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Landwirtschaftliche Nutzung organischer Siedlungsabfälle vor dem Hintergrund eines nachhaltigen Boden- und Verbraucherschutzes

Habilitationsschrift

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Vorwort

"Alle in Fäulnis oder Verwesung übergegangene organische Substanzen enthalten die Materie zur Hervorbringung... jeder angebauter Vegetabilien."
(Albrecht Daniel Thaer 1752 – 1828)

Mit der vorliegenden kumulativen Habilitationsschrift werden Teilbereiche des Forschungsgebietes zur nachhaltigen Nutzung organischer Siedlungsabfälle in der Landwirtschaft vorgestellt. Diese Forschungsdisziplin kann nicht erschöpfend bearbeitet werden, jedoch sollen hier der aktuelle Erkenntnisstand und – daraus abgeleitet – weiterer Forschungsbedarf mit Handlungsempfehlungen vorgestellt werden. Einzelne Schwerpunkte zu den grundlegenden Prozessen im System Abfall-Boden-Pflanze werden hier behandelt, um ein vertieftes Verständnis für eine umweltgerechte Nutzung organischer Abfälle in der Landwirtschaft zu erlangen. Diese Aspekte werden im ersten Teil dieser Arbeit mit den deutschen Zusammenfassungen der im Anhang angefügten Originalarbeiten zusammengeführt.

Dieses angewandte, disziplinenübergreifende Gebiet zu bearbeiten wurde mir ermöglicht am Institut für Landschaftsökologie und Ressourcenmanagement, Professur für Abfall- und Ressourcenmanagement. Das Institut ist seit dem Frühjahr des Jahres 2000 eingebunden in das neu geschaffene Interdisziplinäre Forschungszentrum für biowissenschaftliche Grundlagen der Umweltsicherung (IFZ für Umweltsicherung). Hier wird, nach einer Aufbauphase, interdisziplinäres Arbeiten in besonderem Maße gefördert. Das in dieser anregenden Atmosphäre vorherrschende freundschaftliche Miteinander hat mir mehr als die notwendigen Möglichkeiten und Impulse für meine Arbeit gegeben. Dafür danke ich allen Kollegen, Helfern und beteiligten Diplomanden des Instituts.

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B Düring, R.-A., T. Hoß und S. Gäth (2002): Depth distribution and accumulation behavior of pollutants in long-term differently tilled soils. Soil Till. Res. 66, 183-195.

C Düring, R.-A. und S. Gäth (2002): Utilization of municipal organic wastes in agriculture: where do we stand, where will we go? J. Plant Nutr. Soil Sci. 165, 544-556.

D Düring, R.-A. und S. Gäth (2000): Microwave assisted methodology for the determination of organic pollutants in organic municipal wastes and soils: extraction of polychlorinated biphenyls using heat transformer disks. Fresen. J. Anal. Chem. 368, 684-688.

E Düring, R.-A., H.E. Hummel, X. Zhang, J. Czynski und S. Gäth (2002): Microwave assisted steam distillation with simultaneous liquid/liquid extraction of pentachlorophenol from organic wastes and soils. Anal. Bioanal. Chem., angenommen.

F Düring, R.-A., S. Krahe und S. Gäth (2002): Sorption behavior of nonylphenol in terrestrial soils. Environ. Sci. Technol. 36, 4052-4057.

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J Schug, B.; T. Hoß, R.-A. Düring and S. Gäth (1999): Regionalization of sorption capacities for arsenic and cadmium. Plant Soil 213, 181-187.

K Horn, A., R.-A. Düring, S. Gäth (2003): Comparison of decision support systems for an optimised application of compost and sewage sludge on agricultural land based on heavy metal accumulation in soil. Sci. Tot. Environ., angenommen.

1 Zusammenfassung - Summary

Die Nutzung organischer Siedlungsabfälle in der Landwirtschaft birgt Chancen und Risiken. Zwischen einer Nutzung von Nährstoffen wie der knappen Ressource Phosphat und der Erhaltung der Bodenfunktionen besteht ein Zielkonflikt, der im öffentlichen und politischen Raum thematisiert wird: Ein zusätzlicher Eintrag von Schwermetallen und organischen Schadstoffen in die Böden ist bei dieser Kreislaufführung nicht zu vermeiden. Diese Konfliktsituation kann nur über ein erweitertes Verständnis für die Prozesse im System Abfall-Boden-Pflanze zielführend diskutiert werden.

Mit der vorliegenden kumulativen Habilitationsschrift wird – nach einer Charakterisierung der Böden und der eingesetzten Abfälle – das Verhalten möglicher Kontaminanten dieses Systems auf verschiedenen Skalenniveaus beschrieben.

Böden als Abbau- und Ausgleichsmedium

Zunächst wird der Boden in seiner Sensibilität als Puffer- und Abbaumedium anhand des Einflusses des Bearbeitungsregimes dargestellt. Eine langjährige Verringerung der Intensität der Bodenbearbeitung oder die Unterlassung derselben erhöhen beispielsweise den Humusgehalt an der Bodenoberfläche, der wiederum in hohem Maß für die Bindung von Schadstoffen im Boden verantwortlich ist.

Abfälle mit Nährstoff- und Risikopotenzialen

Mit einem Übersichtsartikel wird die Relevanz der Verwertung organischer Abfälle auf der Fläche herausgestellt, die sich aus hohem Aufkommen bei begrenztem Deponieraum, weltweit limitierten Nährstoffreserven und politischen Vorgaben ergibt. Aus dieser Übersicht geht hervor, dass vor allem die Anreicherung einer unbekannten Zahl organischer Schadstoffe in diesen Abfällen deren flächenhafte Verwertung in Frage stellt. Weiterhin wird deutlich, dass hinsichtlich der Bestimmungsmöglichkeiten und der Vorhersagbarkeit der ökotoxikologischen Wirkung dieser Stoffe erheblicher Forschungsbedarf besteht.

Analytischer Schadstoffnachweis

Dem analytischen Nachweis von Organika in Böden und Abfällen widmen sich zwei Originalarbeiten, die hierzu neue Anwendungsmöglichkeiten der Mikrowellen unterstützten Extraktion präsentieren. Mit diesen Verfahren ist es möglich, selektiv und effizient z. B. polychlorierte Biphenyle (PCB) oder substituierte Phenole aus unterschiedlichen Feststoffen zu extrahieren. Derartige Methoden, die gegenüber herkömmlichen Verfahren eine deutliche Einsparung von Zeit und Lösungsmitteln bei vergleichbarer Nachweisempfindlichkeit bieten, sollten ein breiteres und vertieftes Monitoring organischer Schadstoffe in den unterschiedlichen Umweltkompartimenten ermöglichen.

Schadstoffverhalten im System Abfall-Boden-Pflanze

Nach dem Eintrag der Schadstoffe in den Boden treten diese miteinander in Wechselwirkung. Der grundlegende Prozess der Sorption, der wiederum das Verlagerungs- und Anreicherungsverhalten von Schwermetallen und organischen Schadstoffen bestimmt, wird von der Labor- bis zur Regionalskala in fünf Originalarbeiten behandelt.

Laborebene

Während für die Schwermetalle eine Übertragung in den Landschaftsmaßstab vorgenommen werden kann, muss das Verteilungsverhalten der organischen Schadstoffe häufig zunächst im Labormaßstab charakterisiert werden. In diesem Sinne wurde die Sorption von Nonylphenol, einer sich in anaerob behandeltem Klärschlamm anreichernden toxischen und hormonell wirksamen Verbindung, erstmalig charakterisiert. Nach der Untersuchung anhand von 51 verschiedenen Böden konnte Nonylphenol ein verhältnismäßig lipophiles Verhalten mit einem $\log K_{oc}$ von 3,97 zugesprochen werden. Die Analysen zeigten aber auch, dass das Sorptionsverhalten der zahlreichen Isomere des Nonylphenols unterschiedlich sein kann. Einer vermuteten unterschiedlichen östrogenen Wirksamkeit wurde in einer Studie auf der Basis des E-Screen-Assays nachgegangen. Da eine Trennung der Einzelisomere derzeit nicht möglich ist, und isolierte Standardsubstanzen dieser Isomere nicht verfügbar sind, wurden mittels präparativer GC sechs unterschiedliche Fraktionen des Nonylphenols gewonnen. Zwischen diesen Fraktionen konnten nur geringe Unterschiede ermittelt werden.

Feldversuch

Mit zwei weiteren Publikationen wird das Anreicherungsverhalten und die Bioverfügbarkeit der über Kompost und Klärschlamm eingetragenen Schadstoffe im Rahmen von Feldversuchen vorgestellt. Hierbei zeigte sich, dass für den Verbleib sowohl der Schwermetalle als auch der untersuchten PCB der Humusgehalt des Bodens die entscheidende Rolle spielt. Der Schadstoffeintrag nach gesetzeskonformer Anwendung organischer Abfälle war hier von untergeordneter Bedeutung, auch im Falle ungepflügter Böden, in denen keine Durchmischung des Bodens mit dem Abfall und somit auch kein Verdünnungseffekt anzunehmen war.

Die Abhängigkeit der Schadstoffsorption von bestimmten Schlüsseleigenschaften der Böden gilt es zu quantifizieren, wenn – etwa im Zuge einer Risikoabschätzung – das Verhalten dieser Stoffe im Boden vorhergesagt werden soll. Zu diesem Zweck wurden mit einer weiteren Studie 159 Bodenproben hinsichtlich ihrer Sorptionskapazität für Cadmium und Arsen untersucht. Mittels multipler linearer Regression konnte für Cadmium der Beitrag wesentlicher Bodeneigenschaften an der Sorption quantifiziert und - über die Erstellung von Pedotransferfunktionen – eine Übertragung des Sorptionsverhaltens in andere Landschaften ermöglicht werden. Auf der Basis erweiterter Freundlich-Isothermen wird mit der letzten Publikation ein Entscheidungsmodell zur nachhaltigen Nutzung organischer Abfälle in der Landwirtschaft präsentiert. Mit diesem, auf der Quantifizierung der Sorptionskapazitäten für Cadmium, Blei und Zink basierenden Entscheidungsmodell kann dem Ziel einer nachhaltigen Nutzung organischer Abfälle auf unterschiedlichen landwirtschaftlichen Böden vor dem Hintergrund der Schwermetallbelastung näherungsweise entsprochen werden: Angepasst an die Bodeneigenschaften, können Nährstoffe aus Abfällen genutzt werden, ohne eine langfristige Überschreitung von Schwermetallgrenzwerten bezüglich der Bodenfest- oder Bodenflüssigphase zu riskieren.

Regionalisierung

Für eine nachhaltige Nutzung organischer Abfälle in der Landwirtschaft bedarf es geeigneter Managementmethoden, für die zunächst verlässliche Kennzahlen (z. B. Qualitätsparameter zu Abfällen und Böden, Parameter zu den Stoffeigenschaften) sowie Kontroll- und Prüfinstrumente (analytische Nachweismethoden) bereit gestellt werden müssen. Unter diesen Voraussetzungen ist es wünschenswert, hochwertige Sekundärrohstoffdünger aus dem ländlichen Raum regional in der Landwirtschaft zu verwerten.

Sustainable utilisation of organic municipal wastes in agriculture with special regard to protection of soils and consumers

The use of organic municipal wastes in agriculture holds both chances and risks. There is a conflict of objectives between the substitution of worldwide limited mineral phosphate resources and the conservation of soil functions. This gives reason to political and public debate: With recycling of organic waste in agriculture, an additional input of heavy-metals and organic pollutants into soils is inevitable. However, discussion in this field can only succeed with deeper knowledge of the processes involved in the system waste-soil-plant.

The work presented as a set of original papers outlines some characteristics of both the considered soils and wastes and demonstrates the fate of potential contaminants of this system at different scales.

At first, the sensibility of soils to buffer the input of pollutants is depicted by results of long-term field experiments investigating different intensity of soil tillage. Both reduced soil tillage and no-tillage result in an enrichment of humus at the soil surface and stronger fixation of pollutants.

A review article emphasises the importance of the agricultural utilisation of organic wastes which is due to huge amounts of the wastes at a limited number of controlled landfills, globally limited nutrient resources, and political conditions. This review makes clear that the accumulation of an unknown number of organic pollutants is a questionable approach. The need to further improve analytical techniques and knowledge of the ecotoxicologal impact of those substances is also emphasised in this original paper.

New options to determine organic pollutants in soils and wastes are presented with two articles. The application of microwaves to solid samples provides selective and efficient extraction of i. e. polychlorinated biphenyls (PCB), and substituted phenols, respectively. Those methods, which significantly save time and solvent consumption, should allow for deeper and extensive monitoring of the different environmental media for organic pollutants.

Once introduced into the soil, the fertiliser-derived pollutants interact with the different soil constituents. Sorption as the fundamental process which determines translocation and accumulation of heavy-metals and organic pollutants, is discussed in five articles considering the different scales from a laboratory experiment up to the level of landscapes.

For heavy-metals a transition from the lab scale into regions can be performed, whereas the partition behaviour of many organic pollutants must be studied at first in small scale laboratory experiments. Hence, sorption of nonylphenol, a toxic and endocrine dis-

rupting substance which accumulates in anaerobically digested sewage sludge, was characterised for the first time. Laboratory experiments with 51 different soil samples resulted in a $\log K_{oc}$ of 3.97, indicating a comparatively lipophilic behaviour of nonylphenol. However, it was also shown that sorption behaviour of the various isomers of nonylphenol is likely to be different. Since complete separation into single isomers is presently impossible and isolated standards are not available, six fractions of the technical nonylphenol mixture were obtained by means of preparative GC. Those fractions were examined for their estrogenic activity with the E-Screen-Assay. As a result, only slight differences between fractions could be determined.

Two additional field studies report on accumulation and bioavailability of the fertiliser-derived pollutants. Here, it was shown that the content of organic matter in soil is the key factor determining the fate of heavy-metals and organic pollutants. The input of pollutants via waste application rates which conform to statutory limits was of minor importance. The same was true for untilled soils which received a topical application of the organic waste and therefore showed relatively higher concentrations of pollutants in the top 3 cm of soil analysed.

There is a need to quantify the dependence of sorption on certain key characteristics of the soil if – in terms of a risk assessment – the fate of such elements or compounds in soil should be predicted. To this end, 159 soil samples were studied for their sorption capacity for cadmium and arsenic. By means of multiple linear regression, the contribution of essential soil properties to sorption of cadmium to soil was quantified. This facilitated a transfer of the knowledge on sorption behaviour into other regions of different origin, land use, and climate. With the last publication, a decision support system for a sustainable utilisation of organic wastes in agriculture is presented. This decision support system, which is based on general purpose Freundlich isotherms, quantifies sorption capacities of cadmium, lead, and zinc, respectively, and provides the opportunity for a sustainable use of organic wastes in agriculture. Adapted to soil properties, nutrients derived from the wastes can be beneficially used without exceeding any limit values for the solid or the liquid phase of the soil in the long run.

The sustainable use of organic wastes in agriculture needs management methods with operating figures (i. e., quality indices for wastes and soils, parameters for substance properties) and control measures (high performance analytical procedures). Under these circumstances and specifications, high quality fertilisers derived from organic wastes may be regionally used in agriculture.

2 Einführung

Der Begriff der Nachhaltigkeit wurde bereits im 18. Jahrhundert in der Forstwirtschaft geprägt, um - entgegen früherer Praxis – nicht mehr Holz einzuschlagen, als dem jährlichen Zuwachs entspricht, und damit einen dauerhaften Ertrag zu sichern. Nachhaltige Entwicklung (sustainable development) steht für eine Verbindung von ökonomischer Beständigkeit, dem Erhalt der ökologischen Funktionsfähigkeit des Naturhaushaltes und sozialer Gerechtigkeit (*Brundtland*, 1987). Vor diesem Hintergrund unterzeichneten 1992 auf der UN-Umweltkonferenz von Rio de Janeiro 178 Staaten die Agenda 21, das weltweite Aktionsprogramm für eine dauerhaft umweltgerechte Entwicklung.

Nachhaltige Entwicklung ist gefährdet, wenn – im Zuge der weltweiten Urbanisierung mit verändertem Konsumverhalten – die Qualität der Nahrungsmittelerzeugung aufgrund unerwünschter Begleitstoffe in den Produkten sinkt. Der Eintritt solcher, vom Menschen synthetisierter Stoffe in die Nahrungskette wurde bekannt, seit der Physiker *James Lovelock* im Jahre 1957 den Elektroneneinfangdetektor als hochempfindliches Nachweissystem, insbesondere für chlororganische Verbindungen, entwickelte (*Lovelock,* 1991). Mit dieser Technik, die die moderne organische Spurenanalytik begründete, wurde in den sechziger Jahren offenkundig, dass bestimmte persistente Pflanzenschutzmittel und andere toxische Organika sich ubiquitär in der Umwelt verteilen und in Nahrungsketten anreichern (z. B. *Hutzinger* et al., 1974) . In der Folge wurde die breite Öffentlichkeit u. a. durch das Buch „Silent Spring“ von *Rachel Carson* (1962) für diese globale Schadstoffbelastung sensibilisiert. *Theodora Colborn* erregte in den neunziger Jahren Aufsehen mit ihrem Werk „Our Stolen Future“ (1996) über die Wirkungen alltäglich benutzter Chemikalien auf das Reproduktionssystem des Menschen: Schäden bis hin zur Unfruchtbarkeit könnten auf eine Exposition zu anthropogenen Chemikalien zurückgeführt werden.

Mit zunehmendem Kenntnisstand wurden über politische Maßnahmen und gesetzliche Regelungen Schadstoffeinträge aus punktuellen Quellen in die Umwelt in den entwickelten Industrienationen reduziert (*Chaney* et al., 1996). Der diffuse Eintrag dieser Schadstoffe in verschiedene Umweltmedien findet jedoch permanent statt; für einige persistente Schadstoffe gelten mittlerweile „Gleichgewichtsbedingungen“ z. B. im System Atmosphäre-Boden (*Cousins* et al., 1999*a*).

Der Boden bzw. die Landschaft mit den Schnittstellen zur Atmosphäre und aquatischen Systemen stellen eine Senke für die zivilisationsbedingt diffus emittierten Schadstoffe dar (*Gren*, 1998). Gemäß dem Bundes-Bodenschutzgesetz (*BBodSchG*, 1998) ist Vorsorge gegen das Entstehen schädlicher Bodenveränderungen zu treffen und es gilt, die verschiedenen Funktionen des Bodens im Sinne der Nachhaltigkeit zu sichern.

Neben seinen natürlichen Funktionen erfüllt der Boden Nutzungsfunktionen, die ihn u. a. als möglichen Standort zur Verwertung von Abfällen ausweisen. Die - gemäß dem Kreislaufwirtschafts- und Abfallgesetz (*KrwAbfG*, 1994) - zu schaffenden weitgehend geschlossenen Stoffkreisläufe über die stoffliche Verwertung geeigneter organischer Abfälle vermindern die Notwendigkeit überregionaler Nährstofflieferungen und den Verbrauch begrenzter Ressourcen. Ein zusätzlicher Eintrag organischer und anorganischer Schadstoffe in die Böden ist bei dieser Vorgehensweise jedoch nicht zu vermeiden. Neben den Schwermetallen, die in den verschiedenen Düngemitteln angereichert sein können, akkumulieren zahlreiche organische Schadstoffe in Sekundärrohstoff- und auch Wirtschaftsdüngern (z. B. *Alcock* und *Jones*, 1993; *de la Torre et al.*, 2000; *Hale* et al., 2001; *La Guardia* et al., 2002). Dem Verbleib einer kleinen Gruppe von Leitsubstanzen aus dem breiten Spektrum dieser Stoffe im System Klärschlamm-Boden-Pflanze wurde in den siebziger und achtziger Jahren erhöhte Aufmerksamkeit gewidmet. Die auf der Basis langfristiger Ausbringung hoher Klärschlammfrachten erbrachten Resultate (z. B. *Kampe* 1987; *Kampe* et al. 1987; *Witte* et al., 1989) führten zur Berücksichtigung organischer Schadstoffe in der Novellierung der bundesdeutschen Abfall-Klärschlammverordnung 1992 (*AbfKlärV*, 1992).

Die gegenwärtige, intensiv in Deutschland geführte Diskussion um einen Ausstieg aus der landwirtschaftlichen Klärschlammverwertung stützt sich unter anderem darauf, dass eine Schadstoffanreicherung in Böden vermieden werden muss, um die verschiedenen Nutzungsfunktionen des Bodens langfristig zu sichern. Dabei sollen alle Düngestoffe, einschließlich Kompost, Gülle, Mineraldünger und Klärschlamm, in diesem Sinne bewertet werden. Diese Bewertung basiert momentan auf den Schwermetallgehalten der verschiedenen genannten Düngestoffe. Organische Schadstoffe sind bislang nicht berücksichtigt, da hier die fachlichen Grundlagen, wie z. B. eine leistungsfähige oder gar standardisierte Analytik, für eine Abschätzung des Risikos nicht gegeben sind.

