Yang et al. 2002; Bacardit and Camarero 2010; Catalan 2015), so that fluxes to the lakes can remain positive despite emission reductions.

The peak in ca. 2005 is reflected in the moss monitoring (Schröder and Nickel 2019). An increase in metal concentrations between 2000 and 2005 was also found in, e.g., Finland, Austria, and Switzerland, and is attributed to a chromium mine located on the Kola Peninsula (Kratz and Schröder 2010). Emissions of this mine could have been transported southwards to the lake area by temporary occurring weather systems.

As for local peculiarities, the resemblance in profiles between lakes FH, BL, SL, and CR is probably due to the geographic vicinity of the lakes to each other, and the hydraulic connections between them. Lakes ST and WM show the highest TE concentrations of all studied lakes. This might be in correlation to the high amount of forest in their catchment areas. Tree canopies are known to gather particles and pollutants from air, thereby increasing the input to the underlying soil (forest filter effect; Horstmann and McLachlan 1998; Nizzetto et al. 2006). The extraordinarily high Cu concentrations present in lake ST since 1966 and declining since 1981 could be associated with the adjacent power plant (Kernkraftwerk Rheinsberg) that was operated between 1966 and 1990 (Koschel and Adams 2003): It used water from the neighboring Lake Nehmitz as coolant. The warm waste water, however, was expelled into lake ST (UBA 2004) leading to an increase in average water temperature (O'Reilly et al. 2015). Presumably, the water could have carried Cu from the external cooling system through which it was transferred, as was observed in other power plant effluents (Wright and Zamudal 1991; Friedlander et al. 1996; Bojakowska and Krasuska 2014).

Contrary to expectation, no indication of traffic emissions, i.e., through Pb concentrations mirroring the use of leaded gasoline, was found. Instead, the TE profiles of the lakes mirror emissions from industrial processes (Heinrichs 1993; Wessels et al. 1995). Possibly, emitted Pb did not reach the lakes or it had too little effect on the overall Pb concentration, so that it was masked by significantly higher industrial depositions. In Switzerland, cores from Lake Zurich showed rising Pb concentrations long before the introduction of leaded fuel (Gunten et al. 1997), and in Lake Brêt, the Pb profile roughly followed that of other studied elements, i.e., Cu and Hg (Thevenon et al. 2013). Both observations, which are present in the current study as well, were ascribed to an overall metal pollution from industrial activity as the major source.

Organochlorine pesticides

Of the DDT group of analytes, only TPs DDD and DDE but no traces of the parent compound DDT were detected. The period with the strongest increases and peaks of concentrations was between ca. 1945 and ca. 1975, excluding lake TF featuring the main peak in ca. 1985. Concentrations

of ΣDDX peaked between 30 and 380 µg·kg^{-1} (median 225 µg·kg^{-1}). These are, in fact, comparable to 4 of the 5 Canadian lakes examined by Kurek et al. (2019), which experienced direct aerial spray input of DDT in the 1950s–1970s, with maxima between ca. 130 and ca. 575 µg·kg^{-1}.

MacDonald et al. (2000) developed consensus-based sediment quality guidelines (SEQs) for 28 chemicals of concern in freshwater ecosystems. Among them were a threshold effect concentration (TEC) and a probable effect concentration (PEC; not to be mixed up with predicted environmental concentration) for each analyte of concern. The TEC is intended to identify concentrations below which detrimental effects on sediment-dwelling organisms are not expected. The PEC on the other hand should indicate concentrations above which harmful effects on such organisms are expected to occur frequently. In the cases of ΣDDD and ΣDDE, TECs were 4.88 and 3.16 µg·kg^{-1}, respectively, and PECs were 28 and 31.3 µg·kg^{-1}, respectively. The latter were generally exceeded during the mentioned period of highest concentrations, by 2 to as much as 10 times in the case of ΣDDD, and by almost 3 times in the case of ΣDDE. Thus, detrimental effects for benthic fauna during the period of usage were very likely. Concentrations near the surface of the lake sediment were mostly < 10 µg·kg^{-1}. They were in the same range as other surface sediment samples from anthropogenically influenced lakes. Similar concentrations as those found in our study were also observed in Lake Victoria in Uganda (mean ΣDDX 4.24 µg·kg^{-1}; Wasswa et al. 2011), Chinese Lakes Taihu (ca. 3.7–13.6 µg·kg^{-1}; Zhao et al. 2017), and Songyang (0.4–18.4 µg·kg^{-1}; Gong et al. 2021). In contrast, concentrations of DDD and DDE of some lakes (AR, BL, OR, PL) were similar to those found in remote alpine lakes of Switzerland (< LOD–4.75 µg·kg^{-1}; Poma et al. 2017). Concentrations in these four lakes are well below the TECs, indicating no acute threat to epibenthic fauna. Nevertheless, sublethal and chronic effects might still occur (Chattopadhyay and Chattopadhyay 2015; Marziali et al. 2017; Iliff et al. 2019).

For further considerations, it is important to establish if the concentrations of DDD and DDE as well as the ratio between them have significantly changed over the decades since their deposition. First of all, a transformation of DDD to DDE or vice versa in the sediments is rather unlikely. Although both transformation paths have been reported (Purnomo et al. 2008, 2011), they were catalyzed by brown-rot fungi that require aerobic conditions (Kim and Singh 2000), which does not apply here. Microbial degradation of DDD and DDE under anaerobic conditions has been reported. For DDE, the most probable path of transformation is to DDMU (1-chloro-2,2-bis-(p-chlorophenyl)ethylene) as the next following product via reductive dechlorination (3 times faster than DDD; Quensen et al. 2001; Schulze et al. 2003; Yu et al. 2011). The dominant anaerobic transformation pathway of DDT results in both DDD and DDMS (1-chloro-2,2-bis-(p-chlorophenyl)ethane), as shown, e.g., by Heim et al. (2005) and Yu et al. (2011). Apart from DDD and DDE, other TPs were not analyzed in the current study. Coincidentally, Heim et al. (2005) studied a sediment core from Teltow canal in Berlin, which was severely exposed to DDT and lindane in the former GDR, albeit by a chemical factory (VEB Berlin Chemie). They found DDMS as the second most abundant TP after DDD, which showed at least 2 times higher concentrations. The lowest part of their core had been deposited 7 years before the sampling. Concentrations of DDD were still 44 times above those of DDT and 15 times above DDE. Therefore, we assume that even if degradation of the primary TPs has occurred, the overall ratio of DDD to DDE has not been changed fundamentally up to this point.

For these reasons, we assume two distinctive scenarios: In the first, DDT formulation directly reaches the lake sediment, e.g., because of drift during application on fields and forests (Frank et al. 1994; Craig et al. 1998; Matthews 2014). In this scenario, mainly DDT is deposited, and while minor parts may be transformed to DDE during deposition, most of the DDT is afterwards transformed to DDD anaerobically. In the second scenario, DDT reaches the sediment indirectly via erosion of topsoil some time after agricultural or forest application. The proportion of DDT in the eroded material will be higher at first, but with ongoing dwell time and, thus, transformation in the mostly aerobic soil, DDE concentrations will increase until they finally surpass those of DDT, if no additional DDT formulation is applied (lakes CR, OR, and SL; Dimond and Owen 1996). Depending on the capacity of reservoirs capable of storing DDT surrounding the lakes, a more or less constant leakage input is imaginable, leading to steadily low concentrations in the profiles (lake TF). Such a behavior of persistent chlorinated pollutants was observed in boreal forests of Norway by Bergknut et al. (2011). In reality, these two scenarios will most probably occur coincidentally to different extents in different points of time.

Furthermore, input of DDX into the lakes or their surrounding reservoirs via LRAT is possible and has been reported (Juracek and Mau 2003). However, contributions through this pathway should be minor in regard to the extent of direct depositions that took place in the examined area.

Silva et al. (2019) evaluated the distribution of 76 pesticides in agricultural topsoil samples from across the EU in 2015. Frequently found compounds were DDT and its TPs. They were second only to the herbicide glyphosate which was applied much more recently. Accordingly, the most common TP was 4,4'-DDE with median and maximum of 20 and 310 µg·kg^{-1}, respectively, while for 4,4'-DDD, it was 10 and 40 µg·kg^{-1}. In the current study, concentrations in the youngest layers dating back to 2010–2015 were between < LOD and 15.71 for 4,4'-DDE and < LOD and 22.07 µg·kg^{-1} for 4,4'-DDD. Camenzuli et al. (2016) evaluated data from 73 peer-reviewed articles and calculated median concentrations

for several legacy pesticides of agricultural and background soils from all over the world. The results were divided into two distinct periods: 1993–2002 and 2003–2012. Values of 4,4'-DDT declined from 16.22 to 8.71 $\mu g \cdot kg^{-1}$ in agricultural soils and from 1.23 to 0.91 $\mu g \cdot kg^{-1}$ in background soils. Similar values and trends were shown for 4,4'-DDE: 12.02 to 7.76 $\mu g \cdot kg^{-1}$ and 0.98 to 0.51 $\mu g \cdot kg^{-1}$ in agricultural and background soils, respectively. In the present study, 4,4'-DDD which is assumed to represent its DDT counterpart, is found at a median concentration of 7.66 $\mu g \cdot kg^{-1}$ in the first period and at < LOD in the second. 4,4'-DDE stays more or less the same (7.23 and 8.23 $\mu g \cdot kg^{-1}$), at concentrations comparable to those from agricultural soils in the second period from Camenzuli's study. The predominant TP in other studies concerning OCP concentrations in sediments was DDD (Muir et al. 1995; Hendy and Peake 1996; Pereira et al. 1996; Hoke et al. 1997; Eggen and Majcherczyk 2006; Götz et al. 2007; Thevenon et al. 2013), and in two of them examining river sediments, almost all DDT was converted (Schwarzbauer et al. 2001; Heim et al. 2005). On the other hand, there are also many studies in which DDE was the predominant TP (e.g., Rawn et al. 2001; Juracek and Mau 2003; Franců et al. 2010; Bettinetti et al. 2011). Franců et al. (2010) and Evenset et al. (2007) attributed this to input of mainly strongly weathered soil material (i.e., from agriculture), and little direct input of DDT into the lake.

Historical context

The insecticidal feature of DDT was discovered in 1939 and came to widespread use in agriculture following World War 2 (Mellanby 1992 ex Jürgens et al. 2016; Ricking and Schwarzbauer 2012). In the 1950s and 1960s, the application of DDT increased dramatically. But rising awareness of environmental issues in the 1960s also affected the agricultural sector. By that time, DDT had grown into a model compound in ecotoxicological studies, whose unfavorable results led to waning enthusiasm for the pesticide (Mellanby 1992 ex Jürgens et al. 2016). At the end of the 1960s, the GDR government found itself constrained to react to the global wave of DDT bans, which endangered its own food and crop exports. As a result, a stepwise substitution plan was adopted: From 1971 until 1976, more and more DDT bans for the most application intensive crops were installed, visible in decreasing amounts of distributed DDT in the GDR from ca. 280 $Mg \cdot a^{-1}$ in 1972 to ca. 20 $Mg \cdot a^{-1}$ in 1977 (Heinisch et al. 1993). Handout and assumed applications stayed low until 1983/1984, when the massive spread of the nun moth (*Lymantria monacha*) and associated pests (Riek et al. 2021) in forests of the northern GDR forced the government to divert from the substitution plan. Unofficially, 260,000 ha of the 600,000 ha of infested stands were aviochemically treated with DDT/lindane formulations. After that, handout of DDT dropped back to the previous level of 1970 and quickly declined further, finally coming to an end shortly before Germany's reunification a few years later (Heinisch et al. 1993).

These developments are reflected in the 4,4'-DDD concentrations of the single profiles (Fig. 4). The increase after World War 2 is present in all studied lakes where the core covers this time period (except lake AR which only shows one increase from 1970 and subsequent decrease after 1975). The main application period in the 1950s and 1960s is especially prominent in lakes FH, BL, SL, OR, and even in the forest lake ST. Probably as a result of the stepwise ban, concentrations are lower at the beginning of the 1970s in lakes FH, BL and OR, while the latter is demonstrating a gradual decline. In some areas, local farmers or foresters might have resorted to applying higher rates than usual in order to dispose of their remainders of the soon banned pesticides. This in turn could have led to high concentrations in lakes CR, PL, and AR in the 1970s, and through them to the peak in Fig. 2. In other studies of lake sediments, the main peak of DDX concentration was also found in the mid-1960s to mid-1970s in European countries, e.g., GB (Fox et al. 2001), Germany (Götz et al. 2007), Italy (Bettinetti et al. 2011), and Norway (Evenset et al. 2007), but also in several lakes throughout Canada (Rawn et al. 2001; Kurek et al. 2019) and the USA (van Metre and Mahler 2005). The secret operation against the nun moth in 1983/1984 is impressively visible in lake TF, and is indicated to a lesser extent in lakes BL (ca. 1985) and OR (ca. 1986).