Mit der vorliegenden Schrift sollen Möglichkeiten aufgezeigt werden, diese Defizite zu mindern: Zunächst gilt es, relevante Schadstoffe, die in organischen Abfällen angereichert sind, zu benennen, diese in ihren Eigenschaften zu charakterisieren und deren analytischen Nachweis zu sichern.

Unter Berücksichtigung der Standort- bzw. Bodeneigenschaften, die eine angepasste Nutzung oder eine schonende Bewirtschaftung erfordern, sollte mit verbessertem Kenntnisstand die Nachhaltigkeit einer stofflichen Verwertung organischer Abfälle in der Landwirtschaft geprüft werden. Diese nachhaltige Verwertung erscheint nur sinnvoll, wenn sie im Zusammenhang mit einem regionalen bis hin zu einem globalen Umweltmanagement stehen.

3 Böden als Abbau- und Ausgleichsmedium

Schädliche Bodenveränderungen sind zu befürchten, wenn aufgrund der räumlichen, langfristigen oder komplexen Auswirkungen einer Nutzung oder Maßnahme nachteilige Auswirkungen auf die Bodenfunktionen (*BBodSchG*, 1998) zu erwarten sind. Unter dem Aspekt der Schadstoffbelastung gilt es insbesondere, seine Funktion als Abbau- und Ausgleichsmedium zu erhalten.

Die puffernde Funktion des Bodens gegenüber Umwelteinflüssen wird im wesentlichen von dessen oberflächennaher Schicht, der durchwurzelbaren Bodenzone gesteuert. In ackerbaulich genutzten Böden beschränkt sich diese Zone hauptsächlich auf den mehr oder weniger humosen Bearbeitungshorizont. Um langfristig die Fruchtbarkeit und die puffernde Funktion des Bodens zu sichern, gilt es, diesen sensiblen Bereich besonders zu erhalten.

Das klassisch pflügende Bearbeitungssystem kann - bei ungünstigen Bedingungen - zu Bodenverlusten durch Erosion führen, die weitaus höher sind als jede bekannte Neubildungsrate. Konservierende Bodenbearbeitungsverfahren, die durch einen reduzierten mechanischen Eingriff in den Boden und eine ganzjährige Pflanzendecke bzw. eine Schicht aus Pflanzenresten an der Oberfläche charakterisiert sind, verringern den Bodenabtrag und reichern organische Substanz an der Oberfläche an. Eine konservierende Bodenbearbeitung wird somit den Zielen des Bundes-Bodenschutzgesetzes (1998) über die Wahrung einer optimalen Bodenstruktur und nachhaltigen Ertragsfähigkeit sowie aufgrund der Erhaltung der Filter- und Pufferfähigkeit gerecht. Diese sich vom traditionell pflügenden System abwendende Art der Bodenbearbeitung findet z. B. in den USA seit geraumer Zeit großflächige Anwendung (*Phillips* et al., 1980; *Gebhardt* et al., 1985) und setzt sich zunehmend auf dem europäischen Kontinent durch (*Rasmussen*, 1999). Mit diesen konservierenden Bodenbearbeitungssystemen wird über die ganzjährige Bedeckung des Bodens mit Pflanzenmaterial dessen standorttypischer Humusgehalt erhalten (*Reeves*, 1997). Die Bindungskapazität für Schadstoffe wird somit gesteigert (*Karlen* et al., 1994), das Potenzial für ihre Verlagerung minimiert, jedoch deren Vorrat im Boden selbst vermutlich erhöht (*Franzluebbers* und *Hons*, 1996).

Diese Effekte stellen sich langfristig ein, d. h. der Boden muss sich bei einer Umstellung von der pflügenden zur konservierenden Bodenbearbeitung an die neuen Bedingungen erst adaptieren. Dauerhafte, vergleichende Untersuchungen zum Einfluss des Bearbeitungssystems auf physikalische, chemische und biologische Charakteristika des Bodens mit einheitlichen Standorteigenschaften sind aufwändig, für eine Bewertung der verschiedenen Systeme aber notwendig.

Bezüglich der Langfristigkeit der Versuche sowie der Vielseitigkeit der Standortbedingungen und angewandten Bodenbearbeitungssysteme bieten die Versuchsflächen der Justus-Liebig-Universität Gießen außergewöhnlich gute Voraussetzungen, um Auswirkungen des Bodenbearbeitungssystems auf verschiedene Funktionen des Bodens zu bewerten.

Auf der Grundlage dieser unter der Federführung des Instituts für Landtechnik seit 1979 mit interdisziplinärer Forschung unterhaltenen Versuche werden im folgenden wesentliche Einflüsse unterschiedlicher Bodenbearbeitung auf wichtige Bodeneigenschaften, die wiederum das Stoffverhalten beeinflussen, zusammengefasst.

> Deutsche Zusammenfassung von Anhang A
>
> *Reduzierung der Bodenbearbeitungsintensität – Ergebnisse einer Langzeitstudie in Deutschland -*
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> Diese Arbeit fasst die Forschungsaktivitäten der Justus-Liebig-Universität Gießen zum Einfluss verschiedener Bodenbearbeitungssysteme auf Bodeneigenschaften und –qualität zusammen. Die Auswirkungen nachhaltiger Bodenbearbeitungsvarianten auf zahlreiche Bodeneigenschaften werden anhand ausgewählter Ergebnisse aus langjährig interdisziplinärer Forschungsarbeit dargestellt.
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> Die Versuche basierten auf vergleichender, langjähriger (Versuchsdauer bis zu 18 Jahren) Anwendung entsprechender Bodenbearbeitungsvarianten auf verschiedenen Böden (z. B. Braunerde, Parabraunerde), deren Bodenarten von Sand bis zu schluffigem Lehm reichen. Diese Böden stammen von fünf Standorten mit unterschiedlichen Fruchtfolgen aus Hessen. Die Intensität der Bodenbearbeitung wurde in der folgenden Reihenfolge als abnehmend betrachtet: konventionelle Pflugbearbeitung (CT = conventional tillage), reduzierte Bodenbearbeitung (RT = reduced tillage) und Direktsaat (NT = no-tillage).
>
> Um die Auswirkungen der Bodenbearbeitungsintensität aufzuklären, wurden die Extrema CT und NT verglichen. Der Einfluss der Anwendung von RT auf physikalische Eigenschaften des Bodens wurde als intermediär zwischen CT und NT angesehen. Die Lagerungsdichte war im allgemeinen in der oberen Bodenschicht der Direktsaatböden erhöht, was – verglichen mit RT- und CT- Böden - mit einem Rückgang des Anteils der Grobporen und einer verringerten gesättigten Wasserleitfähigkeit einherging. Die Bodenbedeckung mit Pflanzenrückständen sowie eine höhere Aggregatstabilität unter Direktsaatbedingungen wirkten schützend für die Bodenfruchtbarkeit, indem den Prozessen der Oberflächenverschlämmung und Erosion entgegengewirkt wurde. Laterale Herbizidausträge waren unter Direktsaatbedingungen ebenfalls verringert, wobei die Neigung für einen präferenziellen vertikalen Transport unter diesen Bedingungen noch weiter aufgeklärt werden

> muss. Das Belassen einer Mulchschicht bei den nicht-wendenden Bearbeitungssystemen führte zu einer nützlichen Anreicherung von organischer Substanz und Nährstoffen nahe der Oberfläche der RT- bzw. NT-Böden. Diese Verbesserungen waren verbunden mit erhöhten biologischen Aktivitäten in den Oberböden der RT- und NT-Varianten. Gesteigerte Regenwurmtätigkeit ging mit der Bildung eines Systems kontinuierlicher Makroporen, die die Infiltrationsraten verbesserten, einher. Weiterhin wurde die Strohzersetzung und –einarbeitung über die Regenwurmaktivität verbessert. Böden, die über Jahre hinweg unbearbeitet blieben, waren beständiger gegenüber Fahrzeugverkehr und zeigten infolgedessen geringere Verdichtungserscheinungen. Eindringwiderstandsmessungen deuteten darauf hin, dass sich in langjährig unbearbeiteten Böden eine einheitlich stabile Struktur über die Tiefe ausbildet.
>
> Die Ergebnisse zeigen, dass sowohl das System mit reduzierter Eingriffsintensität als auch das Direktsaatsystem für die untersuchten Bodeneigenschaften förderlich waren. Bei angepasster Fruchtfolge, optimiertem Maschineneinsatz und Pflanzenschutz vermögen diese Systeme die konventionelle Pflugbearbeitung in vielen Fällen in Deutschland zu ersetzen.

Offen blieb im Rahmen dieser Feldversuche die Frage des vertikalen Transports reaktiver Stoffe mit dem Wasserfluss. Zur Beantwortung dieser Fragestellung kann man sich Lysimeterversuchen in unterschiedlichem Maßstab bedienen, die – anhand dieser differenziert bearbeiteten Böden - in der Arbeit von *Düring* und *Hummel* (1999) vorgestellt wurden. Unter verschiedenen Beregnungsregimes (von moderaten, kontinuierlich applizierten Intensitäten bis zu simulierten Starkregenereignissen kurz nach einer Pflanzenschutzmittelanwendung) ergab sich, dass stärkere Adsorption oder auch erhöhte Abbauraten mögliche präferenzielle Transportvorgänge in Direktsaatböden maskieren.

Das Verhalten von Schwermetallen in Böden, die geogenen Ursprungs sind oder anthropogen eingetragen werden, sowie der Verbleib persistenter organischer Schadstoffe in langjährig differenziert bearbeiteten Böden wurde nach der oben besprochenen umfassenden Charakterisierung der Einflüsse von Bearbeitungssystemen auf das Ökosystem Boden in einer weiteren Studie untersucht. Ziel dieser Arbeit war es, die Verfügbarkeit und Tiefenverteilung anorganischer und organischer Schadstoffe im Boden in Abhängigkeit von dessen Bearbeitung zu charakterisieren. Die Ergebnisse lassen sich wie folgt zusammenfassen:

Deutsche Zusammenfassung von Anhang B

Tiefenverteilung und Bioverfügbarkeit von Schadstoffen in langjährig differenziert bearbeiteten Böden

Schadstoffe können über die Anwendung organischer und anorganischer Düngemittel, Pflanzenschutzmittel und atmosphärische Deposition in Böden eingetragen werden. Ziel dieser Arbeit war es, den Einfluss langjährig (9 – 17 Jahre) differenzierter Bodenbearbeitung auf das Schadstoffverhalten in Böden nachzuweisen. Die Bioverfügbarkeit und Anreicherung von Schwermetallen, Arsen und Organika wie den polychlorierten Biphenylen (PCBs) und eines chlorierten Phenols (2,4-DCP) wurden in einer Braunerde und in einer Parabraunerde bei konventioneller Pflugbearbeitung (CT = conventional tillage), reduzierter Bodenbearbeitung (RT = reduced tillage) und Direktsaat (NT = no-tillage) ermittelt.

Die oberflächennahe Schicht der NT-Böden war mit Schadstoffen angereichert, jedoch nahmen deren Konzentrationen mit zunehmender Bodentiefe ab. Die atmosphärische Schadstoffdeposition und Einträge über organische Dünger waren erkennbar in langjährig unbearbeiteten Böden. Zink (59 mg kg^{-1} Gesamtgehalt) war signifikant angereichert in einer Bodentiefe von 0–3 cm der unbearbeiteten Parabraunerde, was auf die höhere Sorptionskapazität für Schwermetalleinträge durch Gülle zurückgeführt wurde. In der Braunerde führte NT zu einer signifikanten Erhöhung Königswasser extrahierbaren Cadmiums in der Ackerkrume von 0-25 cm. Infolge höherer Gehalte organischer Substanz war die langjährige Anreicherung von PCBs in unbearbeiteten Böden stärker ausgeprägt als in den gepflügten Böden. Die mischende Wirkung der Pflugbearbeitung resultierte in homogener Verteilung der Schadstoffe innerhalb der untersuchten Bodentiefe von 0-25 cm.

Die Anreicherung organischen Kohlenstoffs in reduziert (RT) bzw. nicht bearbeiteten Böden (NT) unterstreicht die Rolle der Böden als Schadstoffsenke über ihre Funktion, Schadstoffe vor einem Austrag über das Sickerwasser und dem Übergang in Nutzpflanzen zu puffern.

Während die Anreicherung organischen Kohlenstoffs mit folglich erhöhtem Sorptionspotenzial in unbearbeiteten Böden klar herausgestellt werden konnte, waren die Unterschiede zwischen den verschieden bearbeiteten Böden bezüglich der Schwermetallkonzentrationen mit den Ergebnissen der Arbeit aus Anhang B nur selten abzusichern. Die Konzentrationen der ausschließlich anthropogen eingetragenen polychlorierten Biphenyle waren jedoch in Abhängigkeit der Bodenbearbeitung signifikant verschieden, so dass das Bodenbearbeitungssystem als Steuergröße für den PCB-Status von Böden angesehen werden kann.

4 Abfälle mit Nährstoff- und Risikopotenzialen

Weltweit steigende Bevölkerungszahlen bedingen wachsende Abfallmengen und einen zunehmenden Ressourcenverbrauch. Die natürliche Umwelt wird dabei als Deponie für die Abfallmengen aus Haushalten und der Industrie genutzt. Während die jährliche Abfallmenge pro Kopf in der Bundesrepublik Deutschland mit ca. 480 kg pro Kopf seit Beginn der neunziger Jahre stagniert, ist für die Europäische Union insgesamt eine Zunahme dieser Abfallmengen zu verzeichnen. Im Vergleich dazu weisen die USA mit 720 kg Hausmüll pro Kopf und Jahr deutlich höhere Abfallmengen auf (*Eurostat*, 2002). Die globale Bevölkerung wird zunächst weiter wachsen, aber – nach neueren probabilistischen Vorhersagen – sich vom heutigen Stand von 6,1 Milliarden Menschen in diesem Jahrhundert wahrscheinlich nicht mehr verdoppeln (*Lutz* et al., 1997). Für einen Wachstumsstopp bei nahezu 9 Milliarden Menschen im Jahre 2075 geben *Lutz* et al. (2001) eine Wahrscheinlichkeit von 85% an.

Die urbane Lebensform mit beschleunigter Zersiedelung und Verstädterung wird in den nächsten Generationen weltweit dominieren. Dieser Prozess ist mit einer starken Zunahme des Verbrauches an Ressourcen verbunden. Somit hat der ansteigende Grad der Urbanisierung - neben den steigenden Siedlungsabfallmengen – zur Folge, dass konsumbedingt zunehmend anorganische und organische Schadstoffe in die Umwelt gelangen (*Callender* und *Rice,* 2000; *van Metre* et al., 2000) und sich in diesen Abfällen anreichern.

Da die Funktionstüchtigkeit von Ökosystemen auf Energieflüssen und Stoffkreisläufen beruht, müssen diese Abfallmengen auf lange Sicht wieder in die biogeochemischen Kreisläufe eingebracht werden. Auf dieser Erkenntnis beruht das 1996 in der Bundesrepublik in Kraft getretene Kreislaufwirtschafts- und Abfallgesetz (*KrWAbfG*, 1994), das, gemäß dem bundesdeutschen Rechtssystem, in zahlreichen Verordnungen umgesetzt wird. In diesem Sinne ist die Verwertung organischer Abfälle anderen Beseitigungsoptionen vorzuziehen. Die Verwertung kann grundsätzlich stofflich oder energetisch erfolgen. Vorrang hat die ökonomisch wie ökologisch vorteilhaftere Variante.

Das jährliche Bioabfallaufkommen je Einwohner liegt in der Bundesrepublik Deutschland in Abhängigkeit von Siedlungsstruktur und Jahreszeit zwischen 25 und 150 kg (*Beisecker* et al., 1998). Eine Verwertung dieser Abfälle in der Landwirtschaft kann den Bedarf mineralischer Düngemittel vermindern und, zumindest ökonomisch gesehen, zur nachhaltigen Produktion beitragen. Im Spannungsfeld zwischen der Nutzung von organischer Substanz und Nährstoffen – hier ist insbesondere Phosphat zu nennen – und der Tolerierung einer langfristigen Anreicherung von Schadstoffen im Boden haben sich ein wissenschaftliches Teilgebiet und ein differenziertes Rechtssystem in verschiedenen Industrienationen entwickelt. Ein Überblick zum aktuellen Stand der Forschung auf Grundlage der auszubringenden Siedlungsabfallmengen mit den unterschiedlichen Nähr- und Schadstofffrachten ist mit der Arbeit in Anhang C gegeben und im folgenden zusammengefasst.

> Deutsche Zusammenfassung von Anhang C
>
> *Verwertung organischer Abfälle in der Landwirtschaft: Status und Perspektiven*
>
> Weltweit steigende Mengen organischer Abfälle erfordern Strategien, um diese möglichst umweltverträglich zu verwerten. Die bestehenden Regularien bezüglich der Qualitäten der zu verwertenden Abfälle und der mit ihnen in den Boden eingetragenen Schadstofffrachten unterscheiden sich erheblich zwischen Europa und den USA. Nützliche Effekte, die die Bodenfruchtbarkeit verbessern, wurden häufig ermittelt. Schwermetallanreicherungen wurden auf langjährige Klärschlammausbringungen zurückgeführt, wobei der Effekt auf die Bioverfügbarkeit der Metalle weiterhin aufgeklärt werden muss. Eine Reihe organischer Schadstoffe, wie z. B. hydrophobe persistente organische Verbindungen und Tenside, reichern sich in organischen Abfällen an. Da die hydrophoben Schadstoffe stark mit der organischen Substanz im System Klärschlamm-Boden-Pflanze interagieren, wird deren systemische Aufnahme von der Pflanze als minimal angesehen. Tenside können nachteilige Umweltauswirkungen verursachen, da sie in hohen Frachten in die Kanalisation gelangen und sich im Klärschlamm anreichern. Tenside und einige ihrer Abbauprodukte werden unter schlecht durchlüfteten Bedingungen nicht vollständig abgebaut. Aufgrund ihrer Toxizität und der östrogenen Eigenschaften, z.B. des Nonylphenols, besteht Forschungsbedarf, diese Stoffe analytisch zu erfassen und ihr Verhalten im Boden nachzuvollziehen. Möglichkeiten, die Vorzüge einer landwirtschaftlichen Verwertung organischer Abfälle besser zu nutzen und Risiken zu minimieren, werden aufgeführt: (1) Weitere Reduzierung von Grenzwerten für Schadstoffe und stärkere Eingrenzung der Aufwandmengen; (2) verbesserte Technologien, um Gesamtgehalte und verfügbare Anteile von Schwermetallen und organischen Schadstoffen zu reduzieren; (3) Anpassung der Aufwandmengen an Bodeneigenschaften, wie die Sorptionskapazität für Schadstoffe; (4) Harmonisierung der Analysenverfahren für organische Schadstoffe (Tenside und Metabolite), um ein zuverlässigeres und umfangreicheres Monitoring der organischen Abfälle, die auf Böden aufgebracht werden sollen, zu ermöglichen.

Aus dieser Arbeit geht hervor, dass sich die Forschung – neben der Studie der Verfügbarkeit und Speziierung von Schwermetallen - zunehmend auf das Monitoring, Umweltverhalten und die Analytik organischer Verbindungen konzentriert. Immer noch ist zu wenig über das Vorkommen dieser Stoffe in der Umwelt und in Siedlungsabfällen bekannt. Eine neue, groß angelegte Untersuchung von *Kolpin* et al. (2002) anhand von Wasserproben eines Netzwerks von 139 Strömen in 30 Staaten der USA machte das Vorkommen zahlreicher Pharmazeutika, Hormone und anderer organischer Abwasserschadstoffe offenkundig. Zu den am häufigsten der 95 bestimmten Verbindungen gehörten z. B. bestimmte Steroide, Desinfektionsmittel, aber auch Koffein und Nonylphenol. Diese aufklärende Untersuchung zeigt, dass eine Reduzierung der Überwachung und Analyse auf die z. B. von der obersten amerikanischen Umweltbehörde US EPA (Environmental Protection Agency) oder auch der EU benannten „prioritären Schadstoffe" nicht ausreichend ist. Aufstellungen prioritärer Schadstoffe werden nach den Kriterien Herstellungsmengen, Anwendungsmuster und Umweltgefährlichkeit dieser Leitsubstanzen gemacht, um eine Bewertung von potenziell zu verwertenden organischen Abfällen (Sekundärrohstoffdüngern) auf Basis einer Risikoabschätzung treffen zu können. Bezug nehmend auf die o. g. Studie weist *Eckel* (2002) darauf hin, dass zahlreiche „nicht-prioritäre" Schadstoffe mit der geeigneten Analysentechnik (Kapillargaschromatografie mit massenselektiver Detektion – GC/MS) zumindest annähernd zu identifizieren wären. Weiterhin macht er auf die verstärkte Nutzung von GC-Retentionszeitenindices aufmerksam (siehe auch *Zhang* et al., 2002), die bei heutigem Stand der Technik den qualitativen Nachweis über GC/MS weiter verbessern würde. Damit wären heute „nicht-prioritäre", aber gehäuft auftretende Schadstoffe als solche erkennbar.

5 Analytischer Schadstoffnachweis

Eine Diskussion um die Belastung von Böden mit Schadstoffen, die aus einer Verwertung organischer Abfälle resultiert, entbehrt jeder Grundlage, wenn der sichere Nachweis dieser Substanzen nicht gewährleistet ist. Nur für wenige Stoffe bzw. Stoffgruppen existieren Standardverfahren, die einen selektiven und empfindlichen Nachweis bei vertretbarem analytischem Aufwand garantieren. Die in den letzten Jahren hochentwickelten Analysengeräte werden dem Anspruch gerecht, geringste Schadstoffrückstände sicher und automatisiert aufzuspüren. Als sehr universelles, aber dennoch selektiv und sensitiv einzusetzendes Detektionssystem hat sich mittlerweile die Massenspektrometrie, in Verbindung mit hochauflösenden chromatografischen Verfahren, durchgesetzt. Mit diesen gekoppelten Methoden ist man heute in der Lage, qualitativ und quantitativ höchst präzise Aussagen bezüglich des Schadstoffstatus von Umweltmedien zu treffen (*Richardson*, 2002).

Die Aufbereitung, insbesondere von Feststoffproben, hingegen stützt sich im wesentlichen immer noch auf Verfahren und Prinzipien, die seit Jahrzehnten nicht verändert wurden.

Nach *Pawliszyn* (1993) ist diese Probenaufbereitung - Extraktion und Wiederfindung eines Analyten aus einer festen Matrix - ein fünfstufiger Prozess:

1. Die Desorption der Verbindung von den aktiven Stellen der Matrix
2. Die Diffusion in die Matrix selbst
3. Die Lösung des Analyten im Extraktionsmittel
4. Die Diffusion des Analyten im Extraktionsmittel
5. Die möglichst quantitative Aufnahme der extrahierten Verbindungen.

Bei der Extraktion organischer Schadstoffe aus Feststoffproben, wie z. B. Böden oder Abfällen, ist der erste Schritt häufig der anspruchsvollste, da die Wechselwirkung von Analyt und Matrix oft sehr schwer zu überwinden bzw. schwierig einzuschätzen ist. Traditionelle Extraktionstechniken, die für Feststoffproben angewandt werden, sind z. B. die nach dem deutschen Lebensmittelanalytiker Franz Soxhlet (1848 – 1913) benannte Soxhlet-Extraktion, die Ultraschallbehandlung oder einfaches Ausschütteln. Diese Techniken sind durch mehr oder weniger lange Extraktionszeiten (bis zu 36 Stunden bei der Soxhlet-Extraktion) und hohen Bedarf an Lösungsmittelvolumina - Analysenlabors verwenden weltweit nahezu 100.000.000 L Lösungsmittel pro Jahr (*Environment Canada*,

2002) - gekennzeichnet. Weiterhin erfordern diese Techniken nachfolgende Aufkonzentrierungs- und Aufreinigungsschritte, um die Extrakte analysenfähig zu machen.

Zeitgemäße Extraktionsmethoden, die sowohl den Lösungsmittelbedarf als auch den Zeitaufwand reduzieren und sich in jüngerer Zeit stärker durchsetzen, sind die Extraktion mit überkritischen Fluiden (SFE – supercritical fluid extraction), die beschleunigte Lösungsmittelextraktion (auch bezeichnet als ASE – accelerated solvent extraction oder PSE - pressurized solvent extraction) und die Mikrowellen unterstützte Extraktion (MAE – microwave assisted extraction) (*Camel*, 2001). Außerdem hat sich überkritisches Wasser zur Extraktion auch von unpolaren Schadstoffen bewährt (*Crescenzi* et al., 1999; *Bruno* et al., 2002). Diese Methoden entsprechen dem Geist der „Green Chemistry“, indem sie den Einsatz toxischer Lösungsmittel ausschließen oder drastisch herabsetzen (*DeSimone*, 2002).

Die Nutzung Mikrowellen unterstützter Methoden kann den genannten hohen Verbrauch an toxischen und entsorgungspflichtigen Lösungsmitteln mindestens um den Faktor 10 reduzieren, außerdem ist der Mikrowellen unterstützte Prozess in wenigen Minuten abgeschlossen: Die zur Extraktion organischer Verbindungen erstmals von *Ganzler* et al. (1986) genutzten nicht-ionisierenden Mikrowellen führen hauptsächlich zu Dipolrotationen und, im Zuge der Reibung, zu spontaner Erwärmung geeigneter Proben und Lösungsmittel. Somit ist dieses Prinzip auf Lösungsmittel und Matrices mit polaren Eigenschaften beschränkt. Infolgedessen müssen zur Extraktion hydrophober Schadstoffe polare, durch Mikrowellen anregbare Lösungsmittel zugesetzt werden. Die damit zu erzielende effiziente Extraktion ist jedoch nicht mehr selektiv, so dass nach der Extraktion etwa von polychlorierten Biphenylen (PCB) aus Feststoffen mit einem Lösungsmittelgemisch von Hexan und Aceton in Verhältnissen zwischen 1:3 bis 1:1 zusätzliche Reinigungsschritte erforderlich sind (*Dupont* et al., 1998; *Zuloaga* et al., 1998).

Um polare Lösungsmittel, die die Mikrowellenenergie absorbieren, aber auch unerwünschte Komponenten extrahieren, auszuschließen, wurde mit der im folgenden zusammengefassten Arbeit (siehe Anhang D) der Einsatz von Mikrowellentransformatoren, die der Probe zugesetzt werden, erprobt. Mittels dieser Kunststoffscheiben auf Polytetrafluorethylen (PTFE)-Basis, die mit Kohlenstoff dotiert sind (Weflon®-Scheiben), war es möglich, polychlorierte Biphenyle (PCB) aus verschiedenen Probenmaterialien ausschließlich mit dem unpolaren Lösungsmittel n-Heptan effizient zu extrahieren. Die Extraktion im geschlossenen System ermöglichte – bei erhöhtem Druck - Extraktionstemperaturen deutlich oberhalb des Siedepunktes von n-Heptan, die wiederum sehr kurze Aufbereitungszeiten ermöglichten. Der schematische Aufbau des Mikrowellen unterstützten Extraktionssystems ist in Abb. 1 wiedergegeben.

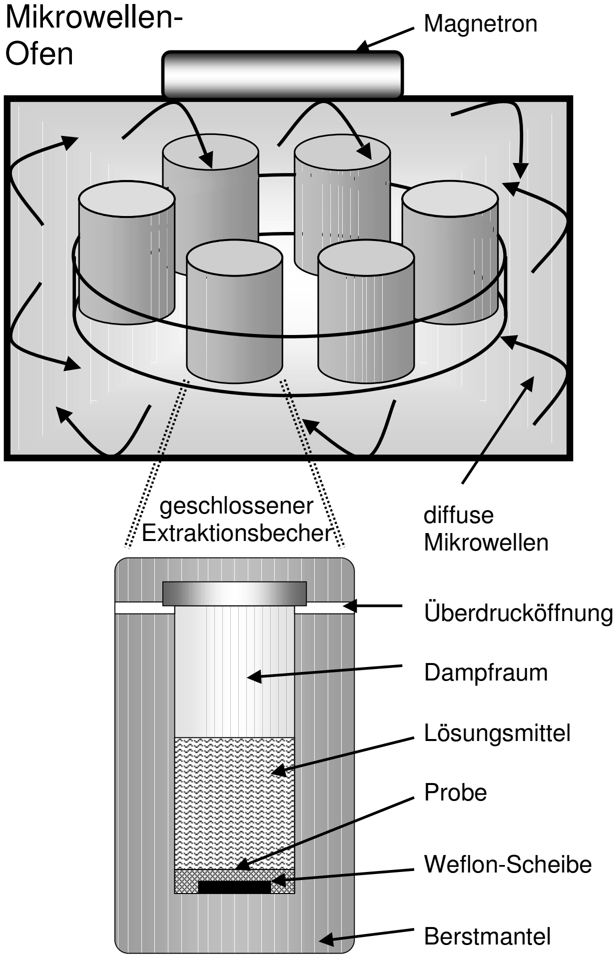

Abb. 1: Prinzip der Mikrowellen unterstützten, unpolaren Extraktion (nach *Camel*, 2001, verändert).

Deutsche Zusammenfassung von Anhang D

Mikrowellen unterstützte Methode zur Bestimmung organischer Schadstoffe aus organischen Siedlungsabfällen und Böden: Extraktion polychlorierter Biphenyle mittels Mikrowellentransformatoren

Die bekannten Vorteile der Mikrowellen unterstützten Extraktion (MAE) von polychlorierten Biphenylen (PCB) aus Feststoffen konnte mit dem beschriebenen Verfahren unter Nutzung von n-Heptan als einzigem Extraktionsmittel bestätigt werden. Die Wärmeübertragung innerhalb der Extraktionsgefäße gewährleisteten Mikrowellentransformatoren, die die Mikrowellenenergie absorbieren und direkt und unabhängig von der im Probe-Lösungsmittelsystem vorherrschenden Temperatur in Wärme umwandeln. Die nachteilige Co-Extraktion polarer Substanzen konnte ausgeschlossen werden; somit reichte eine vereinfachte Probenaufarbeitung für die nachfolgende GC-MS Analyse aus. Der Vergleich mit anderen Extraktionsmethoden bestätigte die Effizienz der Methode auch für gealterte Proben.

Ein weiterer Ansatz zur selektiven und Lösungsmittel einsparenden Mikrowellen unterstützten Extraktion ist in Anhang E dieser Arbeit beschrieben. Hier wird das intrinsische freie Wasser der Probe angeregt, um den Verteilungsprozess des Analyten in das für Mikrowellen transparente und kühlend wirkende n-Hexan zu begünstigen (*Paré* et al., 1994). Am Beispiel des Pentachlorphenol (PCP) wird die besondere Eignung dieses Prinzips (MAP = microwave assisted process) für wasserdampfflüchtige Schadstoffe gezeigt. Die Mikrowellen gestützte Wasserdampfdestillation von PCP aus Böden und Abfällen mit simultaner flüssig/flüssig Verteilung ist im folgenden zusammengefasst:

> Deutsche Zusammenfassung von Anhang E
>
> *Mikrowellen unterstützte Wasserdampfdestillation und simultane flüssig/flüssig Extraktion von Pentachlorphenol aus organischen Siedlungsabfällen und Böden*
>
> Mit dieser Arbeit wird eine effiziente Methode zur Extraktion von Pentachlorphenol (PCP) aus organischen Feststoffproben und Böden vorgestellt. Hierbei werden die feuchten Proben direkt über die Mikrowellenenergie angeregt.
>
> Über die Verteilung des Wasserdampf flüchtigen PCP in das organische Lösungsmittel n-Hexan innerhalb des geschlossenen Systems wurden Wiederfindungsraten von 85 bis 92% erzielt. Nach der Extraktion bildete das kondensierende Wasser eine Grenzschicht zwischen Extrakt und Probe und verhinderte somit eine Rückverteilung des PCP in die Probe. Die Extraktionen nahmen 35 min in Anspruch und die Optimierung der Extraktionsbedingungen deutete auf eine Matrixabhängigkeit dieser Methode. Zur Verbesserung von Selektivität und Sensitivität wurden die Rohextrakte mit Heptafluorbuttersäureanhydrid (HFBA) derivatisiert, um Nachweisgrenzen von 1-2 µg kg^{-1} zu erzielen. GC-MS/MS-Analysen zeigten, dass geeignete Extrakte mit nur geringen Verunreinigungen gewonnen wurden. Übliche Probenaufarbeitungsschritte wie Trocknung, gründliches Mahlen, häufiger Probentransfer sowie Reinigungs- und Aufkonzentrierungsschritte, die alle zu Analytverlusten führen können, konnten minimiert werden. Die Leistungsfähigkeit der Methode wurde anhand des Vergleichs mit einer etablierten Ultraschallextraktionsmethode bestätigt.
>
> Diese Mikrowellen unterstützte, bei Überdruck stattfindende Wasserdampfdestillation mit gleichzeitiger Verteilung des Analyten in eine organische Phase bietet somit eine effiziente Strategie und benötigt keine zusätzlichen Investitionen zur Standardausstattung Mikrowellen unterstützter Extraktionen (MAE). Verluste von Analyten, z. B. durch Abbau, bei längerer Extraktionsdauer müssen berücksichtigt werden.

Die Möglichkeiten der selektiven und effizienten Extraktion bei geringem Lösungsmitteleinsatz werden der Mikrowellen unterstützten Extraktion (MAE und MAP) zukünftig gemeinsam mit der beschleunigten Lösungsmittelextraktion (ASE) verhelfen, althergebrachte Verfahren mehr und mehr abzulösen (*Camel*, 2001).

Die im Anhang E beschriebene Methode, d. h. die Extraktion und Derivatisierung von PCP aus Böden und Abfällen, ist auf andere substituierte Phenole wie z. B. die Alkylphenole übertragbar. Grenzwerte zu diesen endokrin wirksamen Verbindungen, die im Klärschlamm in hohen Konzentrationen auftreten (z. B. *Giger* et al., 1984; *La Guardia* et al., 2001; *Pryor* et al., 2002), sollen in die entsprechende novellierte EU-Richtlinie zur landbaulichen Verwertung von Klärschlämmen in der Landwirtschaft aufgenommen werden (*European Commission*, 2001). Bislang ist hier keine standardisierte Bestimmungsmethode für diese Substanzen verfügbar.

6 Schadstoffverhalten im System Abfall-Boden-Pflanze

In der Bundesbodenschutzverordnung (*BBodSchV*, 1999) sind Schadstoffe als Stoffe und Zubereitungen definiert, die „auf Grund ihrer Gesundheitsschädlichkeit, ihrer Langlebigkeit oder Bioverfügbarkeit im Boden oder aufgrund anderer Eigenschaften und ihrer Konzentration geeignet sind, den Boden in seinen Funktionen zu schädigen oder sonstige Gefahren hervorzurufen."

Schadstoffe unterliegen gemäß ihrer chemisch-physikalischen Eigenschaften zahlreichen Prozessen im Boden. Nach dem Eintrag gelöster Schadstoffe in den Boden treten diese miteinander in Wechselwirkung; die Prozesse Sorption und Desorption mit folgenden Teilschritten bestimmen über ihre Verfügbarkeit für Abbau- und Verlagerungsprozesse:

- Diffusion zur Oberfläche
- Kontakt mit der Oberfläche
- Rückdiffusion in die Lösung oder Sorption
- Ablösung (Desorption) von der Oberfläche

Im Kontext einer stofflichen Verwertung organischer Abfälle auf landwirtschaftlichen Böden sind diese Prozesse auf den Feldmaßstab bis hin zur regionalen Skala zu übertragen. Im folgenden werden verschiedene Arbeiten von der Labor- bis zur regionalen Skala vorgestellt. Diese verschiedenen Skalenniveaus repräsentieren den unterschiedlichen Kenntnisstand zum Verhalten der anorganischen und organischen Schadstoffe im Boden. Während für die Schwermetalle eine Übertragung in den Landschaftsmaßstab hinein möglich ist, muss das Verteilungs- oder auch Abbauverhalten zahlreicher organischer Schadstoffe zunächst im Labormaßstab charakterisiert werden.

6.1 Laborskala

Die oben genannten, für das weitere Verhalten der Schadstoffe fundamentalen Prozesse, versucht man über weitgehend standardisierte Modellversuche im Labormaßstab zu quantifizieren. Neben verschiedenen Ansätzen mit Bodensäulen, die mit dem zu prüfenden Stoff beaufschlagt und bei gegebener Wasserdurchflussrate eluiert werden, haben sich sogenannte Batch-Experimente durchgesetzt, in denen die Verteilung des gelösten Schadstoffs in einer geschüttelten Boden-Lösungssuspension ermittelt wird (*OECD*, 2000). Diese Experimente werden unter der Annahme ausgewertet, dass Gleichgewichtsbedingungen herrschen, d. h. im Zuge der Kinetik der oben genannten Prozesse keine Konzentrationsänderung des vormals eingesetzten Schadstoffs in den verschiedenen Phasen dieses Systems stattfindet.

Der adsorbierende Stoff wird als Adsorbens, die zu adsorbierenden Stoffe in der flüssigen Phase als Adsorptiv bezeichnet. Adsorbens und Adsorptiv zusammen werden Adsorbat genannt.

Die Gleichgewichtskurve, die sich bei isothermen Bedingungen unter Berücksichtigung unterschiedlicher Angebotskonzentrationen des Schadstoffs einstellt, ist die Adsorptionsisotherme (Abb. 2).

Die Anreicherung eines gelösten Stoffes an der Oberfläche von Feststoffen lässt sich modellhaft am einfachsten als Adsorption über die Langmuir-Isotherme (*Langmuir*, 1918; zitiert in *Sparks*, 1995) erklären. Hier beschränkt sich die Adsorption auf die Bildung einer einmolekularen Oberflächenschicht, um sukzessiv die Bindungskräfte der Oberflächenatome des festen Stoffes abzusättigen. Mit steigender Konzentration des Adsorptivs in der Lösung steigt auch die adsorbierte Stoffmenge, bis alle Adsorptionsplätze belegt sind. Somit nähert sich die adsorbierte Stoffmenge einem Sättigungswert. Dieser Ansatz wird mathematisch wie folgt ausgedrückt:

$$S = \frac{bkC}{1 + kC} \qquad \text{(Gl. 1)}$$

S	=	sorbierte Menge je Oberflächeneinheit [µg g^{-1}]
C	=	Konzentration des zur Adsorption kommenden Stoffes [µg mL^{-1}]
b	=	maximale Bindungskapazität des Bodens [µg g^{-1}]
k	=	Größe der initialen Steigung der Sorptionsisotherme [mL $µg^{-1}$].

Im Bereich sehr kleiner (umweltrelevanter) Konzentrationen, bei denen das Sättigungsniveau bei weitem nicht erreicht ist, ergibt sich eine lineare Beziehung, die durch die sogenannte Henry-Isotherme beschrieben wird:

$$S = K_D \cdot C \qquad \text{(Gl. 2)}$$

K_D = Verteilungskoeffizient [mL g^{-1}].

Synonym für den Verteilungskoeffizienten K_D (tiefgestelltes D für Distribution) wird der K_P (tiefgestelltes P für Partition) verwandt. Die Wechselwirkung von Stoffen mit dem Boden ist nicht mit einer „reinen" Adsorption zu beschreiben, andere Prozesse wie z. B. Ausfällung oder Polymerisation finden im Zuge der Interaktion von Adsorptiv und Adsorbent ebenfalls statt. So ist es vorteilhafter, den Begriff „Sorption" im Sinne einer allgemeineren Betrachtung der Affinität des Schadstoffs an den Boden zu wählen.

Der häufig genutzte Ansatz der Freundlich-Isotherme ist rein empirischer Natur und wurde aufgrund des beobachteten logarithmiert linearen Zusammenhangs zwischen der sorbierten Stoffmenge S [µg g^{-1}] und der Gleichgewichtskonzentration C [µg L^{-1}] von *van Bemmelen* (1888, zitiert in *Sparks*, 1995) entwickelt:

$$S = K_f \cdot C^m \tag{Gl. 3}$$

K_f = Verteilungskoeffizient nach Freundlich [L^m mg^{1-m} kg^{-1}]

m = Freundlich-Exponent [-].

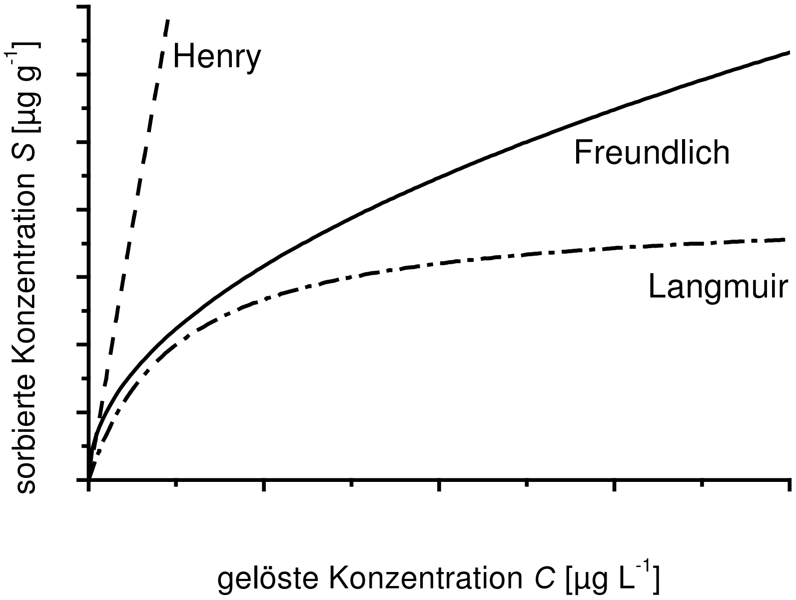

Abb. 2: Sorptionsisothermen zur quantitativen Beschreibung der Wechselwirkung von Schadstoffen mit der Bodenmatrix.