Lakes FH, SL, TF, and OR demonstrate a slight increase in DDD and DDE concentrations after the year 2000. Sabatier et al. (2014) described the same phenomenon in a sediment core from a lake situated downhill of a vineyard in France in the 1990s. According to their theory, legacy pesticides (DDT among others) were remobilized from the soil by increased erosion, which in turn was caused by the application of the herbicide glyphosate, as it leads to a reduction in canopy above the soils, leaving them vulnerable to erosion. A similar effect could be imaginable here.

Regional traits

In the days of the GDR, lakes FH, BL, SL, CR, OR, and TF belonged to one single district (Neubrandenburg), and lakes ST and WM to another (Potsdam). Guidelines of these distinct administrations could play a role in existing similarities within each of these two groups. Still, circumstances on a much more local scale can contribute largely. The group of lakes around lake FH (FH, BL, SL, CR) are close in terms of distance and connection. Nevertheless, they did not show four almost identical profiles but can be divided into pairs: Lakes FH and BL are quite similar, as are lakes SL and CR. Concentrations of OCPs of the four lakes follow

this order: FH ≈ BL < SL < CR. Considering the absolute amounts of agriculture and forest area surrounding these lakes in their hydrological catchment area, there is a similar pattern: FH < BL < SL < CR. The influence of forest area in the vicinity of the lakes needs to be stressed not only for TEs but also for OCPs, although in this case, the contribution of LRAT in conjunction with the forest filter effect was probably minor in comparison to the effect of the direct aerial pesticide applications in the GDR. In Switzerland, Herzig et al. (2019) analyzed the DDX pollution load (among others) in lichens collected in 1995 and 2014. They found significant declines between 56 and 84% and credited this to POP emission regulations in Switzerland as part of central Europe, leading to decreasing direct inputs.

Another important point is the high capability of forest soils to store hydrophobic substances (Holoubek et al. 2009; Riek et al. 2021). This can lead to reemissions long after the last application. Aichner et al. (2013) examined the distribution of POPs including DDT and its TPs in forest soils throughout Germany. They found that concentrations in eastern Germany were much higher than in western Germany (equivalent to the former areas of the GDR and West Germany, respectively). For the region of the sampled lakes, ca. 160–440 $\mu g \cdot kg^{-1}$ for 4,4'-DDT, ca. 40–110 $\mu g \cdot kg^{-1}$ for 4,4'-DDE, and ca. 4–11 $\mu g \cdot kg^{-1}$ for 4,4'-DDD were measured, which was at least one order of magnitude higher than in western Germany. The authors state the severe forest treatment in the former GDR as reason for this. The concentrations in our study are within or below this range.

DDX congener ratios

The mostly unchanging 4,4'-DDD/2,4'-DDD ratios suggest a consistent quality of applied DDT formulations.

Ratios of 4,4'-DDD/4,4'-DDE are in accordance with the two scenarios proposed before. During the officially recorded time range of direct input (ca. 1945–1970), most values are fairly above 1. The decline of 4,4'-DDD/4,4'-DDE ratios that started in the late 1950s could indicate a rising importance of DDE input through erosion after aerobic DDT degradation. By 1985, many lakes have approached values near 1.

HCH

Unlike DDT, for which the ban in the 1970s led to rapidly declining applications, HCH remained an important plant protection product in the GDR until the state's end in 1990. Though a negative trend in the number of licensed products occurred, HCH was produced and used intensively in many fields of the GDR (e.g., agriculture, forest, hygiene, material protection, private), which led to highly contaminated agricultural soils (Heinisch and Klein 1992). Nevertheless, no HCH was found in the current study. This is probably due to its physico-chemical properties (Camenzuli et al. 2016) which influence its overall persistence. This is in line with the study of Bidleman et al. (2021) who examined the dissipation of HCH in Lake Superior, Canada. Between 1986 and 2016, concentrations declined by more than 90%. The authors identified volatilization as main removal process, followed by (hydrolytic and microbial) degradation and outflow through the draining river. Sedimentation was deemed minor.

Conclusion

In this study, 10 sediment profiles from 10 lakes in northeastern Germany (today's Mecklenburg-Western Pomerania and Brandenburg) covering an area of ca. 40,000 km^2 were analyzed for elemental and pesticide concentrations. The generated time series are the first of their kind for the examined area. As intended, they provided evidence of anthropogenic impact in the covered area. Indicators of the Industrial Revolution, the post-war recovery, and the beginning of environmental legislation measures in the 1960s and 1970s were found.

TE concentrations represented air emissions of inorganic pollutants from industrialized areas in western Germany and Europe, indicating industrial activity and policy making with long-range impact. OCP concentrations were consistent with local and regional use in agriculture and forestry, recording periods and single events of pesticide applications and their intensity with rather short-range impact. OCPs also provide evidence for anthropogenic developments and activities hidden from the general public in the former GDR. Concentrations of OCPs in deeper sediment layers exceeded toxic limits, while those on the surface of the lake bottom did not. Both elemental and OCP concentrations were heavily influenced by short- and long-range human activities and respective political and legal measures implemented through time.

Sedimentary TE profiles are in accordance with other forms of long-term monitoring, i.e., the European moss monitoring survey (UBA 2019) and are suited to complement and validate these and others, e.g., the Long-Term Ecological Research Network (LTER) and the Global Lake Ecological Observatory Network (GLEON). Furthermore, sedimentary TE profiles can be used as a relatively cheap and easy dating reference point for northeastern Germany for future paleolimnological works, i.e., as age models solely based on elemental patterns.

Complementing the results from this study with further data from lakes in southeastern Germany and from western Germany would be highly desirable to test for environmental impacts by short- and long-range human activities through time. This would also enable comparison between agricultural and industrial areas. Additional soil samples in combination with satellite observations of the different land-use areas around the lakes could supplement our theories and findings and facilitate inferences about the more recent situation. Lastly, if the analytical portfolio is extended with additional TPs of OCPs, conclusions about the

state of degradation could be made with more confidence. Overall, the current study proves the suitability of dated lacustrine sediments to reliably reconstruct anthropogenic development and disturbance events in the past, as well as retroactively assess the success of legislative regulatory measures.

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Data availability Data for this study were published open access (Simon et al. 2023). Additional figures and tables mentioned in the text are available as part of the Online Resource on the article's webpage (Supplementary file 1; PDF).

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

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3.2 Anhang zu Artikel 2

Electronic supplementary material to article

Dissent in the sediment? Lake sediments as archives of short- and long-range impact of anthropogenic activities in northeastern Germany

(https://doi.org/10.1007/s11356-023-28210-8)

Journal

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Data repository

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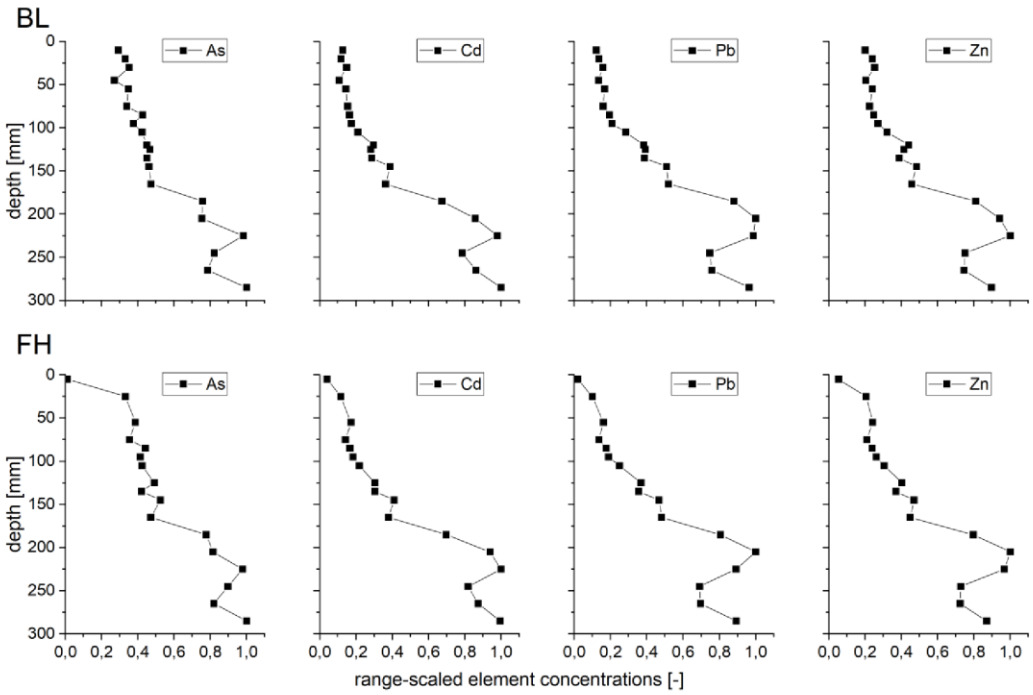

Fig. S1 Normalized concentration profiles of trace elements (TEs) As, Cd, Pb and Zn of cores from Lakes Breiter Luzin (BL) and Feldberger Haussee (FH) demonstrating similarities

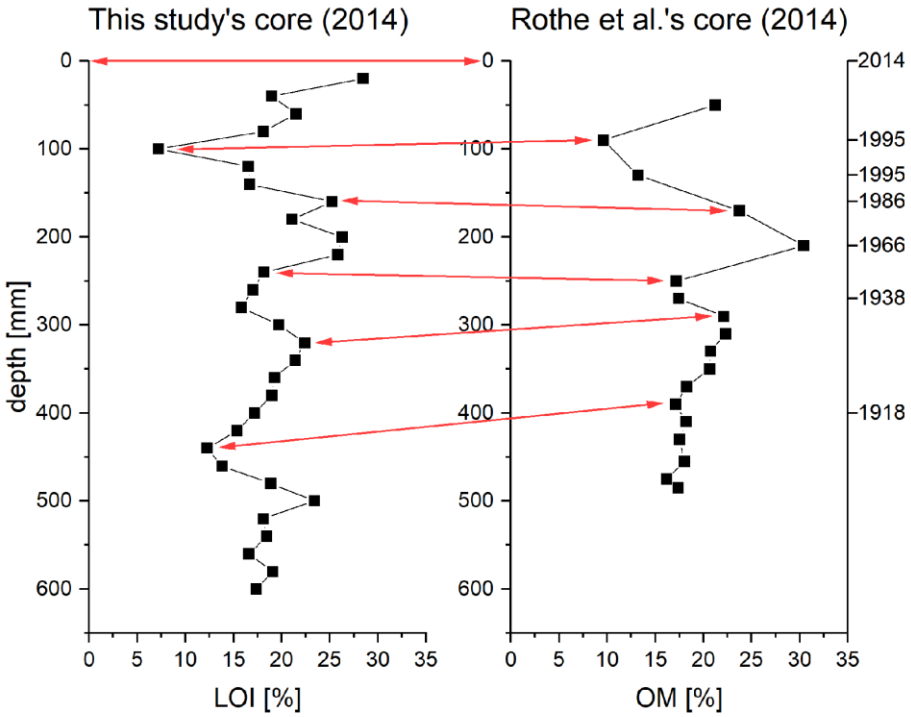

Fig. S2 Alignment of cores from Lake Arendsee (AR) from this study and of Rothe et al. (2015) via content of organic matter. LOI = loss on ignition, OM = organic matter