Neben dieser prinzipiellen Einteilung werden Sorptionsisothermen in vier verschiedene Grundtypen klassifiziert (*Sposito*, 1984; zitiert in *Sparks*, 1995), die der heterogenen Matrix Boden und seiner Interaktion mit unterschiedlichsten Stoffen gerecht zu werden versuchen. Neben dem L- und dem H-Typ, die Sorptionsisothermen unterschiedlicher Steigung mit Sättigungsverläufen beschreiben, existiert noch ein weiterer, der S-Typ. Hierbei wird der Beobachtung Rechnung getragen, dass bei niedrigen Lösungskonzentrationen zunächst geringe Steigungen der Isothermen vorliegen können, die mit zunehmender Angebotskonzentration ansteigen und bei allmählich erschöpften Sorptionsplätzen wieder zurückgehen. Zurückgeführt wird diese Erscheinung auf Konkurrenzbedingungen bei geringen Konzentrationen des Adsorptivs, die zwischen der gelösten organischen Substanz und den Bodenpartikeln um das Adsorptiv bestehen können (*Sposito*, 1998).

Für hydrophobe, nicht-ionische Verbindungen wie z. B. die polychlorierten Biphenyle (PCB) ist die organische Substanz – der Humus - der wichtigste Sorbent in der durchwurzelbaren Bodenzone (*Karickhoff*, 1981; *Chiou* et al., 1988). Bei gegebener geringer Wasserlöslichkeit werden die Verteilungskoeffizienten organischer Schadstoffe zwischen Festphase und wässeriger Lösungsphase häufig aus Henry-Sorptionsisothermen abgeleitet, da z. B. eine Absättigung der Sorptionsplätze mit steigender Konzentration nicht zu erwarten ist und das Verhalten hydrophober Schadstoffe im Boden als reiner Verteilungsprozess verstanden wird (z. B. *Chiou*, 1989; *Pignatello*, 1989; *Brusseau* et al., 1990). Die ermittelten Verteilungskoeffizienten aus der Henry-Beziehung werden auf den Gehalt organischen Kohlenstoffs im Boden bezogen, um ein wichtiges Instrument zur Beschreibung der Verfügbarkeit des Schadstoffes im System Boden-Bodenlösung zu erhalten (*Karickhoff* et al., 1979):

$$K_{OC} = \frac{K_D}{f_{OC}} \qquad \text{(Gl. 4)}$$

K_{oc} = Verteilungskoeffizient, auf den Gehalt organischen Kohlenstoffs im Boden bezogen [L g^{-1}]

f_{oc} = Gewichtsanteil des organischen Kohlenstoffs im Boden [g g^{-1}].

Die Sorption von Schadstoffen an die organische Substanz ist ein zeitabhängiger Vorgang, der im allgemeinen als zweistufiger Prozess verstanden wird (*Pignatello*, 1989; *Spurlock* und *Biggar*, 1994; *Pignatello* und *Xing*, 1996; *Pignatello*, 1998). Die oben beschriebenen unter „quasi-Gleichgewichtsbedingungen“ erstellten Verteilungskoeffizienten basieren auf dem schnellen Sorptionsprozess, der in einer zeitlichen Dimension von Minuten bis maximal etwa einem Tag stattfindet. Diese schnelle Sorption an die organische Substanz ist somit geprägt von Wechselwirkungen ihrer oberflächennahen Bereiche mit dem Adsorptiv, wobei die langsame Sorption ein von der Diffusion gesteuerter Transport bis in deren innere Hohlräume („cavities“) hinein darstellt (*Pignatello*, 1989; *Brusseau* et al., 1990). Diese „zweite Phase“ kann Zeiträume über Jahre hinweg einnehmen und ist daher besonders relevant für Schwermetalle und persistente organische Schadstoffe. Auch das Auftreten von Hysterese zwischen Adsorption und Desorption und die Bildung der so genannten gebundenen Rückstände kann auf eine weit fortgeschrittene intramolekulare Diffusion zurückgeführt werden (*Pignatello* und *Xing*, 1996) und widerspricht somit der Theorie der Bildung kovalenter Bindungen zwischen Schadstoff und Huminstoff (*Scheunert*, 1994).

Diese Langzeiteffekte schmälern die Aussagekraft der im Labormaßstab gewonnenen Kenngrößen zur Sorption; d. h. deren Anwendung, z. B. zur Prognose des Umweltverhaltens der Schadstoffe, muss diesen Einschränkungen Rechnung tragen.

Neben der organischen Festsubstanz stellt die gelöste organische Substanz (dissolved organic matter, DOM; bzw. DOC für dissolved organic carbon) ein für anorganische und organische Schadstoffe attraktives Sorbens dar (*Zsolnay*, 1996; *Marschner*, 1999) und kann als „carrier“ besonders für hydrophobe Stoffe dienen (*McCarthy* und *Jimenez*, 1985; *Chiou* et al., 1987; *McCarthy* und *Zachara*, 1989). Diese gelöste organische Substanz wird über die Anwendung organischer Abfälle wie Klärschlamm, Kompost oder Wirtschaftsdünger in den Boden eingebracht und kann die Bioverfügbarkeit der Schadstoffe beeinflussen (*Maxin* und *Kögel-Knabner*, 1995; *Raber* und *Kögel-Knabner, 1997).* Um diesen Einfluss zu quantifizieren, wurde der K_{DOC} [L g^{-1}] entwickelt (*Maxin* und *Kögel-Knabner*, 1995):

$$K_{DOC} = \frac{X_{DOC}}{C_W} \qquad \text{(Gl. 5)}$$

K_{DOC} = Verteilungskoeffizient, auf den Gehalt gelösten organischen Kohlenstoffs bezogen [L g^{-1}]

X_{DOC} = Analyt, der mit gelöster organischer Substanz assoziiert ist [µg g^{-1}]

C_W = Analyt, frei gelöst [µg L^{-1}].

Den gesamten Gehalt des Analyten in der wässerigen Phase erhält man durch die Addition von frei gelöstem Anteil und dem Anteil, der assoziiert an die gelöste organische Substanz vorliegt.

Der so genannte effektive Sorptionskoeffizient K_{OCeff} [L g^{-1}] lässt sich – unter der Voraussetzung, dass der gelöste Sorbent keine Interaktion mit der Bodenfestsubstanz eingeht - wie folgt beschreiben (*Gschwend* und *Wu*, 1985):

$$K_{OCeff} = \frac{K_{OC}}{(1 + D \cdot K_{DOC})} \qquad \text{(Gl. 6)}$$

K_{oceff} = effektiver Sorptionskoeffizient [L g^{-1}]

D = Konzentration an gelöstem organischen Kohlenstoff [g L^{-1}].

Die aufgeführten grundlegenden Prozesse der Sorption wurden insbesondere für Schwermetalle sehr weitreichend beschrieben und deren quantitativen Zusammenhänge erfolgreich in verschiedenen Modellansätzen angewandt (*Swartjes* et al., 1991; *Streck*, 1993; *Elzinga* et al., 1999).

Innerhalb der unüberschaubaren Gruppe der organischen Schadstoffe dient vor allem bei den Pflanzenschutzmitteln das aus den oben erläuterten Zusammenhängen abgeleitete K_{OC}-Konzept einer Einschätzung ihres Verbleibs in der Umwelt. Chemische Produkte, die vor der Einführung des Chemikaliengesetzes 1980 in Verkehr gebracht, im späteren Verlauf jedoch als organische Schadstoffe erkannt wurden, sind nur selten hinsichtlich ihres Umweltverhaltens charakterisiert, d. h. deren K_{OC}-Werte sind nicht verfügbar.

Zu diesen Verbindungen, die zudem in großen Mengen produziert werden und z. B. über die Abwasserbehandlung in die Umwelt gelangen, gehören die Alkylphenole mit ihrem Hauptvertreter Nonylphenol.

Nonylphenol zählt zu den sogenannten „endocrine disruptors“, den Stoffen, die das Hormonsystem von Mensch und Tier möglicherweise auf folgende Art und Weise beeinflussen (*Sonnenschein* und *Soto*, 1998):

- Nachahmung endogener Hormone wie Östrogene und Androgene
- Hemmung endogener Hormone
- Veränderung der Synthese- und Metabolisierungsmuster natürlicher Hormone
- Modifizierung der Verfügbarkeit von Hormonrezeptoren

Faunistische Beobachtungen über Störungen im Reproduktionssystem und –verhalten, aber auch über Missbildungen bis hin zu Hermaphrodismus werden mit einer Belastung des Hormonsystems über diese Pfade (und wahrscheinlich weitere, noch unbekannte Mechanismen) erklärt (*Colborn* et al., 1993).

Nonylphenol wurde bei Laborversuchen zur Wirksamkeit natürlicher Östrogene zufällig als östrogen wirksam erkannt, da es aus den verwendeten Kunststoffmaterialien in das biologische Material freigesetzt wurde und Effekte somit auch in den Kontrollproben auftraten (*Soto* et al., 1991). Über den schon von *Adolf Butenandt* in den dreißiger Jahren (*Karlson*, 1990) erkannten Zusammenhang zwischen dem Stoffwechsel von Steroiden und dem malignen Wachstum wird dieser *in-vitro* Test mit der Quantifizierung einer zunehmenden Proliferation von Brustkrebszellen zur Abschätzung der östrogenen Wirksamkeit verschiedenster Stoffe eingesetzt.

Alkylphenole gelangen vor allem als Grundbaustein hochwirksamer Tenside (Abb. 3), den Alkylphenolethoxylaten (APEO), in die Umwelt und reichern sich im Klärschlamm und in Sedimenten an (z. B. *Stephanou* und *Giger*, 1982; *Giger* et al., 1984). Gesetzliche Vorgaben bzw. Selbstverpflichtungen der entsprechenden Industriezweige haben nach diesen alarmierenden Ergebnissen bezüglich des Vorkommens von Nonylphenol in Gewässern, Sedimenten und Klärschlamm in einigen europäischen Staaten zu einem Verbrauchsrückgang der APEO geführt. Diese Maßnahmen wurden aufgrund der aquatischen Toxizität des Nonylphenols getroffen; seine östrogene Wirksamkeit war zu diesem Zeitpunkt noch nicht bekannt. Anhand von Untersuchungen archivierter Miesmuscheln aus dem Nordseeküstenbereich lässt sich auf diesen Verbrauchsrückgang eine Verringerung der durchschnittlichen Konzentration von 4 µg kg^{-1} (1985) auf 1,1 µg kg^{-1} (1995) zurückführen, wobei sich die Zahlen seit 1992 auf einem konstanten Niveau bewegen (*Daten zur Umwelt*, 2001; *Günther* et al., 2002*a*). In den USA und in Kanada, wo APEO in großem Umfang eingesetzt werden, bestehen keine vergleichbaren Regelungen. Jüngere Untersuchungen anaerob behandelter Klärschlämme von *La Guardia* et al. (2001) und *Pryor* et al. (2002) zeugen von mittleren NP-Konzentrationen von 754 mg kg^{-1} TS bzw. 1500 mg kg^{-1} TS, die etwa hundertmal höher liegen als die, die derzeitig in deutschem Klärschlamm gefunden werden (HLfU, 1999).

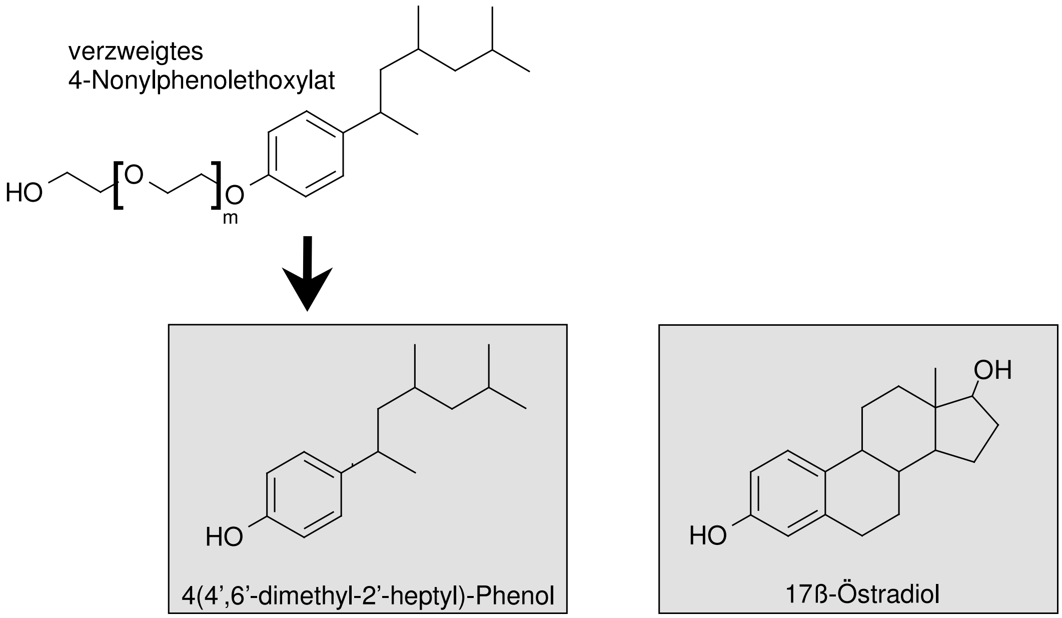

Abb. 3: 4-Nonylphenol als intermediäres Abbauprodukt von 4-Nonylphenolethexylaten. Strukturanalogie zum 17ß-Östradiol (rechter grauer Kasten) am Beispiel eines verzweigten 4-Nonylphenolisomers (linker grauer Kasten).

Das Vorkommen von Nonylphenol in unterschiedlichsten Nahrungsmitteln eines Standardwarenkorbs mit der Schlussfolgerung, dass dieser Stoff ubiquitär verbreitet ist (*Günther* et al., 2002*b*), wirft die Frage auf, welchem Verteilungsverhalten er in der Umwelt unterliegt, um erklären zu können, über welche Pfade er in die Nahrungskette gelangt.

Hierzu existieren Hinweise für dessen moderate Bioakkumulation in aquatischen Organismen (*McLeese* et al., 1981; *Ekelund* et al., 1990), die mit einer weiten Spanne des Oktanol-Wasser-Verteilungskoeffizienten von log K_{ow} 3,01 – 4,48 (*BUA*, 1988; *Ahel* und *Giger*, 1993) gestützt werden. Generell sind die Angaben bezüglich der Bioakkumulationsfaktoren – die zwischen weniger als 100 und mehr als 1.000 schwanken – als unsicher anzusehen. Mittels sogenannter „*in-situ*" Verteilungskoeffizienten, die nach Analyse von Fest- und Lösungsphase in Fließgewässern berechnet wurden, wurde dem Nonylphenol hydrophobes Verhalten und hohe Affinität zur organischen Substanz im Gewässer mit einem logK_{oc} von 4,7 bis 5,9 (*Sekela* et al., 1999; *Solé* et al., 2000*; Isobe* et al., 2001*; Ferguson* et al., 2001) zugeschrieben.

Die oberflächenaktiven Eigenschaften des Nonylphenols erschweren einen sauberen Nachweis und damit eine Quantifizierung seines Sorptionsverhaltens. Mit der Arbeit im Anhang F wird ein Verfahren vorgestellt, das diesen Schwierigkeiten mit einem radioanalytischen Ansatz begegnet, um somit erstmals das Sorptionsverhalten des Nonylphenols in Böden zu beschreiben.

Deutsche Zusammenfassung von Anhang F

Sorptionsverhalten von Nonylphenol in terrestrischen Böden

Nonylphenol (NP) als intermediäres Produkt aus dem anaeroben Abbau vielfach eingesetzter nichtionischer Tenside ist in der Umwelt weitverbreitet. Das Verteilungsverhalten dieser toxischen und das Hormonsystem beeinflussenden Substanz zwischen Boden und Wasser wurde bislang nicht geprüft. Ziel dieser Untersuchung war es, das Sorptions- und Desorptionsverhalten von 4-Nonyl-[^{14}C]-Phenol in einem Satz von 51 Böden mit Hilfe der Batch-Equilibrium Methode zu quantifizieren.

Versuche zur Sorptionskinetik deuteten auf die Einstellung eines scheinbaren Gleichgewichts nach 20 Std. Die Sorption war beeinflusst von der Struktur des Sorptivs, wie anhand des verzweigten 4-Nonyl-[^{14}C]-Phenol und dem linearen Isomer 4-n-NP gezeigt werden konnte. Das Verhalten des linearen 4-*n*-NP differiert von dem des Gemisches der verzweigten 4-NP Isomere. Die Sorption von 4-Nonyl-[^{14}C]-Phenol, getestet anhand von fünf verschiedenen Lösungskonzentrationen, ließ sich mit linear angepassten Sorptionsisothermen beschreiben und ermöglichte die Berechnung der Sorptionskoeffizienten (K_P).

Anhand der Desorptionskoeffizienten ($K_{P\text{-des}}$) konnte Hysteresis beschrieben werden, die unabhängig von den Bodeneigenschaften war und mit zurückgehender eingesetzter NP-Lösungskonzentration abnahm. Die Beziehung zwischen K_p und den Gehalten organischen Kohlenstoffs der entsprechenden Böden ergab einen mittleren $\log K_{OC}$ von 3,97.

Exkurs – isomerenspezifische Betrachtung organischer Schadstoffe

Wie aus der Arbeit in Anhang F auch hervorgeht, besteht technisches Nonylphenol aus einer unbekannten Zahl verschiedener Verbindungen – bislang wurden von *Wheeler* et al. (1997) 22 verzweigte Isomere benannt – , die sich möglicherweise in ihrem Sorptionsverhalten unterscheiden.

Da eine analytische Trennung aller einzelner Isomere bis heute nicht gelungen ist, Ergebnisse zu Synthesen singulärer verzweigter Isomere sich bislang auf drei Verbindungen (*Lalah* et al., 2001; *Vinken* et al., 2002) beschränken, konnte die hormonelle Wirksamkeit oder das Umweltverhalten dieser Einzelisomere noch nicht beschrieben werden.

Große Bedeutung erlangte die isomerenspezifische Analytik von Umweltschadstoffen mit der Auftrennung des theoretisch aus 209 Einzelstoffen bestehenden Gemisches der polychlorierten Biphenyle (*Ballschmiter* und *Zell*, 1980). Vormals nur als Summenparameter zu bestimmen, ist man heute in der Lage, einzelne Vertreter auch aus komplexen Umweltproben zu identifizieren. Von Bedeutung ist dieser analysentechnische Fortschritt nicht nur aufgrund des deutlich unterschiedlichen Umweltverhaltens (z. B. Persistenz, Fugazität) der einzelnen Vertreter – der Kongenere – dieser Stoffgruppe. Je nach Anordnung der Chloratome sind planare Geometrien dieser Moleküle möglich, die deren Toxizität über unterschiedliche Zugänglichkeiten zu den entsprechenden Rezeptoren bedingen. So sind heute bestimmte Isomere der PCBs bekannt, die eine Wirksamkeit ähnlich der der polychlorierten Dioxine aufweisen (*Safe*, 1994). Analytische Probleme bestehen für die Untergruppen der vier-, fünf-, sechs- und siebenfach chlorierten Biphenyle, da diese zahlreiche Stellungsisomere – mit stark unterschiedlicher Wirksamkeit - aufweisen.

Beim Nonylphenol sind sehr viel mehr Stellungsisomere aufgrund der Verzweigung des Nonylrests möglich; bei gleich bleibendem Molekulargewicht ist jedoch deren analytische Auftrennung äußerst schwierig. Mit der im folgenden zusammengefassten Arbeit (Anhang G) wurden einzelne, anhand der präparativen GC aus dem technischen Gemisch isolierte Nonylphenolfraktionen auf ihre östrogene Wirksamkeit mit Hilfe des E-Screen-Assays geprüft.

Deutsche Zusammenfassung von Anhang G

Bestimmung der östrogenen Aktivität verschiedener Nonylphenolfraktionen mit dem E-Screen-Assay

Für eine Reihe ubiquitärer Industriechemikalien wie z. B. Nonylphenol (NP) wurde deren östrogene Aktivität nachgewiesen. Über die Aktivität der einzelnen zahlreichen Isomere, aus denen das technische Nonylphenol-Gemisch besteht, ist kaum etwas bekannt. Unterschiede sind hier – neben dem unterschiedlichen Umweltverhalten – wahrscheinlich.

Um die östrogene Aktivität verschiedener Nonylphenolfraktionen, die mittels präparativer GC gewonnen wurden, zu bestimmen, wurde der E-Screen-Assay eingesetzt. Der Endpunkt dieses in vitro assays ist die Östrogen abhängige Proliferation der humanen Brustkrebszelllinie MCF-7 im Vergleich zur hormonfreien Kontrolle.

Sechs Fraktionen des technischen Nonylphenols und das technische Gemisch selbst wurden mit dem E-Screen-Assay getestet. Geringe, jedoch statistisch nicht signifikante Unterschiede in der östrogenen Aktivität zwischen den einzelnen Fraktionen und zum technischen Gemisch wurden bestimmt.

Der Charakterisierung von Umweltschadstoffen über Biotests bzw. die wirkungsbezogene Analytik (Kombination von chemischer Analytik mit biotechnologischen Testverfahren) wird in jüngster Zeit vermehrt Beachtung geschenkt (*Hock*, 2001). So dienen z. B. Rezeptortests der Ermittlung potenzieller endokriner Disruptoren. Hier wird anstelle von Antikörpern – wie bei indirekten Enzymimmunoassays üblich - ein humaner Östrogenrezeptor genutzt (*Seifert* et al., 1999). Bei zunehmender Standardisierung könnten diese Verfahren eine Basis für eine Risikoabschätzung des Einsatzes organischer Abfälle in der Landwirtschaft darstellen. Inzwischen existieren zumindest für Teilbereiche der Immunanalytik, insbesondere in der Wasseranalytik, Richtlinien zur Validierung und Verwendung derartiger Methoden (*Hock* et al., 1995).

6.2 Feldskala

Böden gelten als Hauptreservoir für halbflüchtige, persistente organische Schadstoffe in der terrestrischen Umwelt (*Brorström-Lundén* und *Löfgren*, 1998; *Cousins* und *Jones*, 1998). Es wird geschätzt, dass der Boden derzeit einen Anteil von über 90% der gesamten Umweltbelastung der ubiquitär vorkommenden polychlorierten Biphenyle (PCB) aufnimmt (*Harrad* et al., 1994). Für den Eintrag dieser Schadstoffe in Böden ist besonders der Belastungspfad über die Atmosphäre zu nennen. Einige ihrer Vertreter werden luftgetragen über weite Strecken transportiert, um z. B. in emittentenfernen Gebieten auf den Boden niederzugehen (z. B. *Mackay* und *Wania*, 1995; *Simonich* und *Hites*, 1995; *Ribes* und *Grimalt*, 2002; *Carrera* et al., 2002). Dieser Transport führt zu einer Verlagerung der PCB und anderer persistenter Schadstoffe innerhalb der nördlichen Hemisphäre – wo sie hauptsächlich produziert und genutzt wurden – weiter in Richtung Norden. Dieses Phänomen wird über die temperaturabhängige atmosphärische Deposition erklärt (*Breivik* et al., 2002). Wenn auch die Konzentrationen der PCBs in der Atmosphäre und vermutlich in den Böden allmählich zurückgehen, werden die weitverbreiteten lokalen Punktquellen (z. B. PCB-haltige elektrische Geräte oder die Beseitigung PCB-haltiger Abfälle) zu einem langandauernden regionalen Transfer dieser Schadstoffe führen (*Backe* et al., 2000).

Organische Schadstoffe werden im Boden vor allem von dessen organischem Kohlenstoff gebunden (siehe Kap. 5.1). Der Gehalt an organischem Kohlenstoff im Boden wiederum ist vom Landnutzungs- und Bewirtschaftungssystem abhängig. Ein Einfluss von Landnutzungssystemen auf PCB-Konzentrationen in Böden ist erkennbar, da z. B. bei forstlicher Nutzung eine Anreicherung der PCB stattfindet: *Brorström-Lundén* und *Löfgren* (1998) ermittelten höhere atmosphärische Deposition von PCB in Waldböden gegenüber der Deposition auf der freien Fläche. *Mackay* und *Wania* (1995) unterscheiden bei der Betrachtung der Schadstoffkonzentrationen in verschiedenen Umweltkompartimenten für den Boden zwischen den Landnutzungen „cultivated soil“ und „uncultivated soil“. Gemäß seines Verteilungsverhaltens und der unterschiedlichen Bodeneigenschaften werden für Hexachlorbenzol unter Gleichgewichtsbedingungen Konzentrationen geschätzt, die im kultivierten Boden 10% unter denen des nicht kultivierten liegen. *Ribes* und *Grimalt* (2002) ermittelten eine starke Abhängigkeit der PCB-Konzentrationen von den Gehalten organischen Kohlenstoffs in subtropischen Gebirgsböden. *Cousins* et al. (1999*b*) schreiben der statistisch signifikanten Beziehung zwischen PCB-Konzentration und dem Gehalt organischen Kohlenstoffs keine große Bedeutung bei der Modellierung der vertikalen Verteilung dieser Stoffe zu. Bei flächenbezogenen Simulationen der PCB-Konzentrationen in Böden empfehlen sie jedoch, den Gehalt organischen Kohlenstoffs in die Berechnungen mit einzubeziehen, um die Genauigkeit Vorhersagen zu verbessern.

Ebenfalls bedeutsam als Senke ist der Boden für anorganische Schadstoffe diffuser Herkunft; z. B. steigen über verschiedene Eintragspfade die Cadmiumkonzentrationen in Böden aus ländlich geprägten Regionen (*Tiktak* et al., 1998). Auch die Bodenbelastung mit Schwermetallen ist von dessen Nutzung und dem angewandten Bewirtschaftungssystem beeinflusst.

Neben diesen langjährigen Prozessen, die von diffusen Schadstoffeinträgen gesteuert werden, gilt es, den Verbleib der über Sekundärrohstoffdünger und Wirtschaftsdünger eingetragenen Schadstoffe zu untersuchen. Üblicherweise werden diese Effekte in Feldversuchen mit stark überhöhten Aufwandmengen mehr oder weniger hoch belasteter Dünger deutlich gemacht und eine Extrapolation in praxis-/umweltrelevante Konzentrationsbereiche impliziert (z. B. *Alcock* et al., 1996; *Eljarrat* et al., 1997). Tatsächlich sind messbare Erhöhungen der Schadstoffkonzentrationen in konventionell gepflügten Böden aufgrund des Verdünnungseffektes erst bei sehr hohen Düngergaben zu erwarten. Mit den im Anhang H und I aufgeführten Arbeiten wurde – bei gesetzeskonformer einmaliger Düngergabe und ausbleibender Bodenbearbeitung - der Verbleib der düngervermittelten Schadstoffe im Boden untersucht. In diesen Arbeiten werden Ergebnisse zu einzelnen Schwermetallen und den polychlorierten Biphenylen (PCB), als Vertreter persistenter organischer Schadstoffe, vorgestellt.

Deutsche Zusammenfassung von Anhang H

Anreicherung von polychlorierten Biphenylen in Böden unter dem Einfluss der Bodenbearbeitung und der Anwendung von Bioabfällen

Die Anreicherung polychlorierter Biphenyle (PCBs) im Boden wird von dessen Eigenschaften wie z. B. dem bearbeitungsabhängigen Gehalt an organischer Substanz oder der Zufuhr organischer Masse mit Abfällen bestimmt. In einem dreijährigen Feldversuch wurde der PCB-Status langjährig differenziert bearbeiteter (konventionelle Pflugbearbeitung gegenüber Direktsaatverfahren) und mit organischen Abfällen (Klärschlamm bzw. Kompost) gedüngter Böden (schluffiger Ton, toniger Schluff, schluffiger Sand) geprüft. Die Anwendung der Abfälle führte innerhalb des Versuchszeitraums zu keiner signifikanten Erhöhung der PCB-Gehalte oder Veränderung der PCB-Muster in den Böden. Deshalb kann die Annahme, PCB-Gehalte im Boden würden über den Austausch Boden-Luft maßgeblich mitbestimmt, bestätigt werden. Der Gehalt organischen Kohlenstoffs war signifikant vom Bodenbearbeitungssystem abhängig und führte zu einer Anreicherung der PCBs in unbearbeiteten Böden. Die lineare Regression der PCB-Belastung mit dem Gehalt organischen Kohlenstoffs der untersuchten unbehandelten Böden war hoch signifikant ($R^2 = 0{,}73$). Aufgrund bereits erhöhter PCB-Gehalte

> in langjährig unbearbeiteten Böden - mit einem Maximalwert von 65 µg kg^{-1} TS in der oberflächennahen Schicht der Kontrollparzellen des tonigen Schluffs - sollten dort weitere Einträge mit organischen Siedlungsabfällen vermieden werden.
>
> Deutsche Zusammenfassung von Anhang I
>
> *Sorption und Bioverfügbarkeit von Schwermetallen in langjährig unterschiedlich bearbeiteten und mit organischen Abfällen beaufschlagten Böden*
>
> Mit dieser Arbeit wurden die Bioverfügbarkeit und Anreicherung von Cd, Zn und Cu in zwei verschiedenen Böden (schluffiger Sand und toniger Schluff), die mit Klärschlamm und Kompost behandelt wurden und verschiedenen Bodenbearbeitungssystemen unterlagen (konventionelle Pflugbearbeitung = CT, Direktsaat = NT), untersucht. Die langjährige Anwendung von NT führte zu signifikanter Zunahme mit Königswasser extrahierbarer Cadmium- und Zinkgehalte in einem Bodenprofil von 0-25 cm Tiefe, speziell in der oberflächennahen Bodenschicht. In der Braunerde wurde eine geringe Zunahme des Cadmiumgehalts mit der Klärschlammbehandlung beobachtet. Die Ergebnisse zu den EDTA-extrahierbaren Schwermetallen waren nicht einheitlich, jedoch waren NH_4NO_3-extrahierbare Anteile in ungepflügten Böden deutlich verringert. Die Bioverfügbarkeit von Schwermetallen war in langjährig ungepflügten Böden reduziert, was sich in einem geringeren Transfer von Cd und Zn in die Pflanze und deren Anreicherung im Boden zeigte. Der Grad der Schwermetallanreicherung im Boden wird von langjährig differenzierter Bodenbearbeitung stärker beeinflusst als von einer gesetzeskonformen Anwendung organischer Abfälle. Langjährig ungepflügte Böden, die mit Schwermetallen angereichert sind, sollten für eine Anwendung organischer Abfälle nicht in Betracht gezogen werden.

Wie aus den Arbeiten hervorgeht, werden die Mobilität und damit die Anreicherungsraten der untersuchten Stoffe vom Bodenbearbeitungssystem beeinflusst. Ein Einfluss der Behandlung mit Sekundärrohstoffdüngern ist im Falle ungepflügter Böden nach relativ kurzen Zeiträumen erkennbar, jedoch im Vergleich zum Effekt einer langjährig differenzierten Bodenbearbeitung von untergeordneter Bedeutung.

Geringere Aufnahmeraten der untersuchten Schwermetalle in die Pflanze bei reduzierter Bearbeitungsintensität unterstützen die Aussagen zur differenzierten Sorptionskapazität infolge unterschiedlicher Bodenbearbeitung.

Bei ansonsten konstanten Standortbedingungen spielt der Humusgehalt des Bodens die entscheidende Rolle etwa bei einer möglichen Verlagerung der Schadstoffe mit dem Sickerwasser oder bei der Aufnahme in die Pflanze. Dieser Humusgehalt gilt als labiler

Bodenparameter, der sich gemäß dem Bewirtschaftungssystem oder der Landnutzung einstellt. Für die hydrophoben organischen Schadstoffe wie z. B. die PCB lassen sich enge Beziehungen zwischen dem Humusgehalt und der Anreicherungsrate bzw. der Sorptionskapazität ableiten. Es ist denkbar, bei ausreichend großem und diesbezüglich heterogenem Probenpool Regeln zu entwickeln, die eine Vorhersage des Anreicherungsverhaltens dieser Stoffe in Abhängigkeit von dessen Humusgehalt erlauben.

Die Sorptionskapazität der Böden für Schwermetalle wird - neben dem Gehalt organischen Kohlenstoffs - als eine Funktion verschiedener Bodeneigenschaften ermittelt (*van der Zee* und *van Riemsdijk*, 1987). Um langfristig eine Gefährdung des Schutzgutes Wasser über die Nutzung des Bodens in seiner Funktion als Puffer- und Ausgleichsmedium zu vermeiden, muss diese Funktion für die unterschiedlichen Böden differenziert auf einer regionalen Maßstabsebene bekannt sein. Ganze Regionen hinsichtlich ihrer Sorptionskapazität für Schadstoffe zu charakterisieren, ist auf der Basis der Erstellung von Sorptionsisothermen äußerst aufwändig bzw. unmöglich.

6.3 Regionale Skala

Für das Schwermetall Cadmium und das Metalloid Arsen wird in der Arbeit im Anhang J ein Verfahren zur Abschätzung der Parameter K_f und m der Freundlich-Gleichung (siehe Gl. 3) vorgestellt. Nach der Bestimmung des Sorptionsverhaltens dieser Stoffe in 159 Bodenproben wurden anhand multipler linearer Regression einiger ausgewählter, leicht bestimmbarer Schlüsseleigenschaften des Bodens mit den Freundlich-Parametern folgende Pedotransferfunktionen erstellt:

$$\ln K_f = konst. + b_1 \cdot pH + b_2 \cdot Ton + b_3 \cdot TOC + b_4 \cdot Fe_d \qquad \text{(Gl. 7)}$$

$$\ln m = konst. + b_1 \cdot pH + b_2 \cdot Ton + b_3 \cdot TOC + b_4 \cdot Fe_d \qquad \text{(Gl. 8)}$$

konst. = Konstante

pH = pH-Wert

Ton = Tongehalt [g g^{-1}]

TOC = Kohlenstoffgesamtgehalt [g g^{-1}]

Fe_d = Gehalt Dithionit löslicher Eisenoxide [g g^{-1}]

Prinzipiell können hiermit Sorptionskapazitäten von Böden für verschiedene Schadstoffe abgeschätzt werden, die, in einem weiteren Schritt, auf den regionalen Maßstab zu übertragen sind.

> Deutsche Zusammenfassung von Anhang J
>
> *Regionalisierung der Sorptionskapazitäten für Arsen und Cadmium*
>
> Um der Funktion der Pufferung von Schwermetallen gerecht zu werden, ist eine Überfrachtung der Böden z. B. mit As und Cd zu vermeiden. Diese Pufferfunktion gilt es im regionalen Maßstab über die Kenntnis der Sorptionskapazitäten der Böden abzuschätzen. Die großflächige Bestimmung dieser Sorptionskapazitäten ist jedoch aufgrund des dafür notwendigen hohen Laboraufwands kaum möglich. Mit den hier präsentierten Daten wird das Rückhaltevermögen für Cadmium und Arsen anhand von Standardbodenparametern abgeschätzt. Batch-Experimente dienten der Bestimmung des Sorptionsverhaltens von 40 Böden aus der Region Freiberg/Sachsen in Deutschland. Die erzielten Sorptionsisothermen aus den Laborexperimenten wurden an die Freundlich-Funktion ($S = k \cdot C^m$) angepasst. Die beiden Konstanten (k, m) dieser Funktion wurden für die multiple lineare Regression herangezogen, um die Sorptionskapazität mit den Bodenparametern zu korrelieren. Als wichtigste Einflussgrößen wurden hierbei der Tongehalt, der pH-Wert, der Gehalt organischen Kohlenstoffs sowie die Dithionit lösliche Eisenfraktion in den Berechnungen berücksichtigt. Aufgrund des langjährigen Erzabbaus in der Region um Freiberg bestehen hier hohe Hintergrundbelastungen für die beiden untersuchten Elemente As und Cd, die in dieser Studie mit zwei unterschiedlichen mathematischen Verfahren berücksichtigt wurden. Die Laborergebnisse wurden vor der Anpassung an die Freundlich-Funktion entsprechend korrigiert, um anschließend Pedotransferfunktionen zu bestimmen. Mittels dieser Transferfunktionen konnten die Parameter k und m für die Sorption von Cadmium mit einer statistischen Sicherheit von 91% bzw. 62% (korrigiertes R^2) geschätzt werden, wobei die Vorhersagbarkeit für die Sorption von Arsen nicht praktikabel ist mit geringen R^2-Werten von 17% bzw. 7%.

Die dargestellte Methode mit dem Anwendungsbeispiel zu einer Region mit hoher Schwermetallgrundbelastung zeigt das regional deutlich differenzierte Vermögen der Böden, als Abbau- und Ausgleichsmedium zu wirken. Hiermit können Flächen ausgewiesen werden, die sich aufgrund ihrer Sorptionseigenschaften für eine stoffliche Verwertung organischer Abfälle eignen. Weiterhin lassen sich bei Variation einzelner sorptionsbestimmender Eigenschaften – etwa durch eine Änderung in der Nutzung oder Bewirtschaftung – Sorptionskapazitäten der Böden prognostizieren.

In Fortführung dieser Arbeit wurden bodenübergreifende, erweiterte Freundlich-Isothermen abgeleitet. Um ein Entscheidungsmodell zur nachhaltigen Anwendung organischer Abfälle in der Landwirtschaft bereit zu stellen (Anhang K), wurden Bodeneigenschaften, etwa wie der pH-Wert, der Gehalt an organischem Kohlenstoff und der Tongehalt, in die Freundlich-Gleichung wie folgt integriert:

$$S = k \cdot C^{m} \cdot (H^{+})^{a} \cdot C_{org}^{b} \tag{Gl. 9}$$

S = Schwermetallkonzentration, sorbiert an die feste Phase [mg kg^{-1}]

C = Schwermetallkonzentration in der Lösungsphase [mg L^{-1}]

(H^{+}) = Protonenaktivität [-]

C_{org} = Gehalt an organischem Kohlenstoff [g g^{-1}]

a, b, m = dimensionslose Exponenten

k = Koeffizient der Freundlich-Gleichung [L^{m} mg^{1-m} kg^{-1}].

In diese erweiterte Freundlich-Gleichung können noch andere, ebenfalls sorptionsrelevante Bodeneigenschaften aufgenommen werden, die für diese Anwendung in möglichst großer Breite zur Verfügung stehen bzw. einfach zu bestimmen oder abzuleiten sind.

Nach dieser Parametrisierung lässt sich mit den abgeleiteten Pedotransfergleichungen unter Berücksichtigung der aufgeführten Bodeneigenschaften die Schwermetallkonzentration in der Bodenlösung und der Bodenfestphase abschätzen (*Streck*, 1993; *Gäth*, 1996; *Ingwersen* et al., 1998; *Gäth* et al., 1999). Mit den berechneten standortabhängigen Sorptionskapazitäten und Informationen zur Sickerwasserrate können schließlich die Geschwindigkeiten der vertikalen Schadstoffverlagerung oder Zeiträume einer Anreicherung bis an Bodengrenzwerte abgeschätzt werden. Mit der Arbeit in Anhang K wird ein Entscheidungsmodell zur optimierten, nachhaltigen Ausbringung organischer Abfälle in der Landwirtschaft, das sich auf erweiterte Freundlich-Isothermen stützt, mit dem eines auf Schwermetallgesamtgehalten basierenden verglichen.

Deutsche Zusammenfassung von Anhang K

Vergleich von Entscheidungsmodellen zur optimierten Anwendung von Kompost und Klärschlamm in der Landwirtschaft vor dem Hintergrund der Schwermetallanreicherung in Böden

Mit dieser Arbeit werden zwei verschiedene Entscheidungsmodelle (DSS – decision support system) zur Anwendung organischer Abfälle in der Landwirtschaft vorgestellt. Beide DSS ermitteln die maximale Applikationsdauer der organischen Abfälle, indem sie die Ausschöpfung des Aufnahmepotenzials der Böden für Schwermetalle berücksichtigen. Mit dem ersten DSS (DSS-AR) wird das Aufnahmepotenzial aus der Differenz der vorliegenden Schwermetallgesamtkonzentration im Boden (nach Königswasseraufschluss) zum entsprechenden gesetzlich festgelegten Grenzwert abgeleitet. Das zweite DSS (DSS-SI) ermittelt die verbleibende Sorptionskapazität des Bodens für ein Schwermetall, d. h. die Differenz eines vorher definierten Maximums zur tatsächlichen Schwermetallkonzentration am Sorbenten. Die Konzentration sorbierten Schwermetalls wird aus Pedotransferfunktionen abgeleitet (erweiterte Freundlich-Isothermen). Hierfür werden Grenzkonzentrationen in der Bodenlösung (WHO Trinkwasserstandards) oder die aktuelle Konzentration löslichen Schwermetalls (nach Extraktion mit Neutralsalzen) herangezogen. Beide Entscheidungsmodelle wurden mittels Modellszenarien unter Nutzung von Bodendaten (grundlegende physikalische und chemische Eigenschaften; Cd, Pb und Zn Konzentrationen) verschiedener landwirtschaftlich genutzter Regionen und den entsprechenden für Deutschland gültigen gesetzlichen Vorgaben bewertet. Hierbei bewies das DSS-SI eine höhere Leistungsfähigkeit als das DSS-AR, d. h. die Aufnahmekapazität des Bodens für Schwermetalle wurde unter Berücksichtigung der Umweltstandards effizienter genutzt. Weiterhin wurde das DSS-SI der natürlichen Variabilität der Bodenbedingungen besser gerecht, indem es einen erweiterten Satz von Bodeneigenschaften kombinierte. Trotz dieser Hinweise für dessen hohe Leistungsfähigkeit besteht weiterer Verbesserungsbedarf des DSS-SI: Die implementierten Pedotransferfunktionen bedürfen einer weiteren statistischen Absicherung, um den Vorhersagebereich zu konsolidieren und zu erweitern. Die Güte des Entscheidungsmodells DSS-SI ist abhängig von der Datenverfügbarkeit und gilt in der betrachteten regionalen Skala nur unter den gegebenen Umweltbedingungen und der gegenwärtigen Rechtslage. Ein direkter Transfer der Ergebnisse dieser Studie in andere Regionen mit abweichender Gesetzgebung und Naturausstattung ist kritisch zu beurteilen. Eine individuelle Prüfung der beiden Entscheidungsmodelle ist somit vor einem beabsichtigten Transfer – als Einführung in den Entscheidungsprozess - unabdingbar.