2

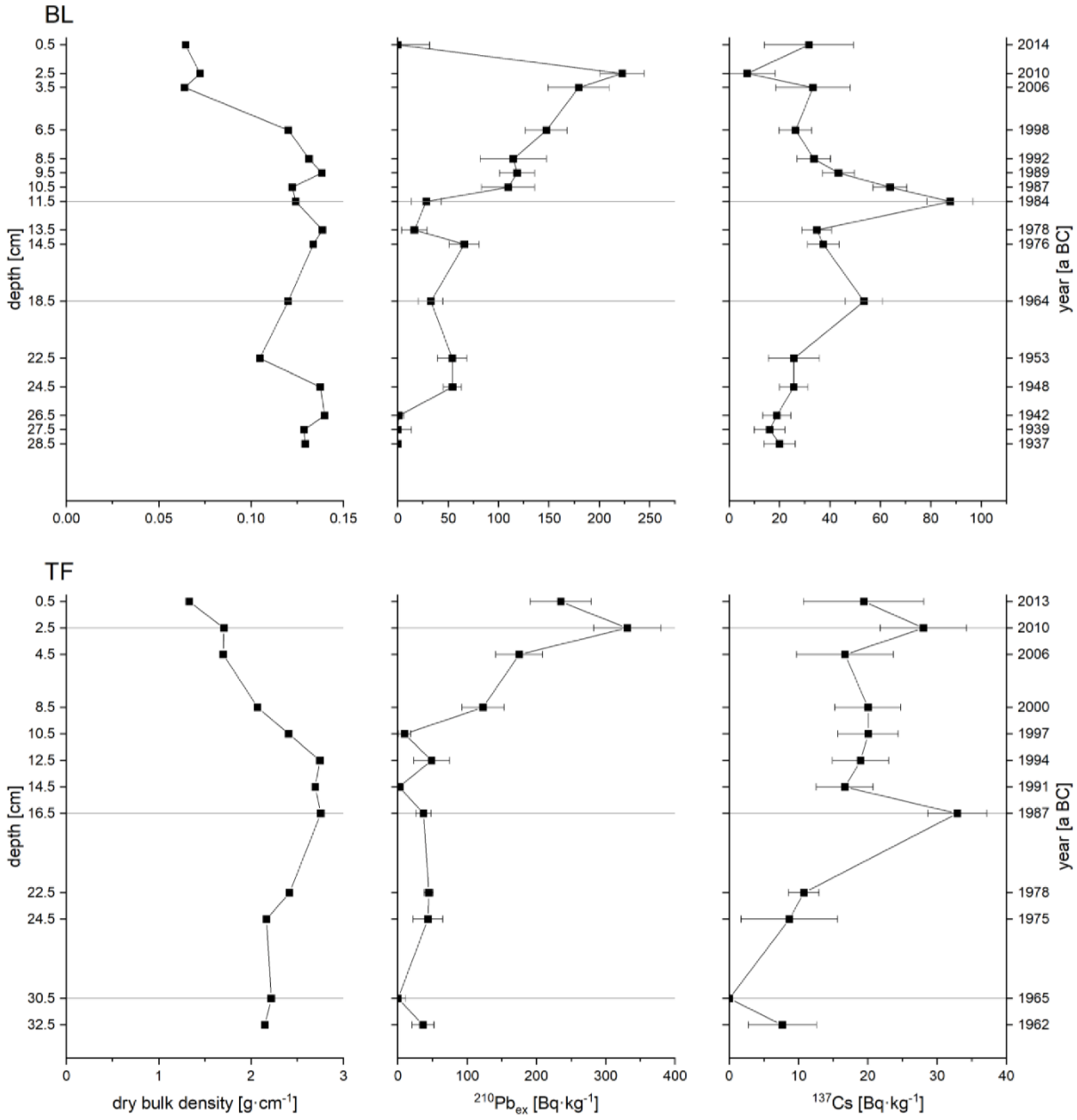

Fig. S3 Re-evaluated age models of cores from Lakes Breiter Luzin (BL) and Tiefwaren (TF)

Table S1 Microwave program for MAE-AR extraction

	Power (W)	Limit Temp. (°C)	Hold time (min)
Step 1	250	–	1
Step 2	250	–	15
Step 3	500	–	10
Ventilation	–	–	30

Table S2 Composition of the applied internal standard mix (stock solution)

Component	Concentration [µg·mL^{-1}]	Final concentration in sample [ng·mL^{-1}]
4,4'-DDE-D_8	5	1
4,4'-DDD-D_8	10	2
^{13}C-2,4'-DDT	15	3
^{13}C-4,4'-DDT	15	3
α-HCH-D_6	15	3

Table S3 Retention times and ions used to identify and quantify the analytes. RT = Retention time, IS = Internal standard. α-HCH-D_6 was used to correct all HCH congeners. 4,4'-DDE-D_8 was IS for both DDE congeners, and 4,4'-DDD-D_8 for both DDD congeners. The ^{13}C substituted IS were used to correct their respective unmarked counterparts

Name	Purpose	RT [min]	Quantifier [m·z^{-1}]	Qualifier [m·z^{-1}]
α-HCH-D_6	IS	21.15	224	185
α-HCH	Analyte	21.36	219	181
γ-HCH	Analyte	22.70	219	181
β-HCH	Analyte	23.92	219	181
δ-HCH	Analyte	24.98	219	181
2,4'-DDE	Analyte	29.02	246	318
4,4'-DDE-D_8	IS	30.37	254.2	326
4,4'-DDE	Analyte	30.46	246	318
2,4'-DDD	Analyte	30.82	235	165
^{13}C-2,4'-DDT	IS	32.00	247	177
2,4'-DDT	Analyte	32.01	235	165
4,4'-DDD-D_8	IS	32.38	243	173
4,4'-DDD	Analyte	32.50	235	165
^{13}C-4,4'-DDT	IS	33.68	247	177
4,4'-DDT	Analyte	33.68	235	165

Table S4 Number of data points included of each lake in the periods used to create the overview graph for *sum of trace elements* in Fig. 2

Period	Lake										No. of data points	No. of lakes included
	FH	BL	SL	CR	TF	OR	PL	AR	ST	WM		
2017-2013	1	1	0	1	0	2	1	0	1	0	7	6
2012-2008	1	2	1	1	2	1	1	1	1	1	12	10
2007-2003	0	1	1	1	2	1	1	1	1	1	10	9
2002-1998	1	1	1	0	1	2	0	2	0	1	9	7
1997-1993	1	1	0	1	2	2	1	1	1	0	10	8
1992-1988	2	2	1	0	1	3	1	1	0	1	12	8
1987-1983	2	2	1	1	2	2	1	1	0	0	12	8
1983-1978	2	3	0	0	1	1	0	2	1	1	11	7
1977-1973	1	1	1	1	0	2	1	1	0	1	9	8
1972-1968	1	1	1	1	1	1	1	1	0	1	9	9
1967-1963	1	1	0	0	1	1	1	1	1	1	8	8
1962-1958	1	1	1	0	1	1	1	1	0	1	8	8
1957-1953	1	1	0	1	1	1	0	1	0	1	7	7
1952-1948	1	1	1	0	0	0	1	1	0	1	6	6
1947-1943	0	0	0	0	0	1	1	2	1	1	6	5
1942-1938	1	1	1	1	0	0	1	1	0	1	7	7
1937-1933	1	1	1	0	0	0	0	1	0	1	5	5
1932-1928	0	0	0	0	0	0	1	1	0	1	3	3
1927-1923	0	0	0	1	0	0	0	2	1	1	5	4

Table S5 Number of data points included of each lake in the periods used to create the overview graph for *sum of DDX* in Fig. 2

Period	Lake										No. of data points	No. of lakes included
	FH	BL	SL	CR	TF	OR	PL	AR	ST	WM		
2017-2013	1	0	1	1	0	2	1	0	0	0	6	5
2012-2008	2	1	1	1	2	1	1	1	1	0	11	9
2007-2003	1	2	0	1	2	1	1	1	1	0	10	8
2002-1998	1	1	1	0	1	2	0	1	0	0	7	6
1997-1993	1	1	0	1	2	2	1	0	0	0	8	6
1992-1988	2	2	1	0	1	3	1	0	0	0	10	6
1987-1983	1	2	1	1	2	1	1	0	0	0	9	7
1983-1978	1	2	0	0	1	1	0	2	2	0	9	6
1977-1973	0	1	1	1	0	2	1	1	1	0	8	7
1972-1968	2	1	1	1	1	1	1	0	1	0	9	8
1967-1963	1	1	0	0	1	1	1	1	1	0	7	7
1962-1958	1	1	1	0	1	1	1	0	2	0	8	7
1957-1953	2	1	0	1	1	1	0	0	1	0	7	6
1952-1948	1	1	1	0	0	0	1	0	0	0	4	4
1947-1943	1	0	0	0	0	1	1	0	1	0	4	4
1942-1938	1	1	1	1	0	0	1	0	1	0	6	6
1937-1933	0	1	1	0	0	0	0	0	0	0	2	2
1932-1928	1	0	0	0	0	0	1	0	1	0	3	3
1927-1923	0	0	0	1	0	0	0	0	2	0	3	2

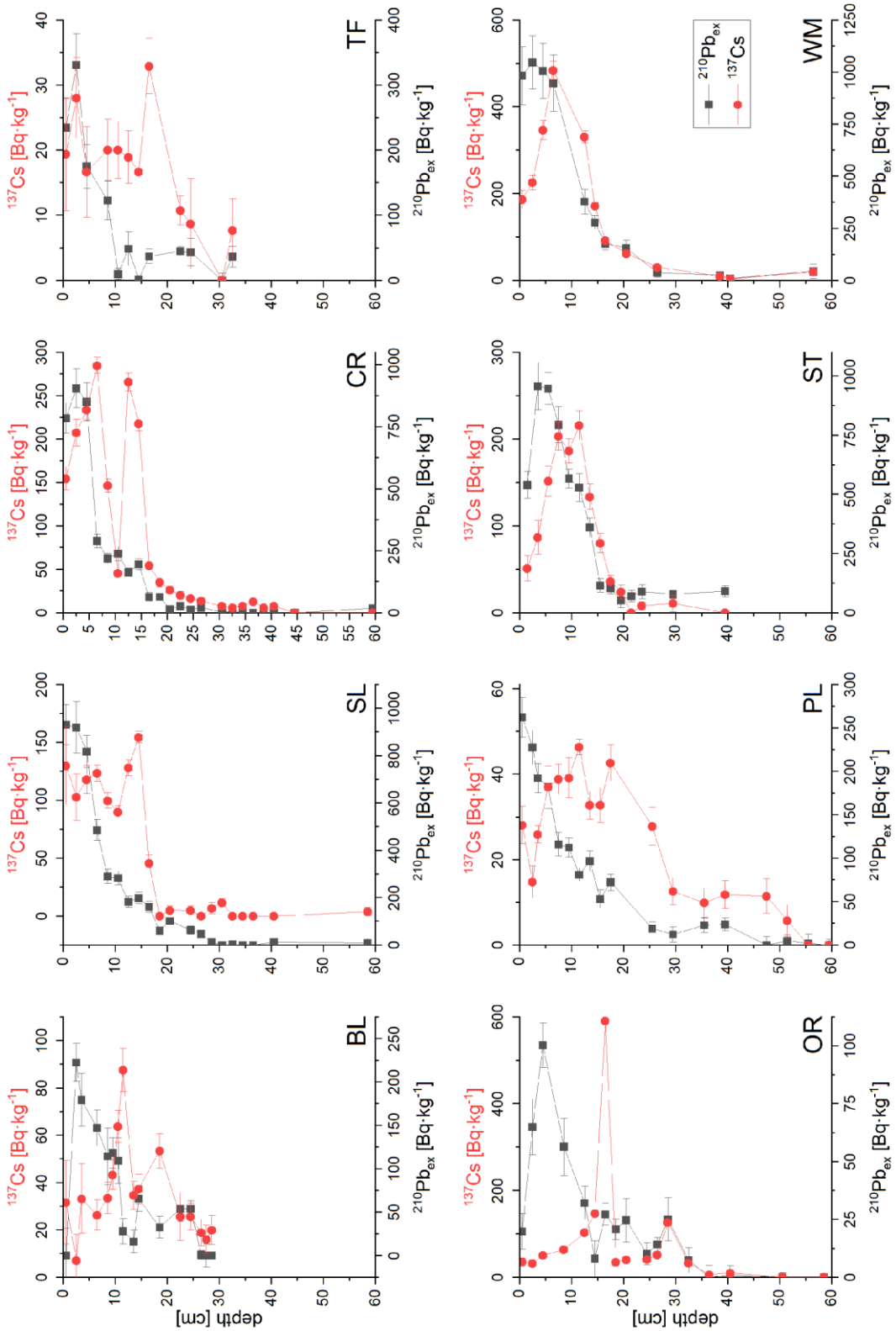

Fig. S4 Activities of isotopes ^{210}Pb (red) and ^{137}Cs (dark gray) per depth in each lake profile. Error bars depict standard deviation