7 Ausblick

Die Qualität der Sekundärrohstoffdünger ist ein Spiegel unserer Konsumgewohnheiten und kann vor allem verbessert werden, wenn der umweltoffene Einsatz umweltschädlicher Produkte auf ein Minimum reduziert wird. Dieser Grundsatz gilt für Klärschlamm, Biokompost und ebenfalls für Wirtschaftsdünger aus der landwirtschaftlichen Tierhaltung. Das Schließen von Nährstoffkreisläufen über die stoffliche Verwertung dieser Abfallstoffe muss vor der Zielsetzung geschehen, eine Anreicherung von Schadstoffen im Boden auszuschließen. Da sich diese Zielsetzung nicht kurzfristig realisieren lässt, muss man sich ihr über ständig zu verbessernde, nachweisbare Qualitätsziele annähern.

Im Sinne eines Qualitätsmanagements müssen die Ursachen für eine übermäßige Belastung dieser potenziellen Nährstofflieferanten offengelegt und sukzessive behoben werden. Sekundärrohstoffdünger sollten, unter Anlegung höchster Qualitätsansprüche, als Produkt verstanden werden. Im Zuge dieser Produktrealisierung ist es selbstverständlich, durch Optimierung der einzelnen Teilprozesse über geeignete Kontrollmaßnahmen ein den Erfordernissen eines nachhaltigen Pflanzenbaus entsprechendes Erzeugnis zu verwirklichen.

Eine kontinuierliche Ausweitung einer stets zu verbessernden Analytik zur Produktprüfung ist unausweichlich, wenn Sekundärrohstoffdünger als wertvolle Nährstoffträger aus organischen Abfällen verstanden werden sollen. Dies ist besonders vor dem Hintergrund der zahlreichen organischen Schadstoffe mit zum größten Teil unbekannten Wirkungsmustern notwendig.

Die Mehrzahl dieser, zumeist erst während der letzten 60 Jahre produzierten organischen Verbindungen, sind hinsichtlich der verschiedenen Ökotoxizitätskriterien noch ungeprüft. Diese Wissenslücken gilt es mit noch größeren Anstrengungen als bisher zu schließen, um die fachliche Grundlage zu haben, Konsequenzen, wie z. B. Anwendungsbeschränkungen, zu ziehen.

Ähnlich der Analyse der Schadstoffe in Muttermilch könnte die Ermittlung der Belastung des Klärschlamms als Indikator für die aktuelle Umweltbelastung durch Schadstoffe gelten. Hierfür müssen kontinuierlich Analysenmethoden verfeinert werden, um auch dem Phänomen Rechnung zu tragen, dass Ersatzstoffe von inzwischen verbotenen Chemikalien sich in Nahrungsnetzen anreichern, und es ihren „Vorgängern“ unglücklicherweise gleichtun. Die Kombination von Biotest und chemischer Analytik sollte als wirkungsspezifische Analytik stärker berücksichtigt werden, um z. B. mögliche additive

Effekte verschiedener Hormone oder hormonähnlicher Chemikalien, die über das Abwasser oder den Klärschlamm in die Umwelt gelangen, zu erfassen. Eine Möglichkeit wäre der im Anhang G vorgestellte robuste E-Screen-Assay, der bereits erfolgreich zur Bewertung der östrogenen Wirksamkeit von Kläranlagenabläufen eingesetzt wurde. In Verbindung mit einer heute verfügbaren leistungsfähigen und kosteneffizienten instrumentellen Analytik ließe sich eine angemessene Endprüfung des Produkts Sekundärrohstoffdünger realisieren.

Die weitergehende Qualitätsprüfung des Klärschlamms, die nur bei dessen stofflicher Verwertung ökonomisch sinnvoll erscheint, ist als Instrument zur Analyse des menschlichen Einflusses auf Ökosysteme zu sehen. Diese Analyse wird – zum heutigen Zeitpunkt durchgeführt – nur wenige Klärschlämme mit geringer Schadstoffbelastung für eine vorzugsweise regionale Verwertung in der Landwirtschaft zulassen.

Mit oberster Priorität ist den Anforderungen des Bodens gerecht zu werden, d. h. zunächst müssen dessen Spezifika bekannt sein. Nicht nur sein Nährstoffanspruch, auch die zumutbare Fracht an schädlichen Stoffen müssen kontinuierlich evaluiert werden. Der Landwirt und die Fachberatung müssen noch mehr als bisher an Methoden des Managements herangeführt werden. Vertrauen kann die Landwirtschaft nur über die Zertifizierung ihrer Managementmethoden wiedererlangen, wie sie seit längerer Zeit in nahezu sämtlichen anderen Branchen selbstverständlich ist.

Wie mit der vorliegenden Arbeit gezeigt wurde, findet eine messbare Schadstoffanreicherung im Boden über sehr lange Zeiträume statt. Vor diesem Hintergrund ist eine Kreislaufführung bei kontinuierlich zu verbessernden Qualitäten der eingesetzten Materialien möglich: Derzeit ist an eine regionale Verwertung hochwertiger Sekundärrohstoffdünger aus dem ländlichen Raum zu denken; höher belastete organische Dünger gilt es zunächst von Schadstoffen zu entfrachten, um sie langfristig ebenfalls für eine stoffliche Verwertung vorzusehen.

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Anhang A

Reducing tillage intensity - a review of results from a long-term study in Germany -

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Soil & Tillage Research 1999, 53, 15-28

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Abstract

This paper reviews research performed at the Justus-Liebig-University of Gießen, Germany into the impact of different tillage systems on soil properties and quality. The impact of intensive soil tillage treatments on several soil properties was described by means of selected data obtained through long-term interdisciplinary research.

The experiments were based on comparative application (long-term, up to 18 years investigations) of the respective tillage options on different soils (e. g. Eutric Cambisol, Eutric Fluvisol) ranging in texture from sand to a silt loam. These soils are located at five field sites with different crop rotations in the central German state of Hesse. Tillage intensity of the systems was considered to decrease in the following sequence: Conventional plough tillage (CT), reduced tillage (RT), and no-tillage (NT).

For elucidating the impact of tillage intensity, the tillage extremes CT and NT were compared. Physical conditions of soil as influenced by the application of RT were considered to be intermediate between CT and NT. In general, bulk density in the upper layer of NT soils was increased, resulting in a decrease in the amount of coarse pores, and a lower saturated hydraulic conductivity when compared with the CT and RT soils. Surface cover by crop residues and higher aggregate stability under NT protected soil fertility by avoiding surface sealing and erosion. Lateral losses of herbicides were also reduced under NT conditions, whereas the susceptibility for preferential vertical transport of herbicides needs further evaluation. Accumulation of organic matter and nutrients near the soil surface under NT and RT were favorable consequences of not inverting the soil and by maintaining a mulch layer on the surface. Those improvements were associated with enhanced biological activities in NT and RT topsoils. Increased earthworm activity in NT treatments was associated with a system of continuous macropores which improved water infiltration rates. Earthworms support decomposition and incorporation of straw. Soils which have not been tilled for many years were more resistant to vehicle passage; consequently, the compaction by traffic was lower. Penetration resistance curves indicate that a uniformly stable structure had developed over the years in NT soils.

Overall, the results show that RT and NT were beneficial to the investigated soil properties. If crop rotation, machinery, and plant protection are well adapted for the introduction of conservation tillage, these systems may replace conventional ploughing systems in many cases in German agriculture.

Soil Till. Res. 1999, 53, 15-28

Introduction

Recent European Union negotiations about agricultural policy may force German farmers to consider reducing tillage intensity and other purchased inputs in order to remain economically competitive. The availability of reliable chemical weed control, improved tillage and planting designs, and predominantly large field sizes in the eastern part of Germany will increase the extent of application of those tillage systems that reduce the costs for crop production. Benefits of conservation tillage systems from the ecological point of view are assumed in agricultural practice, administration, advice, and research in Germany. Experiences in the application and research of conservation tillage in the U.S. have revealed the beneficial long-term effects of these tillage systems on soil physical, chemical, and biological properties *Hubbard* et al., 1994; *Karlen* et al., 1994). Conservation tillage methods will likely become the favored approach in many regions of Germany because of economical and ecological influences (*Tebrügge* and *Böhrnsen*, 1997).

We present here the effects of decreasing tillage intensity on several soil properties from a comprehensive interdisciplinary research project carried out on different soils in Germany (Fig. 1). This research was initiated by the Institute for Agricultural Engineering of the University of Gießen in 1979 (*Eichhorn* et al., 1991).

Soil physical properties discussed herein are those considered most relevant to crop growth and to the protection against undesirable losses of soil and agrochemicals through erosion and/or leaching. Three tillage systems were considered, conventional tillage (CT): use of a moldboard plough; conservation or reduced tillage (RT): non inversion tillage; and no-tillage (NT) where the only soil disturbance is caused by planting. The comparison between tillage extremes of CT and NT was utilized to determine the effects of tillage intensity on a range of soil properties.

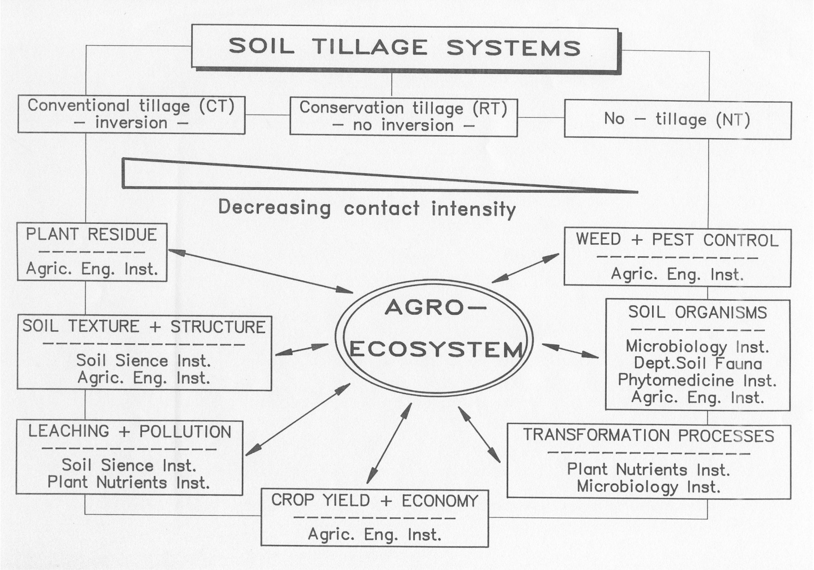

Fig. 1: Institutes and research subjects involved in the joint project on the interrelations of soil tillage systems and the soil ecosystem.

Materials and methods

Experimental Sites

Five field sites with different soil properties were selected (Table 1). Full-sized plots (200 m long, 12 m wide) in two replicated experiments were used to compare the tillage treatments on these sites. The tillage treatments were mainly applied to cereal crops, sugar beet (*Beta saccharifera* L.), maize (*Zea mays* L.), or rape (*Brassica* sp.).

Tillage Systems

The tillage systems had been applied consecutively to the same plots for several years (Table 1). The different tillage methods used in the investigations and the decreasing impact of the implements to the soil (from CT to NT) as well as their influence on agrotechnical aspects are illustrated in Fig. 2.

Table 1: Characteristics of the field sites under investigation.

Soil	Texture [g kg^{-1}]			Soil type	Precip. [mm year^{-1}]	Mean temp. [°C]	Crop rotation	Beginning year
	Clay	Silt	Sand					
Silt loam	310	530	160	Eutric-Fluvisol	600	8	cereal (8 yr.) silage maize (3 yr.)	1986
Loam	265	559	176	Stagnic Luvisol	625	7.6	Cereal (14 yr.) Rape (3 yr.)	1980
Loam	212	673	115	Luvic Phaeozem	575	9	Cereal (13 yr.) sugar beet (4 yr.)	1980
Loam	138	667	195	Luvisol	630	8	Cereal (7 yr.) Rape (2 yr.)	1988
Sand	57	293	650	Eutric Cambisol	600	9	Cereal (8 yr.) sweet maize (4 yr.) sugar beet (5 yr.)	1980

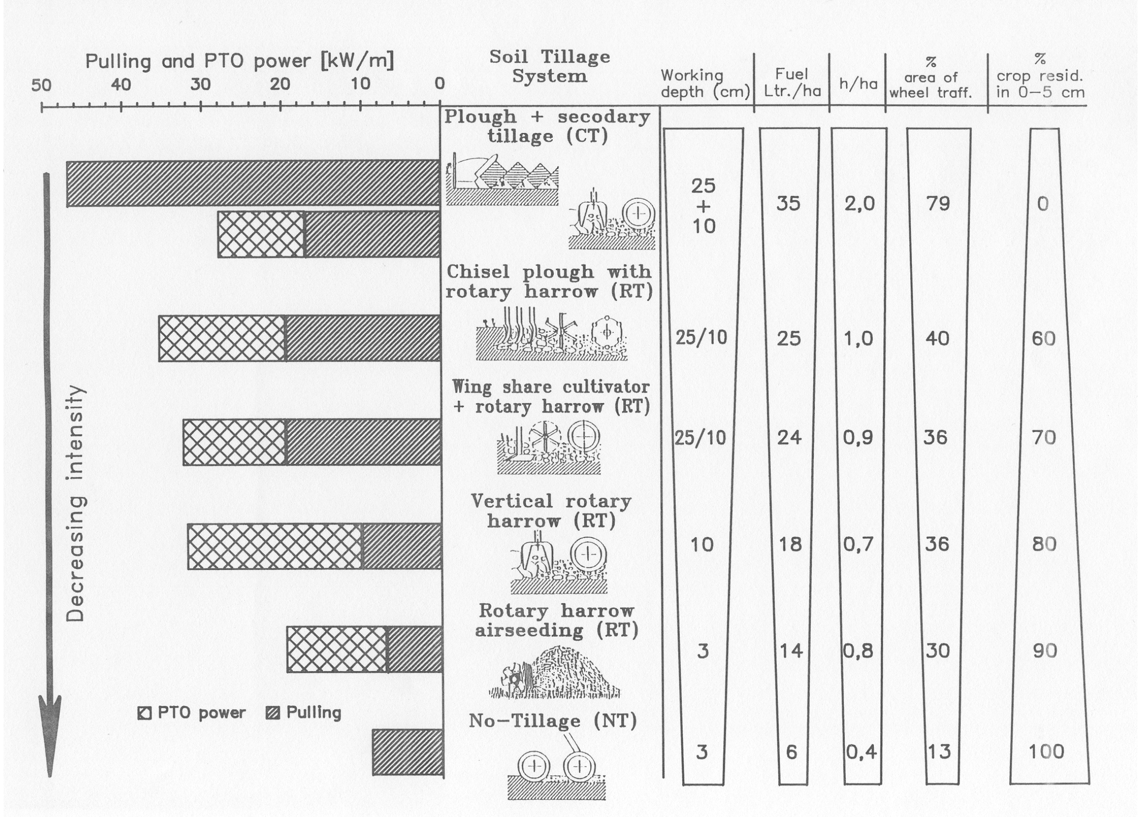

Fig. 2: Applied tillage systems and their effects on performance and requirements. Impact on soil depth and soil surface.

Determination of soil physical properties

Bulk density and water content

Bulk density was determined by taking soil-core samples of 100 cm^3 and 250 cm^3 at 15 and 35 cm soil depths (10 replicates per plot), dried to 105°C and weighed. Soil moisture status on the Stagnic Luvisol in spring (27.04.1993) was quantified by gravimetric moisture content.

Penetration resistance

A hand-operated penetrologger (*Bush-Penetrometer-Eijkelkamp*) with a 60° cone of 12.83 mm diameter and an area of 130 mm² was used to measure penetration resistance down to a depth of 500 mm (ten readings per soil profile). The measurements were carried out on the Stagnic Luvisol at the same time to sampling for water content determination between the rows of winter wheat (*Triticum* sp.).

Pore volume and pore size distribution

The pore volume in soil depths of 2-6, 12-16, 20-24, and 36-40 cm was determined by the collection of undisturbed soil cores of 100 cm^3 volume. After saturation of the samples in the laboratory, they were drained by a pressure plate outflow method with pressures of -2.5, -6, -10, -30, and -100 kPa (*Richards* and *Fireman*, 1943). Pore size distribution was estimated according to the water desorption characteristic, as suggested by *Hartge* (1978).

Trafficability

By means of a pressure gauge (according to *Bolling*, 1987) soil stress under the vehicle wheel was determined on the *Luvic Phaeozem* (20.04.1988). A tractor with a front wheel load of 20.85 kN and a rear wheel load of 13.50 kN was used for the tests. Soil stress at 20 cm and 40 cm depth was determined (ten replicates) during passage. In addition to these measurements, soil samples were taken before and after each passage and analyzed for bulk density and pore size distribution.

Additionally, the behaviour of the soil under increasing pressure was observed by means of a triaxial shear experiment (*Lang* and *Huder*, 1985) in the laboratory.

Aggregate stability

Aggregate stability was determined using a single drop rainfall experiment for the aggregate size class 5.6 mm - 6 mm (*Farres* and *Cousen*, 1985; *Roth*, 1991). Furthermore, stability of moist aggregates was determined by the crushing test according to *Horn* and *Dexter* (1989) and *Mitschke* et al. (1991).

Saturated hydraulic conductivity

The method for measuring the saturated hydraulic conductivity is given by *McIntyre* (1958) and *Hartge* (1971). To indicate the tendency towards surface crusting, the hydraulic conductivity of both crusted and non crusted (after removing the crust) samples was measured throughout the growing period. A quotient can be calculated from both values to give the sealing index (*Groß*, 1996).

Organic carbon

Soil samples from the *Eutric Cambisol* were taken at 0-2.5, 2.5-5, 5-10, 10-15, 15-20 and 20-25 cm depth (10 replicates). The organic carbon content was determined by wet oxidation (*Schlichting* and *Blume*, 1966).

Abundance of earthworms and channels

Small plots (0.25 m^2), surrounded by a stainless steel frame were treated with formalin. All worms which appeared on the surface after 0.5 h were collected, and counted (*Friebe* and *Henke*, 1992). Subsequently, the soil was excavated to 35 cm and the number of inactive earthworms determined.

Additionally, the number of earthworm channels on the *Luvic Phaozem* were counted in 20 cm and 40 cm depth in May and October 1989 (according to a method of *Edwards* et al., 1988). The quantization of the visible biopores (Ø > 1 mm) was improved by digital image analysis (*Beisecker*, 1994).

Runoff, soil erosion, and lateral losses of herbicides

On the *Luvisol*, eight irrigation experiments on small inclined plots (1.8 m x 4.3 m; slope: 12.75%; tillage treatments CT and NT) were carried out. By means of a rainfall simulator (*Kainz* and *Eicher*, 1990), artificial rainfall (63 mm h^{-1}) was applied. This rate simulated a worst case heavy storm event.

For estimation of herbicide losses, the plots were treated two hours before rainfall event (worst case conditions) with herbicide formulations containing the following active ingredients: isoproturone, terbuthylazine, and metolachlor. Sorption kinetic studies revealed that sorption of triazines and phenylureas occurs with an initial rapid rate followed by a slower rate of sorption also under nonequilibrium conditions (*Kookana* et al., 1992). However, under the given conditions some sorption of the herbicides will occur, so differences among herbicides with different properties should be evaluated. Herbicides were chosen according to their solubility in water, affinity to soil, and their relevance in agricultural practice. These properties and their application rates are given in Table 2.

Immediately after sample collection, water and sediment fractions were separated, then extracted for each herbicide and analyzed by HPLC (*Düring*, 1996).

Table 2: Water solubility, sorption index (K_{oc}), and half lives of herbicides used (*Tomlin*, 1995).

Common name	Isoproturon	Metolachlor	Terbuthylazine
Chemical name	3-(4-isopropylphenyl)-1,1-dimethylurea	2-ethyl-6-methyl-n-(2-methoxy-1-methyl-ethyl)-chloro-acetanilide	2-tert.-butylamino-4-chloro-6-ethylamino-1,3,5-triazine
Application rate	2000 g ha^{-1}	1680 g ha^{-1}	840 g ha^{-1}
Water solubility [g l^{-1}]	0.06	488	0.0085
Sorption index (K_{oc}*)	72 - 158	121 - 309	162 - 278
Half life in soil [days]	6 - 29	ca. 30	30 - 60

*K_{oc} = Soil sorption index: Index of the degree of adsorption of a compound to soil normalised for carbon content; the higher the K_{oc} value, the stronger the compound is adsorbed to soil.

Results and discussion

Organic carbon content

Accumulation of organic carbon in the upper soil layer of the Eutric Cambisol is evident under long-term no-tillage conditions and has also been identified by others (*Blevins* et al., 1983; *Rhoton* et al., 1993; *Singh* et al., 1994). The difference in soil organic matter distribution between CT and NT soil is given in Fig. 3.