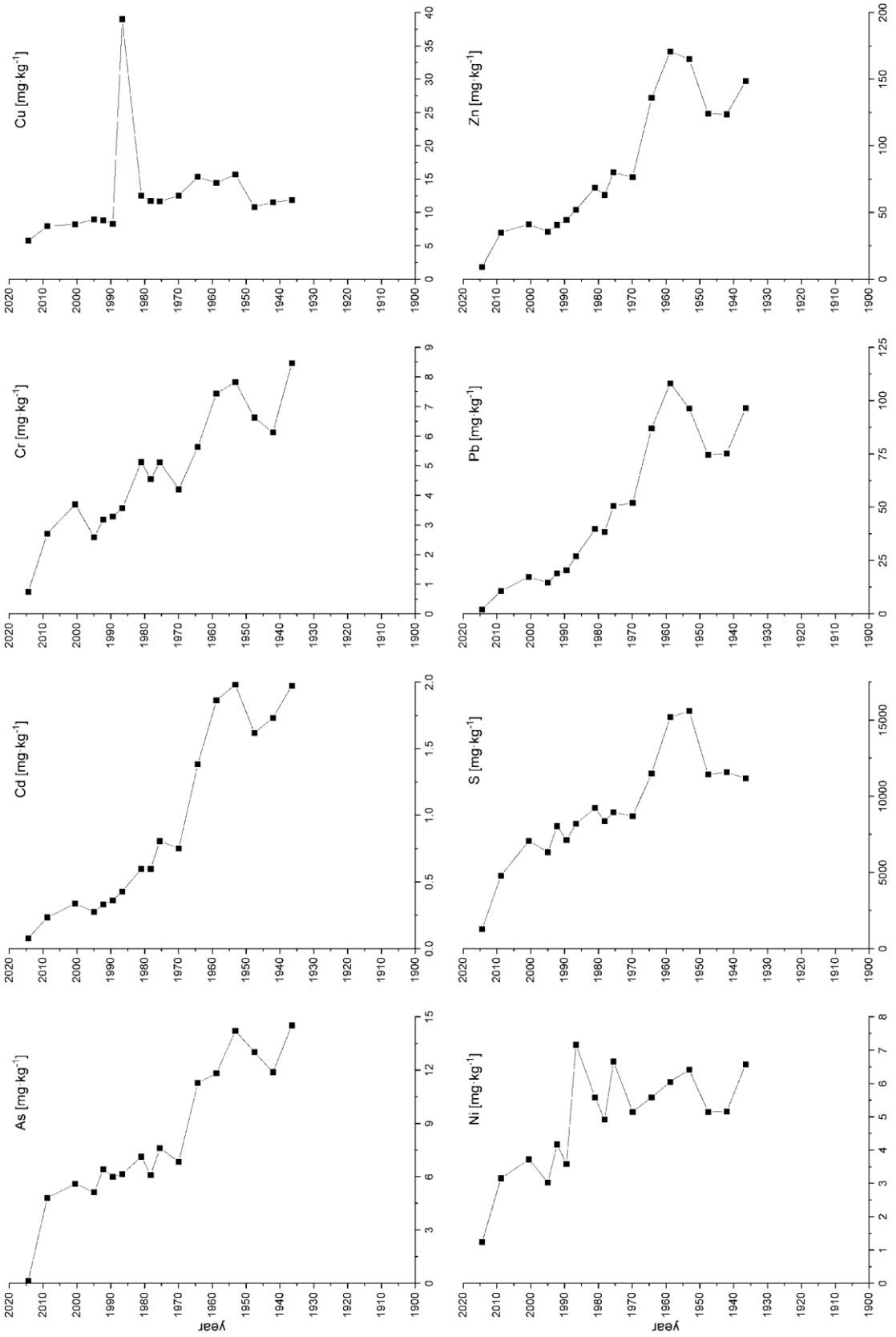

Fig. S5 TE concentrations of the core from Lake Feldberger Haussee (FH) in mg·kg^{-1}. Please note the differing x-axes

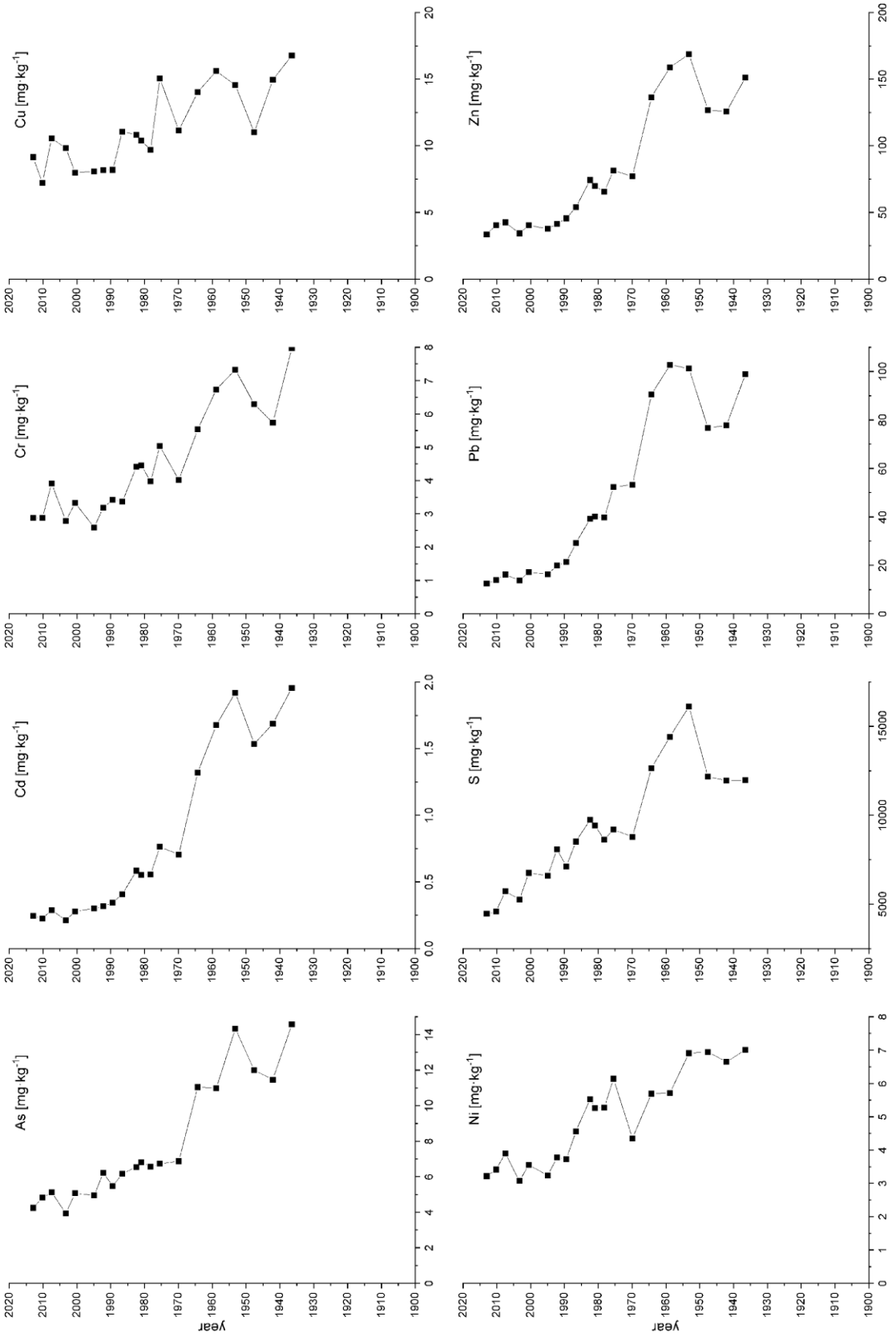

Fig. S6 TE concentrations of the core from Lake Breiter Luzin (BL) in mg·kg^{-1}. Please note the differing x-axes

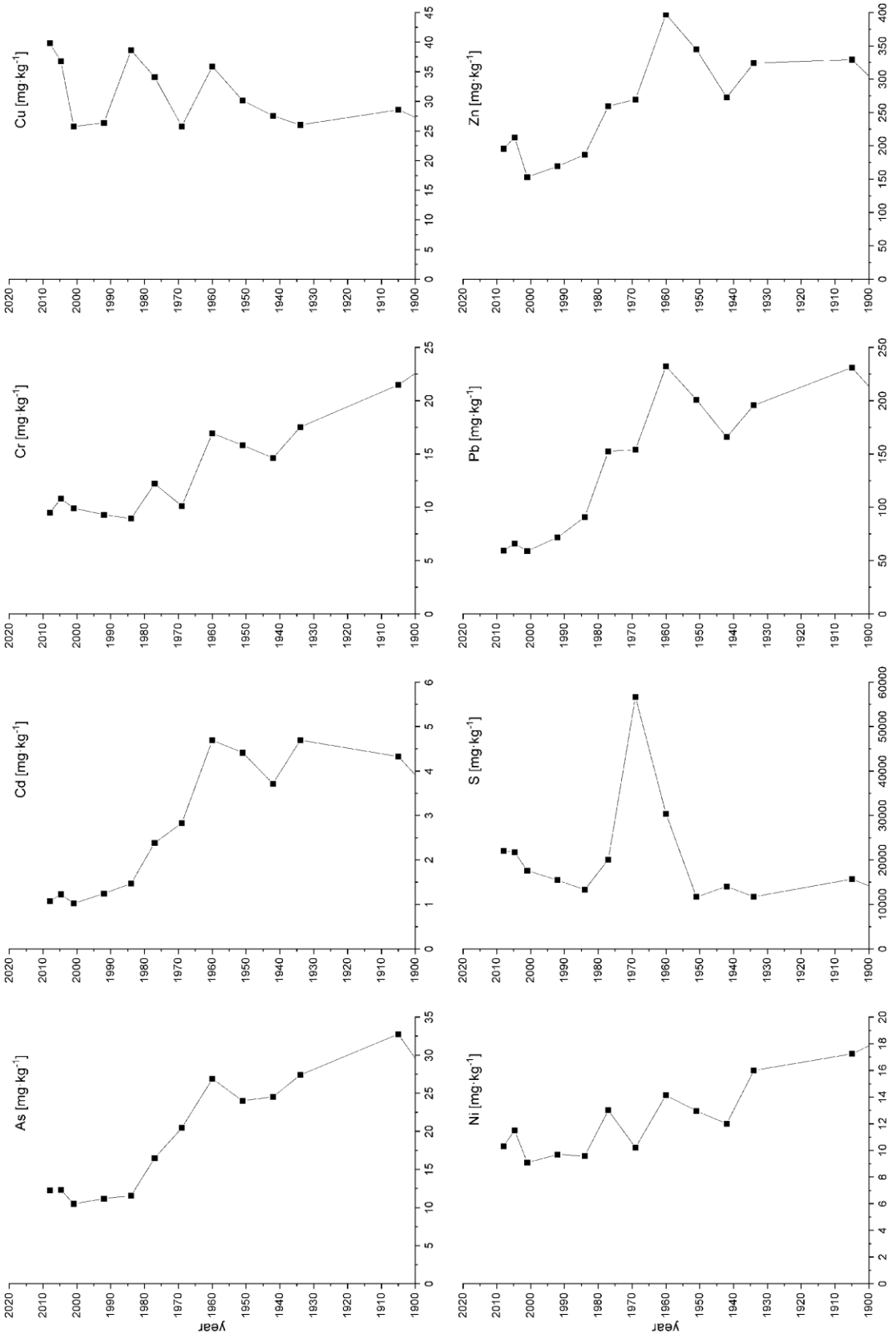

Fig. S7 TE concentrations of the core from Lake Schmaler Luzin (SL) in mg·kg^{-1}. Please note the differing x-axes