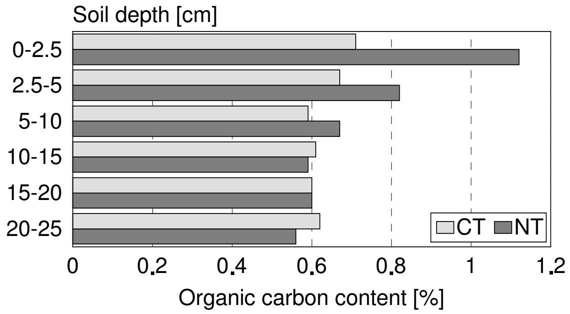

Fig. 3: Effect of long-term applied tillage systems on organic matter contents in soil, expressed by the content of organic carbon in the top soil of the *Eutric Cambisol* (according to *Grocholl*, 1991).

The organic matter stratification is mainly due to the remaining plant residue cover on the soil surface (Fig. 4) which favors the accumulation of organic matter near the soil surface (*Tebrügge* et al., 1991). The litter left on the surface of non-ploughed soils can be considered as a key factor for promoting microbial activity, improving aggregate stability, protecting against erosive water forces, and herbicide behavior.

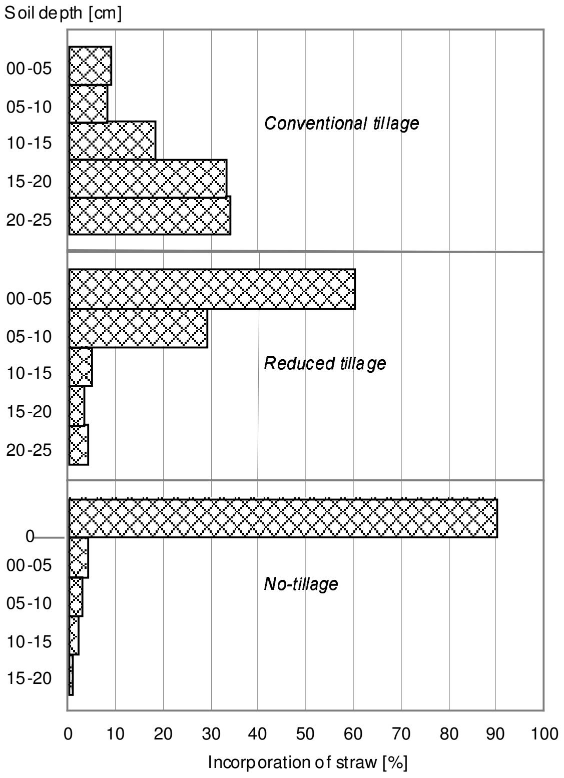

Fig. 4: Degree of incorporation of straw [%] in the soil horizon as affected by soil tillage systems (*Schmidt* and *Tebrügge*, 1989).

Dynamics of bulk density and penetration resistance

Decreasing tillage intensity from the conventional system to no-tillage generally resulted in an increase in bulk density of the upper soil (*Beisecker*, 1994; *Richter*, 1996). However, non-tilled soils show significantly decreased bulk densities directly (0-3 cm depth) at the surface. This would be related to the existing mulch layer (see Figure 3) on top of non-tilled soils (*Beisecker*, 1994) that provides organic matter and food for soil fauna, which loosens surface soil by burrowing activities.

Compaction of NT soil was found at all locations especially at the 0-10 cm soil depth. However, directly below the sub-surface layer (25 - 30 cm soil depth), bulk density of the tilled soils usually was higher than in the non-tilled plots. Compaction in conventionally tilled soils in 25 - 30 cm depth is illustrated (Fig. 5) by the given values for bulk density and the regression curve for penetration resistance. Penetration resistance [MPa] of the soil can be regarded as a factor determining the quality of its structure. No change in resistance with increasing soil depth under no-tillage contrasted with lower resistance under ploughing in the upper soil zone (Fig. 5). At 25 - 30 cm depth, where the tractor wheels compact the soil during ploughing, compaction of the soil (bulk density, 1.51 $Mg \cdot m^{-3}$) could be confirmed by means of this technique, whereas NT did not show this compaction (1.41 $Mg \cdot m^{-3}$). These measurements taken like a snapshot on one day can not give any impression of the dynamics of soil structure over the whole growing season.

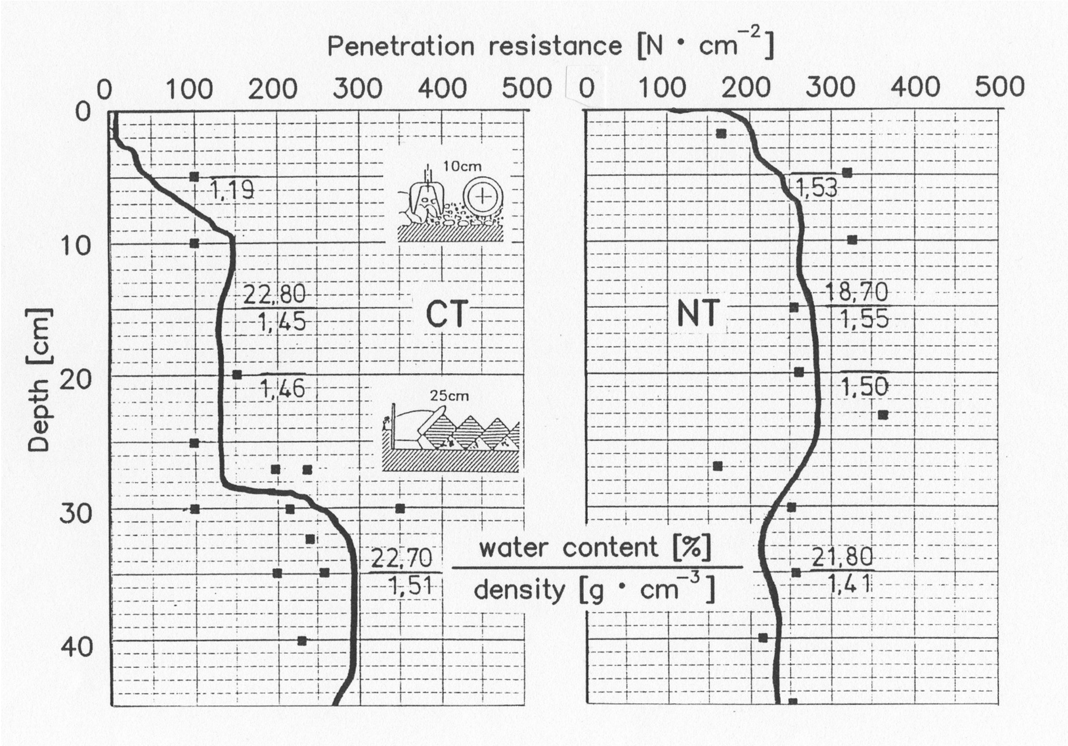

Fig. 5: Penetration resistance, water content, and bulk density in soil dependent on tillage intensity and soil depth - *Luvic Phaeozem*.

Table 3 shows changes in soil bulk density over time. The bulk density after conventional tillage operations in October was very low and was further reduced during a freezing period in December. Later, in the period up to May, a constant increase of bulk density was measured. In contrast, during the same period, the higher bulk densities of the NT-system were progressively reduced. The reason for that can be a self-mulching effect of the *Eutric Fluvisol* which contains 31 % clay and/or an increase of biological activity in springtime.

Table 3: Dynamic of bulk density in different depths of a differently tilled soil (n=12), *Eutric Fluvisol.*

Tillage treatment	Soil depth [cm]	October	December	March	May
		Mean value (range) [$Mg \cdot m^{-3}$]			
CT	4 - 8	1.18 (1.10-1.24)	1.03 (0.96-1.07)	1.17 (1.09-1.21)	1.36 (1.21-1.45)
CT	20 -24	1.26 (1.18-1.51)	1.18 (0.96-1.24)	1.29 (1.19-1.35)	1.42 (1,33-1,49)
NT	4 - 8	1.52 (1.37-1.67)	1.50 (1.43-1.56)	1.37 (1.25-1.49)	1.4 (1.15-1.61)
NT	20 - 24	1.61 (1.52-1.67)	1.45 (1.38-1.52)	1.48 (1.39-1.53)	1.52 (1.47-1.59)

Pore volume, pore size distribution and trafficability

The recurring tillage of CT in October creates an artificial inter-aggregate pore system in the topsoil, which contains nearly 50 % of the total pore volume with pores >120 µm. However, these macropores are unstable as indicated by their volume-reduction over the winter time. The NT plots on the *Eutric Luvisol* showed lower total pore volume (illustrated in Fig. 6 as per cent of soil volume) over the same period with relatively constant values of pore size >10 µm.

The increase in soil stress after wheeling determined by means of pressure gauges showed lowest amounts in the non-tilled plots. Highest pressure was recorded on the ploughed soil at the 20 cm soil depth which was significantly different (0.05 level) from the respective measurements in the NT soil. At the 40 cm soil depth, a similar tendency with lower levels above all tillage treatments was observed. Hence, the most rapid decrease in soil pressure occurred in the non-tilled plots (*Gruber*, 1993).

Further comparison of the results for pore size distribution in the trial plots on the *Luvic Phaeozem* before and after wheeling by a heavy tractor also provided evidence of the varying effects of different tillage systems on the soil structure (Fig. 7). After only one pass, there was a greater reduction of the pore area down to a depth of 40 cm in CT than in NT. Up to 50% of the volume of coarse pores (>50 µm) was reduced by the pressure of the tractor wheels in the CT-system. Hence, the pore surface area in which gas exchange, water drainage and root development occur, was reduced. The reduction of pore volume by a single pass in the NT plots was only 10% at 12 cm depth and 20% (from a higher total volume) at

20 cm depth. No influence of traffic loading was measured at 40 cm depth. Rut depth, which can be taken as a measure of soil surface damage, showed distinctly lower values in NT plots (1 cm) compared to CT (8 cm). Regarding the driving distance which is necessary for conventional tillage operation (approximately 3 fold when compared to NT) the resulting compaction is a serious inherent problem of the CT-system (*Tebrügge* and *Wagner*, 1995).

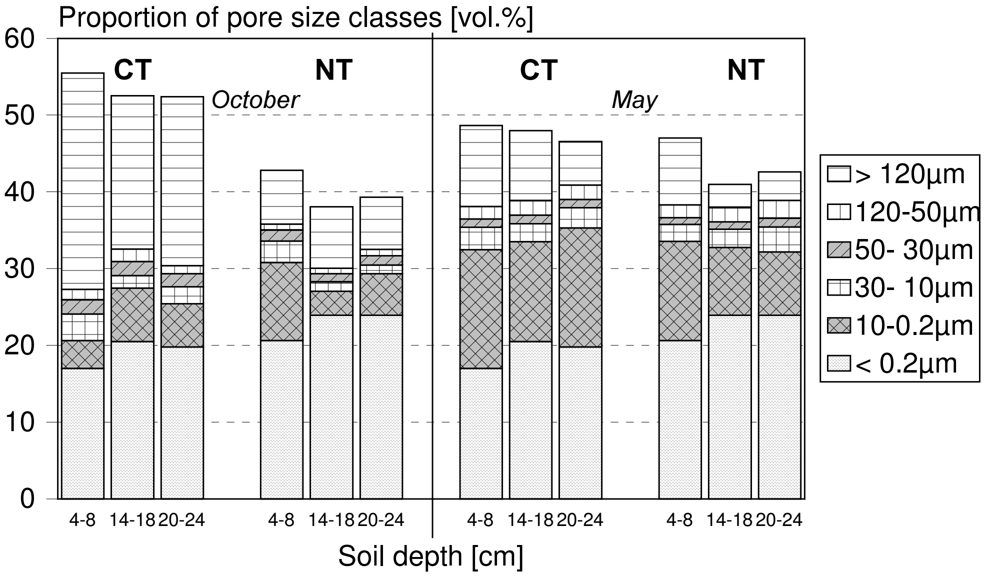

Fig. 6: Pore size distribution (as percent of soil volume) in different depths at different times of conventionally (CT) and non-tilled soil - *Eutric Fluvisol*.

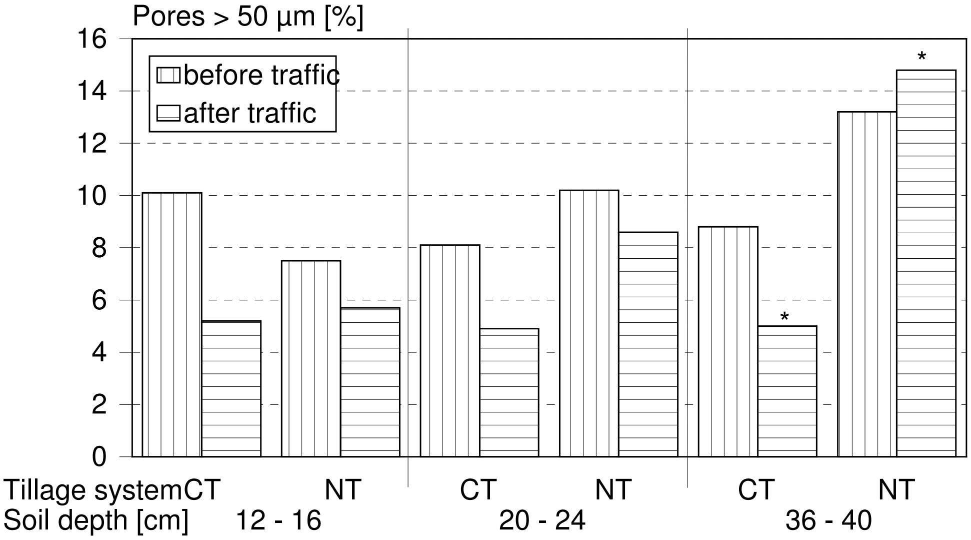

Fig. 7: Pore size distribution before and after traffic in a conventionally tilled (CT) and a non-tilled (NT) soil (*Luvic Phaeozem*). Significant differences (0.05 level) are marked by *. Pore size expressed as percent of soil volume.

Under laboratory conditions triaxial tests give detailed information concerning stress states, as they appear in the soil under load (*Gruber* and *Tebrügge*, 1990). The sample taken from the ploughed plot reacted to the exerted pressure with the highest volume change. Fracture occurred at an axial pressure of less than 0.4 MPa. The soil samples of the non-tilled plot were characterized by the smallest volume changes and therefore had the highest load resistance. Fracture only occurred at an axial pressure of more than 0.7 MPa. Comparing stress conditions, showed that for the NT treatment axial pressure was twice as high as for the CT sample (Fig. 8).

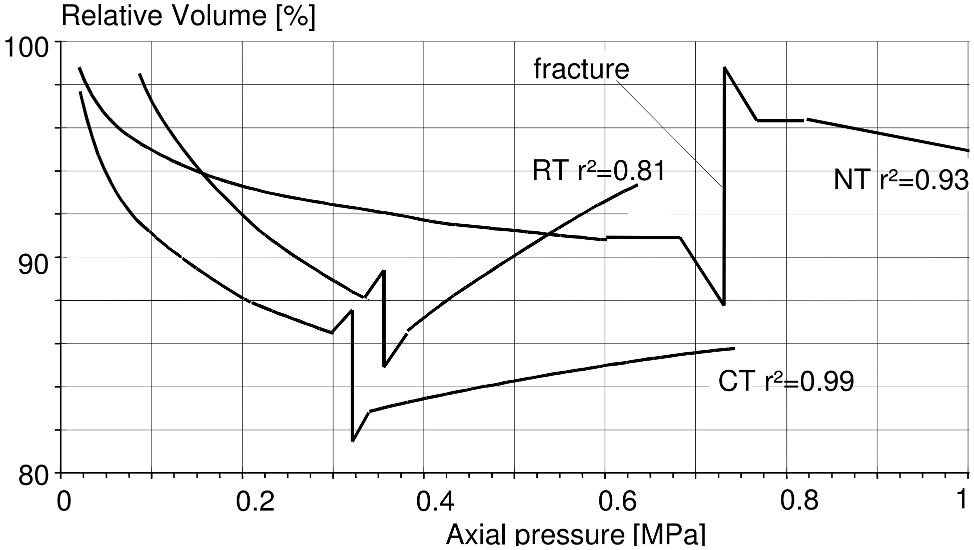

Fig. 8: Relative alteration of volume of soil samples (2 - 12 cm) of different tillage systems (triaxial-test) - *Eutric Fluvisol*, silty loam (*Gruber*, 1993).

The regression curves given in Fig. 8 were derived from non-linear regression equations, based on measured data from three replicates. Results of the experimental studies indicate that soils in an NT-system were more resistant to vehicle passage. Lower soil stresses and track depths confirmed this phenomenon, as well as negligible change in macropore volume on soil loading. For NT, air permeability results suggest a vertical orientation of pore spaces, which produces a high stability to vehicle traffic.

Abundance of earthworms and channels

The intensity of soil tillage strongly influences earthworm populations and, by their activity, the amount of biopores. The long-term application of RT and NT resulted in significantly higher earthworm populations. On the *Luvic Phaeozem* they were approximately 7 times higher in NT than in CT soil (*Friebe* and *Henke*, 1992). The digital image analysis of the visible biopores (> 1 mm) showed higher abundance of these pores in the NT soil (Fig. 9).

However, differences between tillage treatments in the soil at 10 cm depth were not significant. At a depth of 40 cm significant differences between the differently tilled plots have been proven by *Beisecker* (1994). The extent of area of biopores related to the uncovered surface areas in this analysis was less than 2%. However, percentages of 0.89% and 1.58% in depths of 10 cm and 40 cm, respectively, in the NT soil would have significant importance for water infiltration (*Ehlers*, 1975; *Zachmann* et al., 1987; *Edwards* et al., 1988).

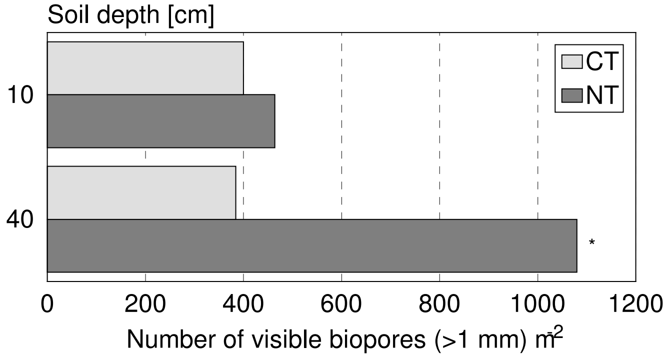

Fig. 9: Visible biopores (> 1 mm) in 10 cm and 40 cm depth of the *Luvic Phaeozem*, dependent on the tillage system (CT = conventional tillage, NT = no-tillage). *Indicates significant differences (0.05 level) (adapted from *Beisecker*, 1994).

In the CT soil, the area covered by biopores with respect to soil depth was 0.22% (10 cm) and 0.23% (40 cm). Deep digging earthworms (e.g. *Lumbricus terrestris*) can build up continuous vertical biopores, and were detected ten times more frequently in NT, where the plant residues remained on the soil surface, than in CT (*Friebe* and *Henke*, 1992). The authors found that in NT treatments, especially in the boundary between topsoil and subsoil, there are considerably more biopores visible than in CT. These biogenic macropores with vertical orientation in the soil profile are very resistant to pressure loading, shown by the trafficability test illustrated in Fig. 7.

Aggregate stability and surface sealing

Aggregate stability on all soils was lowest in the CT treatments. However, with increasing clay contents of the soils, differences in aggregate stability between the treatments decreased (Fig. 10). In addition, resistance of the aggregates against the impact of raindrops was assessed on a monthly basis throughout the growing period on the *Luvic Phaeozem*. For all treatments, the aggregate stability was characterized by fluctuations over time. Despite these fluctuations, increased aggregate stability from CT to RT to NT was clearly observable at all times. It was observed that in the first period after planting on April 20, 1993, aggregate stability decreased in all soils tested. This phenomenon has been reported by *Brunotte* (1990) and was identified as being caused by mechanical disturbance due to tillage and planting operations. As the phenomenon is strongly related to aggregate stability, soil crusting was examined for the different tillage systems after the sowing of sugar beets on the *Luvic*

Phaeozem under natural rainfall conditions. Surface crusts are characterized by a low saturated hydraulic conductivity in comparison to the undisturbed soil. Because of these crusts, the potential for surface runoff and soil erosion and therefore the loss of agrochemicals on such sealed soils is increased.