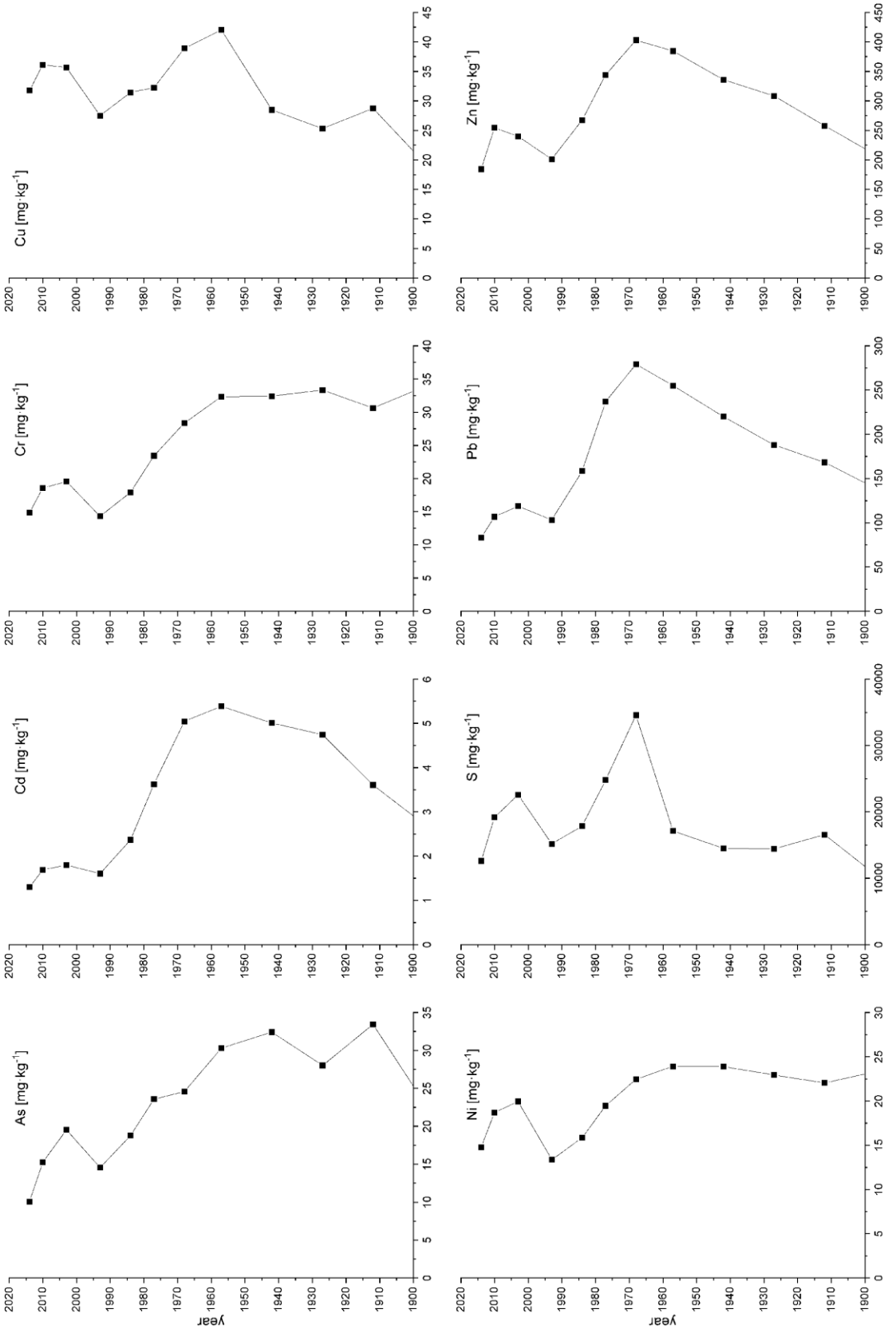

Fig. S8 TE concentrations of the core from Lake Carwitzer (CR) in mg·kg^{-1}. Please note the differing x-axes

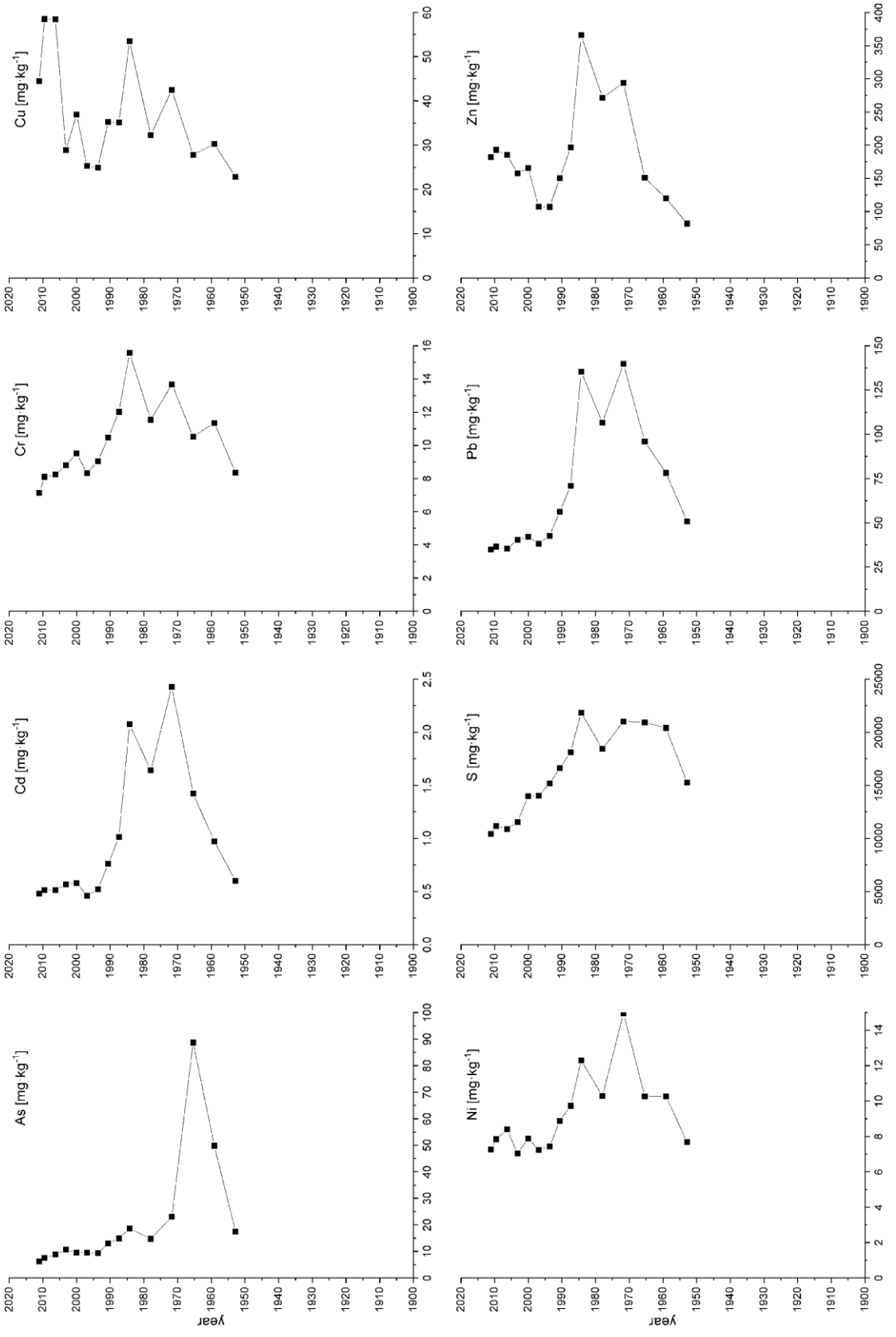

Fig. S9 TE concentrations of the core from Lake Tiefwaren (TF) in mg·kg^{-1}. Please note the differing x-axes

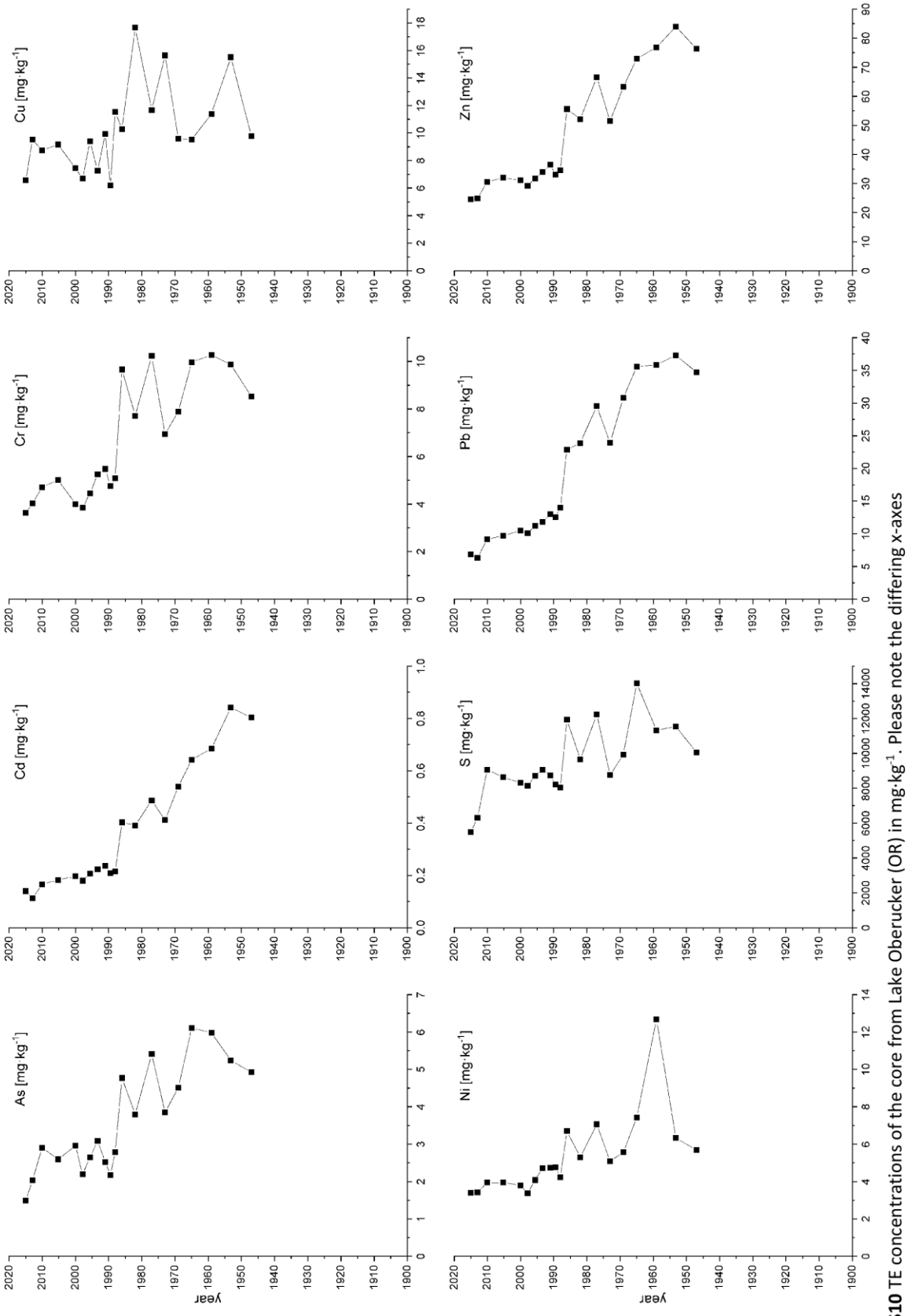

Fig. S10 TE concentrations of the core from Lake Oberucker (OR) in mg·kg^{-1}. Please note the differing x-axes

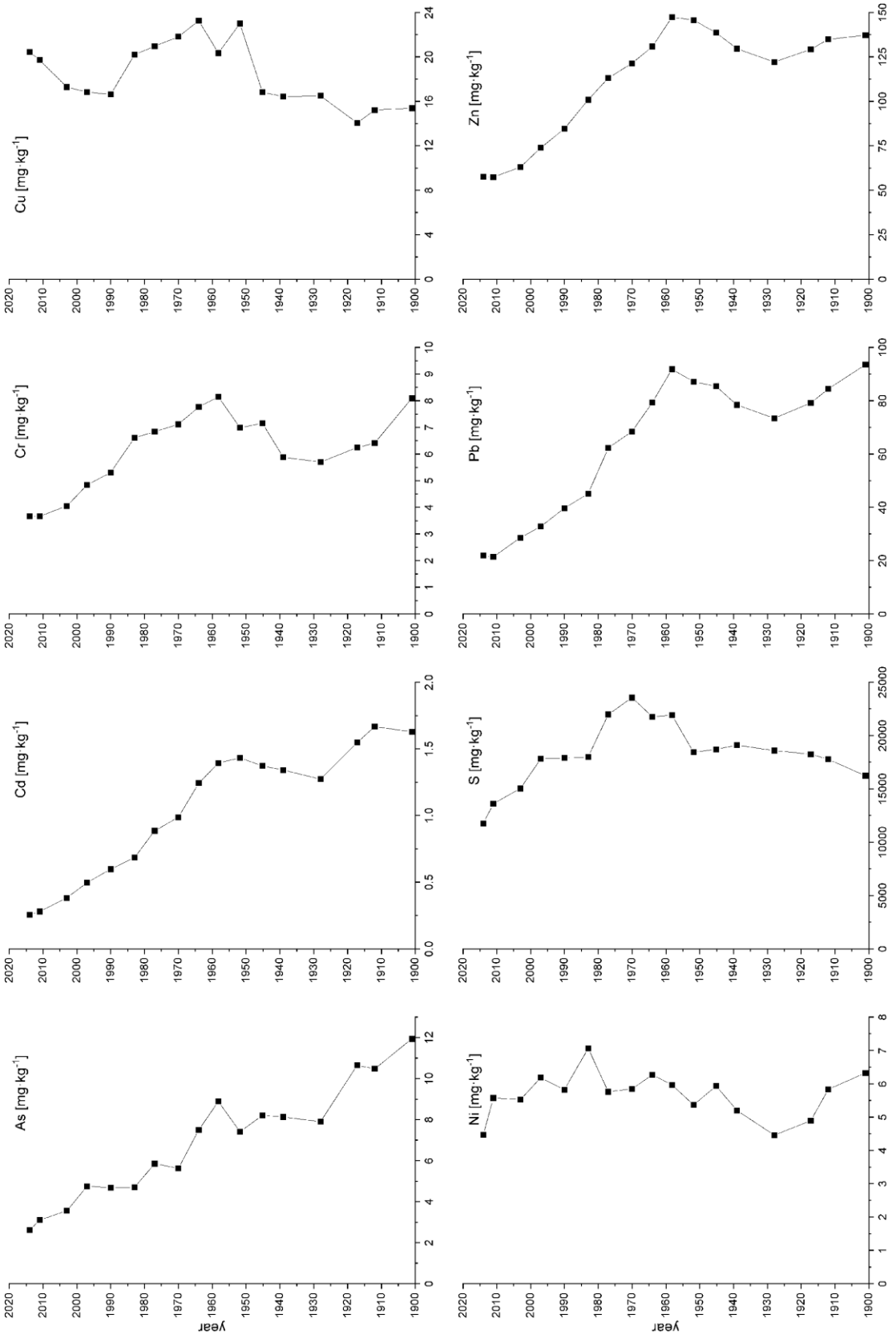

Fig. S11 TE concentrations of the core from Lake Scharmützel (PL) in mg·kg^{-1}. Please note the differing x-axes

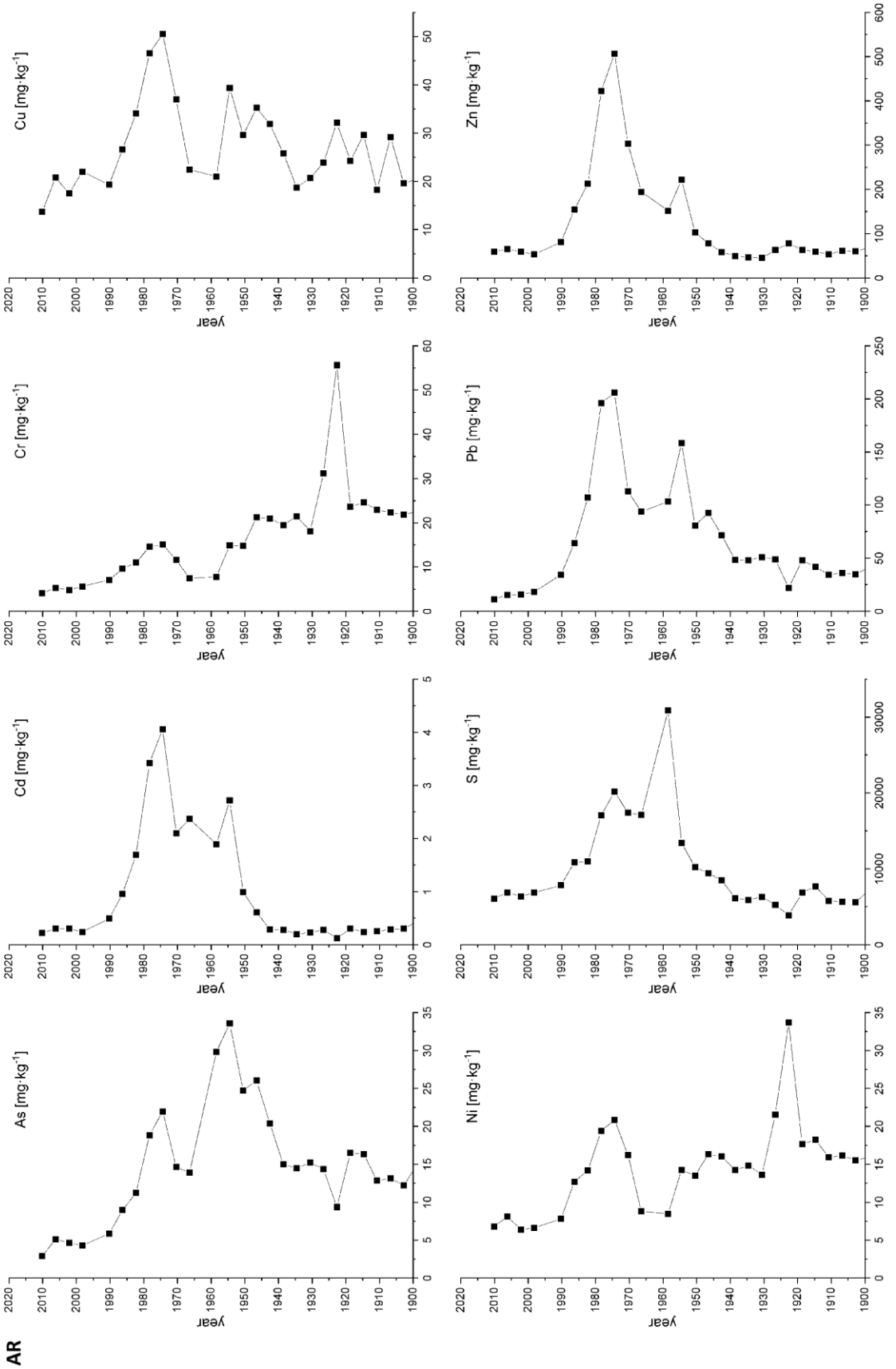

Fig. S12 TE concentrations of the core from Lake Arend (AR) in mg·kg^{-1}. Please note the differing x-axes

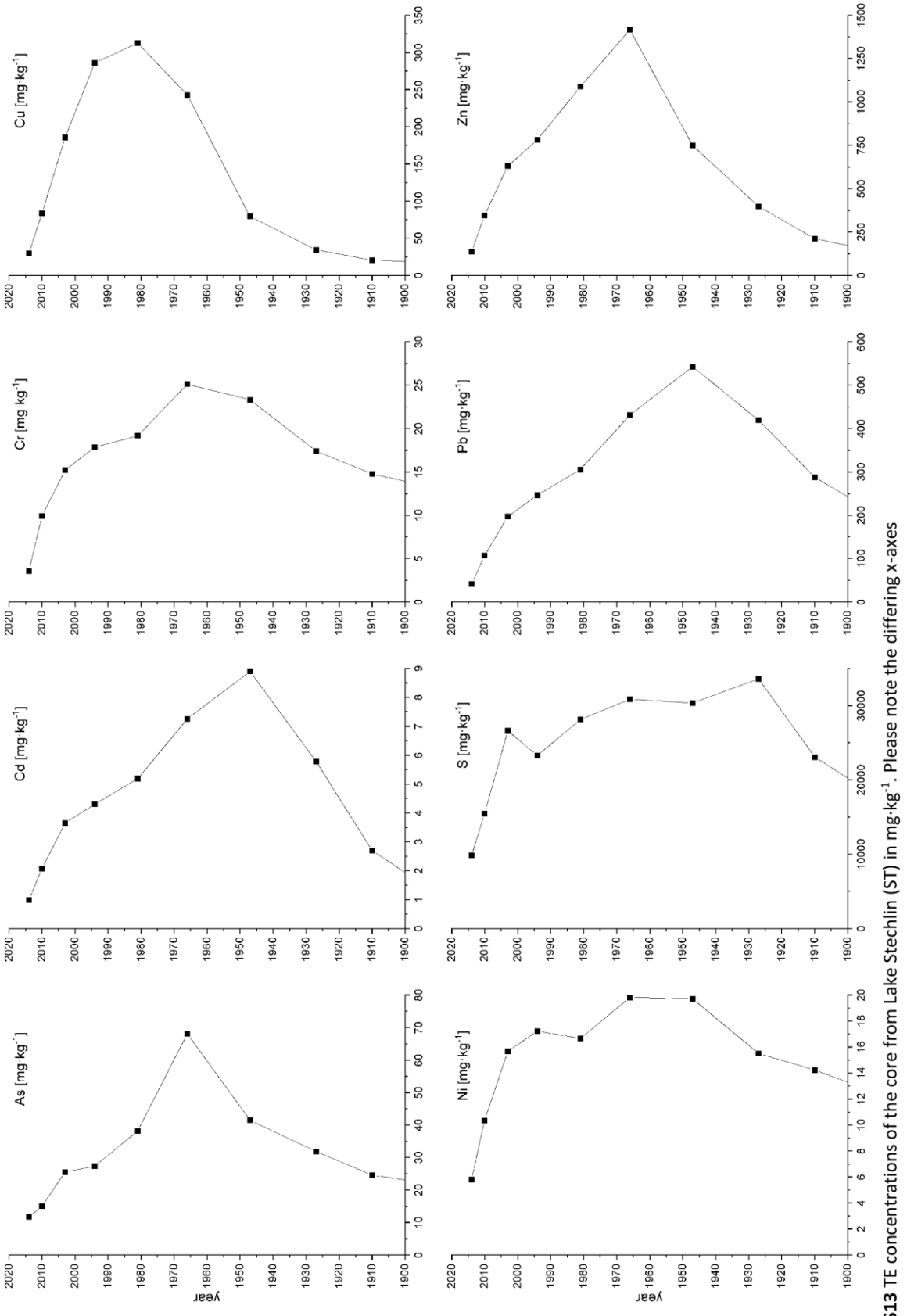

Fig. S13 TE concentrations of the core from Lake Stechlin (ST) in mg·kg^{-1}. Please note the differing x-axes

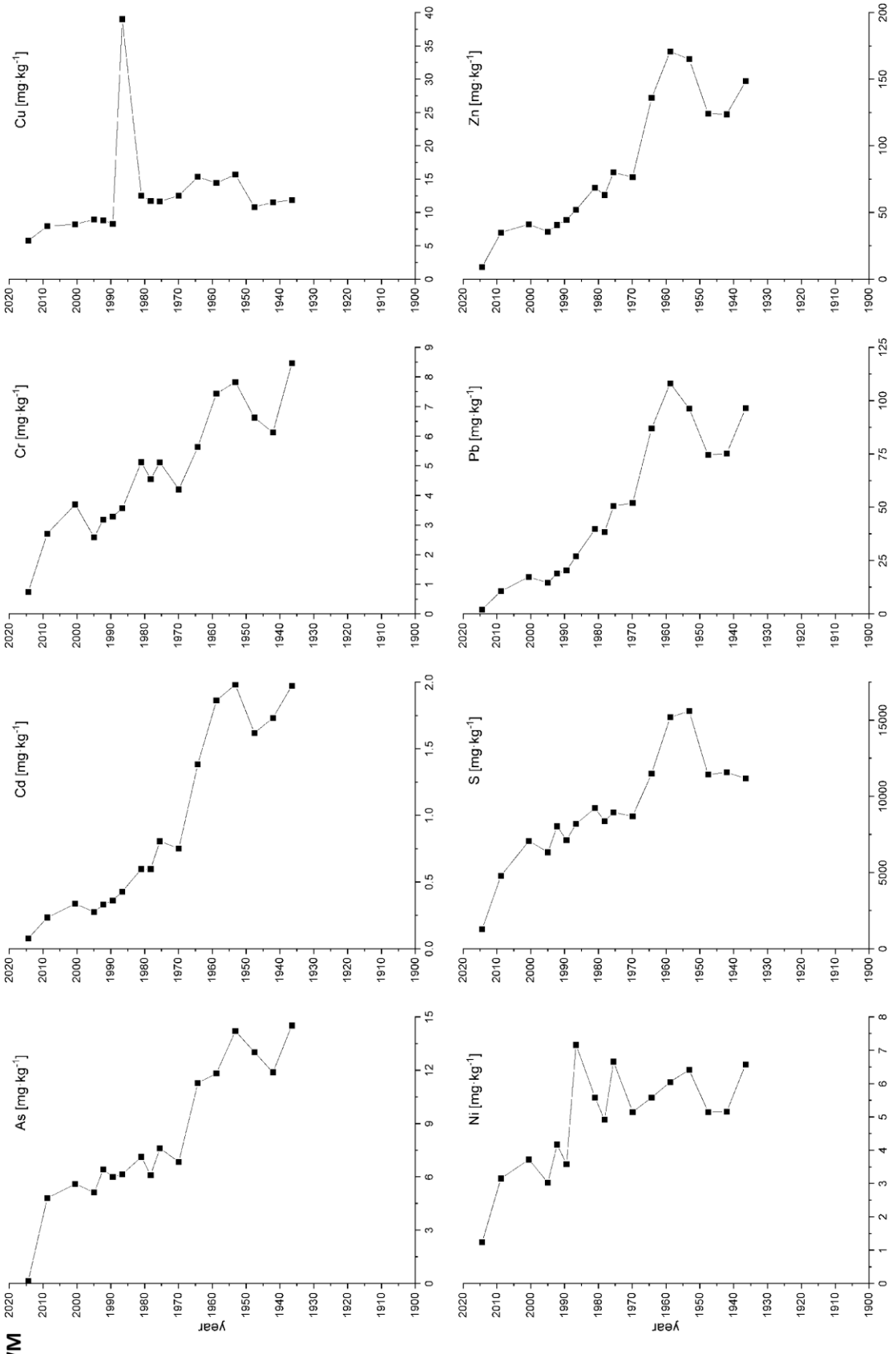

Fig. S14 TE concentrations of the core from Lake Wumm (WM) in mg·kg^{-1}. Please note the differing x-axes

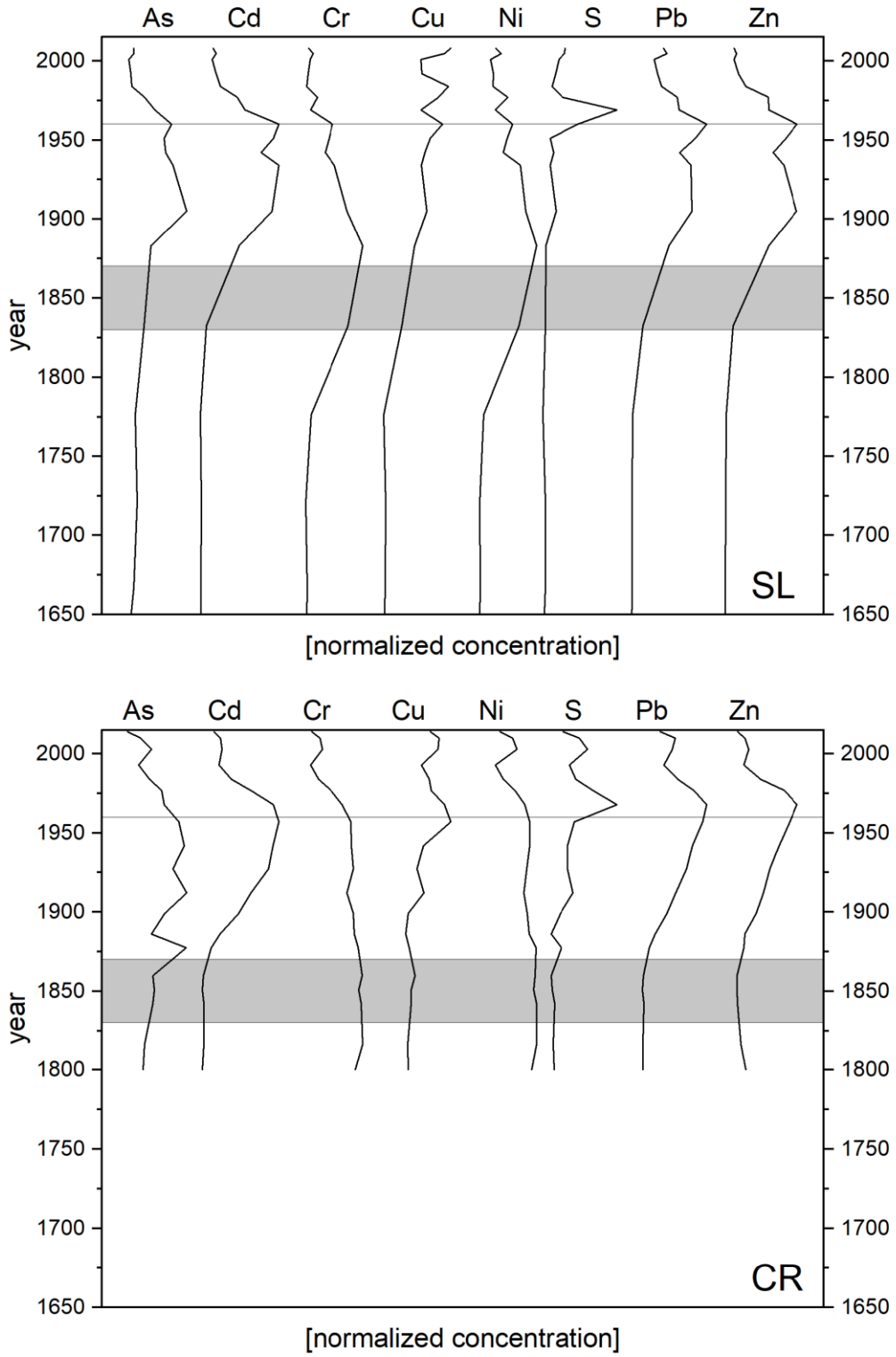

Fig. S15 Normalized TE concentrations of the cores from Lakes Schmaler Luzin (SL) and Carwitzer (CR) that cover time periods before 1900. Gray area shows beginning phase of Industrial Revolution in Germany. Gray line shows the year 1964 when West Germany implemented its first air pollution control regulation

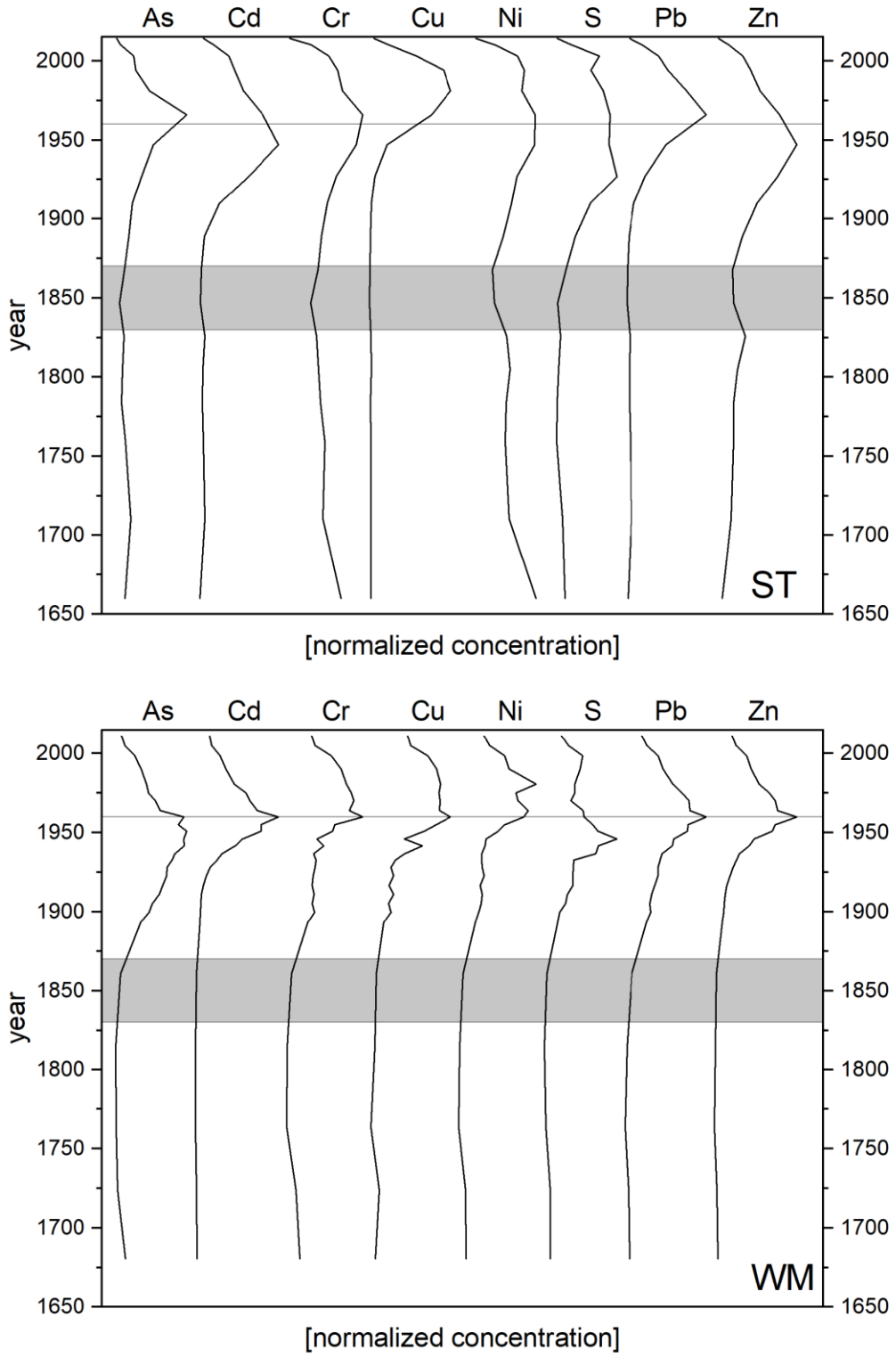

Fig. S16 Normalized TE concentrations of the cores from Lakes Stechlin (ST) and Wumm (WM) that cover time periods before 1900. Gray area shows beginning phase of Industrial Revolution in Germany. Gray line shows the year 1964 when West Germany implemented its first air pollution control regulation

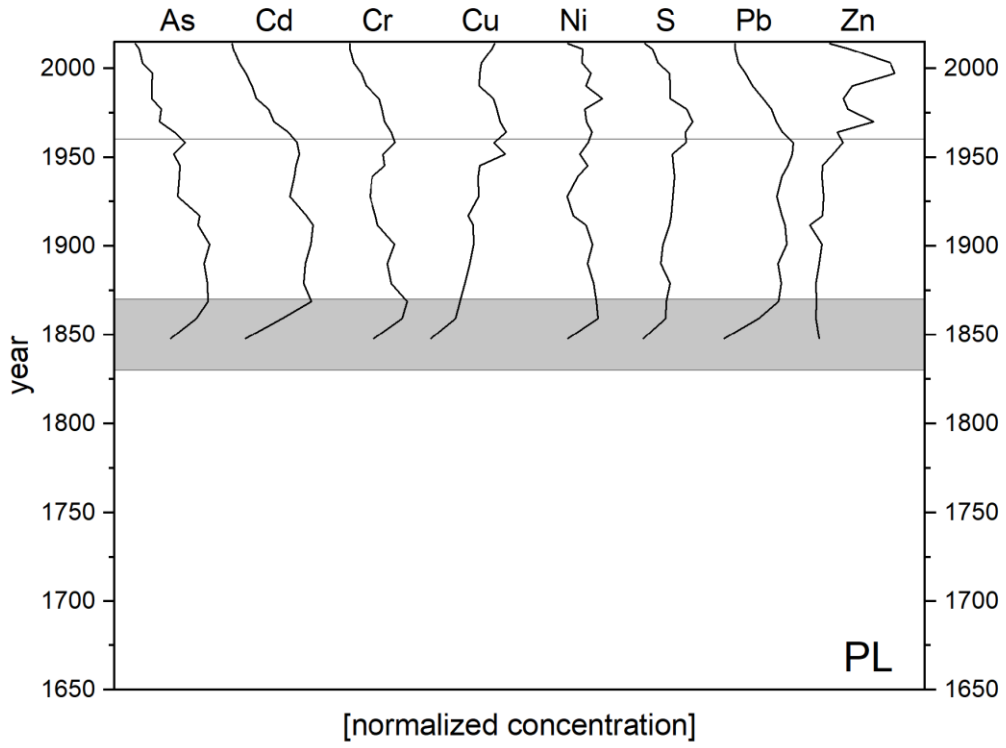

Fig. S17 Normalized TE concentrations of the core from Lake Scharmützel (PL) that covers time periods before 1900. Gray area shows beginning phase of Industrial Revolution in Germany. Gray line shows the year 1964 when West Germany implemented its first air pollution control regulation

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Rothe M, Kleeberg A, Grüneberg B, Friese K, Pérez-Mayo M, Hupfer M (2015) Sedimentary Sulphur:Iron Ratio Indicates Vivianite Occurrence: A Study from Two Contrasting Freshwater Systems. PLoS ONE 10:e0143737. https://doi.org/10.1371/journal.pone.0143737

4 Liste begutachteter Veröffentlichungen

Die untenstehende Liste zeigt alle begutachteten Publikationen, die während der Promotionsphase angefertigt wurden:

Woldetsadik, D., **Simon, M.P.**, Knuth, D., Hailu, H., Gebresilassie, A., Dejen, A., Düring, R.-A. (2021) Exposure to DDT and HCH congeners and associated potential health risks through khat (*Catha edulis*) consumption among adults in South Wollo, Ethiopia. Environ Geochem Health 43, 3597–3613. DOI: 10.1007/s10653-021-00846-w

> Beteiligung der Autor:innen: *Desta Woldetsadik*: Konzept, Verfassen der Erstfassung des Manuskripts, Korrektur des Manuskripts, Probenahme. **Marcel Pierre Simon**, *Dennis Knuth*: Probenvorbereitung, Entwicklung und Validierung der chemischen Analyse, Korrektur des Manuskripts. *Hillette Hailu*, *Araya Gebresilassie*, *Asmare Dejen*: Probenahme, Berechnung von Gefährdungsindex (hazard index, HI) und Krebsrisiko (cancer risk, CR), Korrektur des Manuskripts.

Simon, M.P., Knuth, D., Böhm, L., Wiltschka, K., Schatz, M., Düring, R.-A. (2022) A miniaturized method for fast, simple, and sensitive pesticide analysis in soils. J Soils Sediments 22, 496–508 (2022). DOI: 10.1007/s11368-021-03080-0

> Beteiligung der Autor:innen: **Marcel Pierre Simon**: Entwicklung und Validierung der Methode, formale Analyse, Untersuchung, Datenkuratierung, Verfassen der Erstfassung des Manuskripts, Korrektur des Manuskripts, Visualisierung. *Dennis Knuth*, *Katrin Wiltschka*: Entwicklung und Validierung der Methode, formale Analyse, Untersuchung, Korrektur des Manuskripts. *Marlene Schatz*: Entwicklung und Validierung der Methode, Untersuchung, Korrektur des Manuskripts. *Rolf-Alexander Düring*: Konzept, Entwicklung und Validierung der Methode, Untersuchung, Ressourcen, Korrektur des Manuskripts, Betreuung, Fördermittelakquise, Projektverwaltung.

Lud, D., Schwemm, A., Kalandadze, B., Babaev, E., **Simon, M.P.**, Weller, P., Düring R.-A. (2022) Pesticide handling and waste management: a case study on DDT and HCHs from the Southern Caucasus. SN Appl. Sci. 4, 112. DOI: 10.1007/s42452-022-04999-w

> Beteiligung der Autor:innen: *Daniela Lud*: Konzept, Methodik, formale Analyse, Untersuchung, Verfassen der Erstfassung des Manuskripts, Korrektur des Manuskripts, Fördermittelakquise, Betreuung. *Annika Schwemm*: Konzept, formale Analyse, Untersuchung, Verfassen der Erstfassung des Manuskripts, Korrektur des Manuskripts. *Besik Kalandadze*: formale Analyse, Untersuchung, Korrektur des Manuskripts. *Elbay Babaev*, **Marcel Pierre Simon**, *Philipp Weller*: Korrektur des Manuskripts. *Rolf-Alexander Düring*: Konzept, Methodik, Korrektur des Manuskripts, Fördermittelakquise, Betreuung.

Simon, M.P., Schatz, M., Böhm, L., Papp, I., Grossart, H.-P., Andersen, T.J., Bálint, M., Düring R.-A. (2023) Dissent in the sediment? Lake sediments as archives of short- and long-range impact of anthropogenic activities in northeastern Germany. Environ Sci Pollut Res 30, 85867–85888. DOI: 10.1007/s11356-023-28210-8

Beteiligung der Autor:innen: **Marcel Pierre Simon**: Methodik, Validierung, formale Analyse, Untersuchung, Datenkuratierung, Verfassen der Erstfassung des Manuskripts, Korrektur des Manuskripts, Visualisierung. *Marlene Schatz*: Methodik, Validierung, formale Analyse, Untersuchung, Korrektur des Manuskripts. *István Papp*: Validierung, Korrektur des Manuskripts. *Hans-Peter Grossart*: Ressourcen, Korrektur des Manuskripts. *Thorbjørn Joest Andersen*: Validierung, Untersuchung, Korrektur des Manuskripts. *Miklós Bálint*: Konzept, Methodik, Validierung, Untersuchung, Ressourcen, Korrektur des Manuskripts, Betreuung, Projektverwaltung, Fördermittelakquise. *Rolf-Alexander Düring*: Konzept, Validierung, Ressourcen, Korrektur des Manuskripts.

Darin zitierter, veröffentlichter Datensatz:
Simon, M.P., Schatz, M., Böhm, L., Papp, I., Grossart, H.-P., Andersen, T.J., Bálint, M., Düring R.-A. (2023): Concentrations of selected elements and organochlorine pesticides in layers of dated sediment cores of ten lakes in northeastern Germany [dataset]. PANGAEA. DOI: 10.1594/PANGAEA.951049

Woldetsadik, D., **Simon, M.P.**, Knuth, D., Hailu, H., Sims, D.B., Asmame, B., Seid, A., Motuma, M., Düring, R.-A. (Eingereicht 2024) Distribution, source apportionment and potential risk of DDT and HCH congeners and metal(oid)s in soils under different land-use types in Ankerkah sub-watershed, South Wollo, Ethiopia. Environ Geochem Health. Hillette Hailu:

Beteiligung der Autor:innen: *Desta Woldetsadik*: Konzept, Probenahme, Verfassen der Erstfassung des Manuskripts, Korrektur des Manuskripts. **Marcel Pierre Simon**, *Dennis Knuth*, *Rolf-Alexander Düring*: Probenvorbereitung, Entwicklung und Validierung der chemischen Analyse, Korrektur des Manuskripts. *Hillette Hailu*: Konzept, Probenahme, Datenkuration, Validierung, Korrektur des Manuskripts. *Douglas B. Sims*: Datenkuration, Validierung, Korrektur des Manuskripts. *Birhan Asmame*, *Ali Seid*: Probenahme, Datenkuration, Validierung, Korrektur des Manuskripts. *Mohammed Motuma*: Datenkuration, Validierung, Korrektur des Manuskripts.

5 Liste von Tagungsbeiträgen als Erstautor

Die folgende Liste zeigt alle Beiträge die auf Tagungen präsentiert wurden – entweder in Form eines Posters oder Vortrags:

Simon, M.P., Düring R.-A.: OCP-belastete Böden im Südkaukasus: Monitoring und Minderung. Tagung der Deutschen Bodenkundlichen Gesellschaft (DBG) 2017, Göttingen, Deutschland. Poster.

Simon, M.P., Bálint, M., Düring, R.-A.: Ein Jahrhundert Landnutzungswandel in Mecklenburg-Vorpommern: Organochlorpestizide und Metalle in Seesedimentbohrkernen. Tagung der Society of Environmental Toxicology and Chemistry – German Language Branch (SETAC-GLB) 2017, Neustadt/Weinstraße, Deutschland. Poster.

Simon, M.P., Schmid, H.M., Thiel, M., Düring, R.-A.: Dissipation von Ivermectin – Spielt die Aufnahme in Pflanzen eine Rolle? Tagung der SETAC-GLB 2018, Münster, Deutschland. Poster.

Simon, M.P., Babayev, E.R., Kalandadze, B., Lud, D., Weller, P., Düring, R.-A.: Tensidverstärkte Phytoremediation organochlorpestizidbelasteter Böden. Tagung der DBG 2019, Bern, Schweiz, sowie Tagung der SETAC-GLB 2019, Landau, Deutschland. Poster.

Simon, M.P.: Reconstructing Agriculture and Industrial Activity with Lake Sediments. First Digital GGL Annual Conference 2020, Gießen, Deutschland. Vortrag.

6 Danksagung

Auch wenn es vielleicht den Anschein haben mag, schreiben sich wissenschaftliche Arbeiten nie völlig allein. Manch eine:r mag nun an die wohlbekannte Phrase »Zwerge auf den Schultern von Riesen« denken, die aussagt, dass jede:r Wissenschaftler:in auf dem gesammelten Wissen und der Arbeit aller vorherigen Generationen aufbaut. Damit liegen sie nicht verkehrt. Doch meine ich hier allem voran die Unterstützung im Zwischenmenschlichen, Nichtakademischen.

Ich danke meinem Doktorvater Prof. Dr. Rolf-Alexander Düring. Zu allererst dafür, mir unbekannterweise die Chance gegeben zu haben, einen Projektantrag zu verfassen und schließlich eine Promotion zu beginnen. Aber vor allem natürlich danke ich für die unermüdliche Betreuung, dass ich immer fragen konnte und er sich Zeit für mich nahm. Auch bin ich dankbar dafür, dass ich Gelegenheiten hatte, meine Fühler außerhalb meines Promotionsthemas auszustrecken.

Ich möchte ebenfalls Prof. Dr. Holger Zorn für sein Interesse am Thema sowie seine Bereitschaft danken, als zweiter Gutachter zu fungieren. Ebenso danke ich Prof. Dr. Thomas Degenkolb und Prof Dr. Till Kleinebecker dafür, die Rolle der Prüfer zu übernehmen.

Ich danke besonders meinen Kolleg:innen und Mitstreiter:innen. Der Austausch und die Unterstützung – weniger auf fachlicher, vielmehr auf persönlicher Seite – war unbezahlbar. Ganz besonders dankbar bin ich Andre Heinrich, Benjamin Heyde, Katrin Wiltschka und Nadja Küpper. Ich weiß nicht, ob ich es ohne euch geschafft hätte.

Ich danke den TAs der Bodenkunde: Elke Müller, Elke Schneidenwind und Jolanta Lyko. Vielen Dank für die Einarbeitung im Labor, die Hilfe mit den Messungen, das offene Ohr und den Zuspruch.

Ich möchte mich bei allen HiWis und Studis bedanken, die dazu beigetragen haben, dass diese Promotion vollendet wurde. Hätte ich alle Extraktionen selbst erledigen müssen – ich säße wohl immer noch daran. Vielen Dank Dennis Knuth und Leoni König, aber auch allen anderen, die ich hier nicht namentlich nenne.

Mein ganz besonderer Dank geht an meinen Friedel Martin, für den Rückhalt und das Verständnis – vor allem in den schwierigen Zeiten. Aber auch dafür, mir zu zeigen, dass es neben Promotionen tatsächlich noch andere Dinge in der Welt gibt.

Zu guter Letzt danke ich meiner Familie: meinen Eltern Erika und Karlheinz und meiner Schwester Nadine. Vielen Dank, dass ihr mich auf dem Weg begleitet und wie selbstverständlich unterstützt habt. Ohne das wäre ich wohl nicht, wo ich jetzt bin.

7 Eidesstattliche Erklärung

Ich erkläre: Ich habe die vorgelegte Dissertation selbstständig und ohne unerlaubte fremde Hilfe und nur mit den Hilfen angefertigt, die ich in der Dissertation angegeben habe. Alle Textstellen, die wörtlich oder sinngemäß aus veröffentlichten Schriften entnommen sind, und alle Angaben, die auf mündlichen Auskünften beruhen, sind als solche kenntlich gemacht. Ich stimme einer evtl. Überprüfung meiner Dissertation durch eine Antiplagiat-Software zu. Bei den von mir durchgeführten und in der Dissertation erwähnten Untersuchungen habe ich die Grundsätze guter wissenschaftlicher Praxis, wie sie in der „Satzung der Justus-Liebig-Universität Gießen zur Sicherung guter wissenschaftlicher Praxis“ niedergelegt sind, eingehalten.

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Marcel Pierre Simon