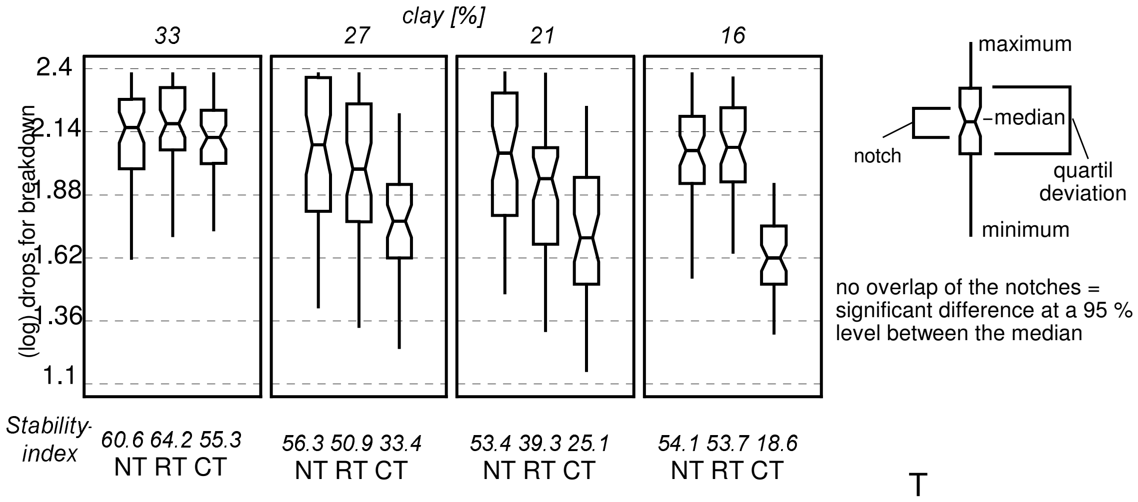

Fig. 10: Aggregate stability for CT, RT and NT on sites with different clay contents. Values are expressed by the number of drops required to break down one aggregate for size class 5.6 - 6mm (*Luvic Phaeozem*). Descriptive statistics by means of notched box-and-whisker plots (*Groß*, 1996).

Although the soil was covered by similar degrees of frozen intercrops throughout all plots, a clearly differentiated sealing with time was measured in the test period (Table 4). The sealing indices were obtained by relating saturated water conductivity of unsealed and sealed soil after one vegetation period, and indicate that the sealing was greatest on the CT soil. Considerably lower indices were obtained in the case of the RT treatment. Hardly any difference was measured between the conductivity of the sealed and unsealed samples on the NT treatment. The calculated rainfall energy and the sealing indices were correlated on different field sites for the differently treated soils. The resulting factors which describe the increase in sealing with time are given in Table 4 and are marked there as sealing susceptibility. The r^2-values for all these linear regression functions are also given.

Table 4: Saturated hydraulic conductivity of sealed and unsealed soil samples, indices for sealing and the calculated susceptibility for sealing at the end of the respective growing periods in relation to the cumulative rainfall energy (*Groß*, 1996).

Field site	Tillage system	Cumul. Rainfall energy [J m^{-2}]	Saturated hydraulic conductivity [cm d^{-1}] unsealed	sealed	Sealing index	Sealing susceptibility	r^2
Eutric	CT	2857	2812	1190	2.36	0.59	0.85
Fluvisol	RT	2857	2950	1790	1.59	0.27	0.87
	NT	2857	450	380	1.18	0.05	0.08
Eutric	CT	2815	923	263	3.51	0.84	0.85
Cambisol	RT	2815	1090	589	1.85	0.33	0.69
	NT	2815	290	238	1.22	0.05	0.11
Luvic	CT	3025	1659	348	4.76	1.20	0.85
Phaeozem	RT	3025	1734	598	2.90	0.67	0.92
	NT	3025	1511	835	1.81	0.28	0.98

Given the high r^2-values, the dependence of sealing on rainfall energy could be proven. However, for the NT treatments on the *Eutric Fluvisol* and the *Eutric Cambisol* no coherence between rainfall energy and surface sealing could be observed. On these soils, plant residues remained on the surface of the conservation tillage treatments. Regarding the *Luvic Phaeozem*, a uniform secondary tillage treatment was applied removing any plant residues from the soil surface. This explains the high correlation between sealing and rainfall energy also for the NT soil. On the *Eutric Fluvisol* swelling and shrinking and high biological activity on the NT plots probably influenced the sealing process. For the *Eutric Cambisol*, the single-grain structure could not contribute to protection against surface sealing. Hence, the residue cover on the soil surface provided protection against splashing energy of the precipitation water. The different tendency towards sealing of the treatments with equal degrees of cover on the *Luvic Phaeozem* was caused through increased organic matter content at the soil surface (see Fig. 3), resulting in higher aggregate stability with decreasing tillage intensity.

Runoff, soil erosion, and lateral losses of herbicides

Water erosion causes severe problems in Germany, especially on silty soils. The factors responsible for this are as follows: decreased infiltration caused by hampered percolation due to subsoil compaction, a lack of pore continuity and buffer capacity of the soil during heavy showers, and surface sealing due to poor aggregate stability.

The rainfall simulation experiments revealed the strong influence of tillage intensity on erosion as numerous authors have shown (i.e., *Packer* et al., 1982; *van Doren* et al., 1984; *Radcliffe* et al., 1988). The soil protective effect of the no-tillage system could be confirmed by significantly lower amounts of both runoff, and more pronounced sediment loss for this silty soil. The cumulative data for runoff and soil losses are illustrated in Fig. 11. The total amounts of runoff after one hour of 63 mm of precipitation were 39 mm (CT) and 24 mm (NT). Sediment losses of 6400 kg ha^{-1} (CT) and 900 kg ha^{-1} (NT) highlighted the soil protective potential of the no-tillage system (*Fischer* et al., 1995).The results regarding the lateral path for losses of the herbicides isoproturon, metolachlor, and terbuthylazine are related directly to the erosion data. In Fig. 11 the different proportions of herbicides lost when compared to the application rates are given. A reduction down to 30% of the loss on the conventionally tilled plots could be achieved on the no-tilled plots.

However, increased infiltration rates and the phenomenon of preferential flow of free water via the macropores may, under certain conditions, increase the downward movement of plant protection agents (*Isensee* et al., 1990; *Edwards* et al., 1992; *Sigua* et al., 1993). This effect may be reduced by enhanced adsorption phenomena as indicated by *Düring* (1996). Furthermore, increased microbial activity (*Böhm* et al., 1991; *Grocholl*, 1991) along with accelerated degradation of herbicides (*Levanon* et al., 1994) and resistance against inhibitory effects of herbicides on the microflora (*Fernau*, 1996) can work against losses of herbicides via leaching. An investigation to determine the relationship between soil tillage and herbicide dissipation was undertaken recently on a European scale (*Borin* et al., 1997).

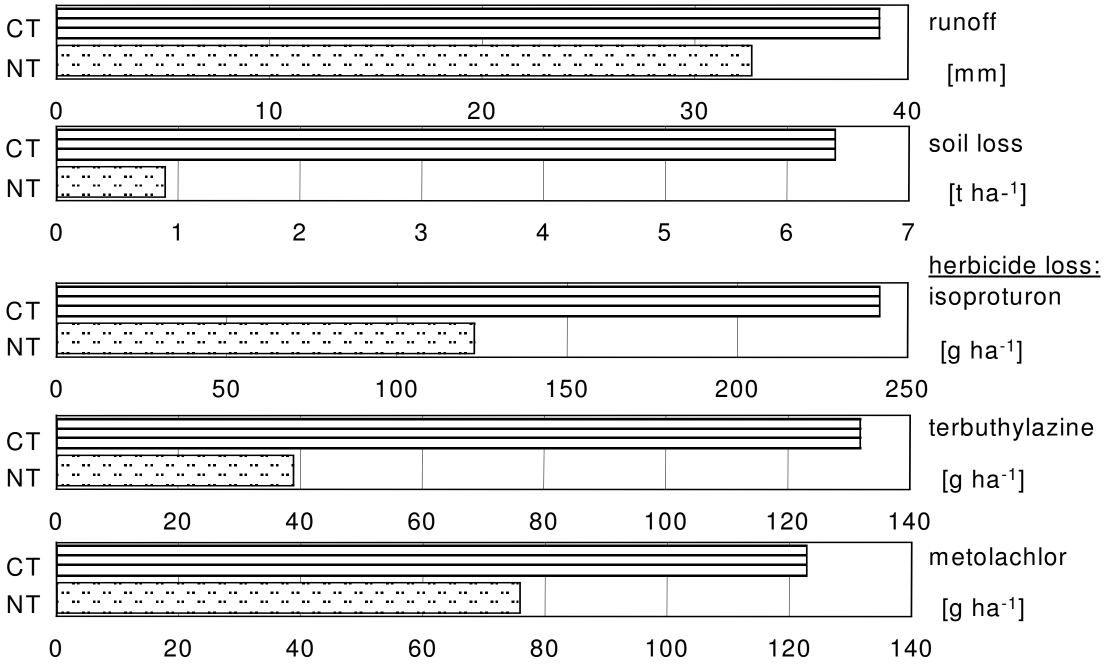

Fig. 11: Runoff, soil loss, and herbicide losses via lateral translocation in a rainfall simulation experiment (63 mm·h^{-1} for one hour); comparison of two different tillage treatments on the *Luvisol* (according to *Fischer* et al., 1995).

Conclusion

Within the given experimental conditions, several soil properties were improved as a consequence of decreased disturbance and the maintenance of cover by crop residues in reduced or no-tillage systems. Soils that have undergone long-term no-tillage were characterized by a higher resistance against stress from vehicle load and by a higher stability of aggregates against the impact of raindrops. Lower susceptibility for soil crusting and erosion and a high abundance of vertically oriented continuous earthworm burrows resulted in increased infiltration rates and reduced soil losses. Moreover, losses of agrochemicals via the lateral path may be clearly reduced under no-till conditions. However, under certain conditions, such as short time intervals between application and a heavy shower event, the downward movement of plant protection agents may be increased. Further research is needed in this field through the cooperation of soil tillage experts and those who study the fate of the various pesticides.

From the results of this long-term research project it was shown that tillage systems which reduce the impact on the soil structure have several beneficial effects. Since the environmental conditions of Germany are quite similar to those in the mid-western and northern States of the U.S., conservation tillage principles and techniques should be applicable.

The large data set from the long-term tillage experiment shows that environmentally sound production can be achieved by tillage systems which reduce the negative impact on soil. Under the premise of increased know-how by the farmer who observes suitable crop rotations, the application of RT and NT systems will increase in significance in Germany. This may be particularly the case for Eastern parts of Germany where large field sizes, soil conditions and climate favour the purchase and usage of improved machines for the application of these tillage systems.

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Anhang B

Depth distribution and bioavailability of pollutants in long-term differently tilled soils

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Abstract

Pollutants can be introduced to soil through the application of organic and inorganic fertilizers and pesticides and through atmospheric depositions. The objective of this research was to evaluate the influence of long-term (9-17 years) tillage systems on the behavior of pollutants in soils. Bioavailability and enrichment of heavy metals, arsenic, and organics, i.e. polychlorinated biphenyls (PCB) and a chlorinated phenol (2,4-DCP) were measured in a Eutric Cambisol and a Luvisol under conventional tillage (CT), reduced tillage (RT), and no tillage (NT). Soil samples were collected from 0-3, 3-10, and 10-25 cm depths.

The upper layer of NT soils was enriched in pollutants, but concentrations decreased with increasing soil depth. Atmospheric deposition of pollutants and input via organic fertilizers was noticeable in soils under long-termNT. Total amount of zinc (59 mg kg^{-1}) was significantly enriched in the 0-3 cm depth of the Luvisol under NT and this was attributed to higher sorption capacity for heavy metal input via liquid manure. In the Eutric Cambisol, NT resulted in significant increase of cadmium extracted by aquia regia in the arable layer of 0-25 cm. As a result of higher soil organic C, long-term accumulation of PCB in NT soils was more pronounced than in plowed soils. In plowed soils the mixing effect resulted in homogeneous distribution of pollutants within a soil depth of 0–25 cm.

The enrichment of organic C in RT and NT soils emphasizes the role of soils as a sink for pollutants, buffering the contaminants against leaching and transfer into crops.

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Introduction

Due to human activities during industrialization, hazardous substances like heavy metals and organic pollutants have been introduced into soils via the atmosphere, irrigation water, and the disposal of wastes. It is essential to understand the fate, i.e. accumulation and leaching, of those substances in soils because they may pose adverse health effects to future generations of people and organisms.

Tillage results in an alteration of soil properties at different depths depending on the type of tillage tool and how it displaces soil. A difference in organic matter content of long-term plowed soils and soils under long-term conservation tillage has been shown (*Blevins* et al., 1983; *Rhoton* et al., 1993; *Singh* et al., 1994). No-tillage can enrich the soil surface with various elements as a result of plant residues left on the soil surface. For example, humus concentrations stratify and decrease with depth within the arable layer (*Lavado* et al., 1999; *Franzluebbers* et al., 1999). In plowed soils, concentrations of elements in the plow pan can increase (*Campbell* et al.,1998; *DeMaria* et al.,1999; *Rasmussen*, 1999; *Bayer* et al., 2000). Stratification due to crop residues leading to enhancement of the cation exchange capacity has been shown to determine soil quality and substance behavior in the enrichment layer (*Karlen* et al., 1994).

Enrichment of heavy metals and micronutrient cations in the surface layer of soils has been shown by *Shuman* and *Hargrove* (1985), *Davis* et al. (1988), and *Franzluebbers* and *Hons* (1996). *Davis* et al. (1988) found specific accumulations of seven heavy metals in a pasture soil which was previously amended with sewage sludge. Lack of plowing resulted in 60 to 100% of the metal load residing in the top 5 cm of the soil. *Sloan* et al. (1998) recovered approximately 100% of the investigated elements in plowed soils 16 years after the application of sewage sludge. The homogeneous distribution of pollutants within a soil depth of 0 to 30 cm was explained by the mixing effect of plow tillage. *Lavado* et al. (1999) observed the stratification and changes in concentration of organic matter, macronutrients and other soil components under the influence of tillage. For example, DTPA-extractable Zn stratified significantly in different patterns between NT and CT. The authors ascribed the increased surface concentrations of some extractable metals to fertilizer applications.

Persistent compounds and some heavy metals in elemental form can accumulate to elevated concentrations with atmospheric deposition and input by fertilizers and plant protection agents that exceed plant uptake (*Gäth* et al., 1999).

Vertical distribution patterns of organic pollutants were also observed for undisturbed soils. However, these investigations were restricted to forest and uncultivated soils, respectively (*McGrath*, 1995; *Krauss* et al., 2000).

A 20-year field research project in Germany has demonstrated the significant impact of tillage intensity on soil physical and chemical properties. Non-inverting tillage systems were beneficial to most soil properties investigated (*Tebrügge* and *Düring*, 1999). These systems may replace conventional plowing systems in German agriculture mainly due to economic benefits. However, behavior of pollutants originating from diffuse and point sources in these differently tilled soils is not known. Tillage-dependent soil properties will likely affect the behavior (accumulation and transport processes) of different pollutants in soil. The purpose of this paper was to investigate the bioavailability and depth distribution of pollutants in soil under different intensity of tillage.

Material and methods

Soils

This study was based on a long-term field experiment involving various tillage systems on different soils. Some sorption relevant and tillage affected properties of the soils, ranging in texture from sand (*Eutric Cambisol*) to a silt loam (*Luvisol*) are given in Table 1. These soils are located at two fields with different crop rotations in the central German state of Hesse. Tillage intensity of the systems was considered to decrease in the following sequence: conventional plough tillage (CT), reduced tillage (RT), and no-tillage (NT). The CT (working depth 25 cm) used a moldboard plow followed by a secondary treatment for seedbed preparation (rotary harrow with a working depth of 10 cm); the RT (working depth 25 cm) did not invert but loosened the soil with a chisel plow; and NT minimized soil disturbance by directly seeding. The tillage systems had been applied repeatedly to the same plots for several years (*Luvisol*: 9 yr, *Eutric Cambisol*: 17 yr) until sampling. Characteristics of the field sites and tillage systems with their influence on agro-technical aspects are given in more detail in *Tebrügge* and *Düring* (1999).

Table 1: Soil properties relevant for the behavior of the investigated pollutants[a].

Luvisol	No-tillage				Reduced tillage				Conventional tillage			
Soil depth [cm]	TOC [g kg^{-1}]	Clay [g kg^{-1}]	CEC [cmol kg^{-1}]	pH ($CaCl_2$)	TOC [g kg^{-1}]	Clay [g kg^{-1}]	CEC [cmol kg^{-1}]	pH ($CaCl_2$)	TOC [g kg^{-1}]	Clay [g kg^{-1}]	CEC [cmol kg^{-1}]	pH ($CaCl_2$)
0-3	27.0	188	19.56	6.6	12.9	117	17.39	6.4	11.3	132	14.33	6.1
3-10	16.7	177	15.85	6.6	16.0	129	13.63	6.5	11.6	155	14.72	6.1
10-25	10.3	168	13.73	6.4	11.2	150	13.30	6.5	11.3	143	14.49	6.2

Eutric Cambisol

Soil depth [cm]	TOC [g kg^{-1}]	Clay [g kg^{-1}]	CEC [cmol kg^{-1}]	pH ($CaCl_2$)	TOC [g kg^{-1}]	Clay [g kg^{-1}]	CEC [cmol kg^{-1}]	pH ($CaCl_2$)	TOC [g kg^{-1}]	Clay [g kg^{-1}]	CEC [cmol kg^{-1}]	pH ($CaCl_2$)
0-3	11.7	43	9.74	5.7	7.5	45	5.71	5.4	5.7	50	4.77	5.5
3-10	9.0	44	8.99	5.4	7.4	47	5.61	5.3	5.6	54	5.34	5.4
10-25	5.8	49	7.87	6.1	6.2	50	5.50	5.5	6.0	51	4.72	5.2

[a] TOC, total organic carbon; CEC, cation exchange capacity

Soil sampling and pretreatment

To determine the stratification of the reactive substances soil samples were taken according to the working depths of the distinctive tillage systems i. e. 0 – 3 cm, 3 – 10 cm, and 10 – 25 cm, respectively. The differently tilled soils were each sampled on two replicated fields. Each field provided two subsamples. Both subsamples were represented by composite samples pooled from at least 10 randomized cores. Surface soil (0 – 3 cm) was sampled carefully with at least 10 randomized soil cores of 8 cm diameter which were also subsequently pooled. The samples were frozen at –18°C immediately after transfer to the laboratory. The samples were air-dried and sieved (2 mm) for further treatment within the heavy metal analysis procedure.

Chemical analysis

Heavy metals

Soils were digested with *aqua regia* (5 g soil, 24 mL *aqua regia*) for 2 h at 120°C (VDLUFA, 1991). Ethylene diamine tetra acetic acid (EDTA)-extracts (5 g soil, 50 mL 0.025 M Na-EDTA, shaken for 90 min) were carried out to determine the potentially available fraction of heavy metals in the soils (*Zeien*, 1995), and extracts in NH_4NO_3 (20 g soil, 50 mL 1 M NH_4NO_3, shaken for 120 min) represented the mobile fraction of heavy metals (*Zeien*, 1995). Heavy metal concentrations in the extracts were analyzed by atomic absorption spectroscopy (Spectra AA10, Varian, Darmstadt, Germany).

Organic pollutants

PCBs were extracted from freeze dried samples under microwave irradiation. After chromatographic clean-up the extracts were analyzed via gas chromatography-mass spectrometry (GC-MS) for the congeners #28; #52; #101; #153; #138; and #180, according to the numbering of International Unions of Pure and Applied Chemistry (*Ballschmiter* and *Zell*, 1980). This method is described in detail in *Düring* and *Gäth* (2000).Aqueous and filtrated solutions obtained from sorption experiments with 2,4-dichlorophenol (2,4-DCP) were analyzed by reversed phase high performance liquid chromatography (RP-HPLC) with an ultraviolet detector.

Sorption experiments

Sorption capacities of the differently tilled soils were examined in laboratory studies with the batch equilibrium method. Spiked soil suspensions were shaken until apparent equilibrium between dissolved and adsorbed pollutant concentrations was achieved. Sorption isotherms were performed on the heavy metals cadmium (Cd), lead (Pb), and zinc (Zn), the metalloid arsenic (As) and 2,4-DCP. Equilibrium time was determined by preliminary kinetic experiments. Phase separation was accomplished by centrifugation and membrane filtration

(0.45 µm pore size).The setup for the sorption experiments with solutions of different concentrations of heavy metals and 2,4-DCP in 0.01 M $CaCl_2$ is given in Table 2.

Table 2: Experimental setup for the estimation of sorption of elements and 2,4-DCP ontwo different soils.

	Applied concentration [mg L^{-1}]						Soil : solution ratio	Equilibration time [h]
zinc	30	160	470	940	-	-	1 : 2.5	16
lead	187.5	250	312.5	375	-	-	1 : 2.5	24
cadmium	$6 * 10^{-4}$	0.06	11	55	110	-	1 : 2.5	16
arsenic	25	62.5	125	250	-	-	1 : 2.5	16
2,4-DCP	6.25	12.5	25	62.5	125	250	1 : 5	6

For reasons of lower detection limits and more accurate determinations, the sorption experiments with cadmium were carried out spiking the samples with the radioactive isotope ^{109}Cd. The remaining activity in the solutions was determined by γ-counting and served for the calculation of sorption parameters (*Schug* et al., 1999a).

Sorption parameters for Zn, Pb, Cd, and As were determined by Freundlich-isotherms which relate the amount of heavy metal adsorbed to the heavy metal concentration remaining in solution at equilibrium:

$$S = K_f \cdot C^n \tag{1}$$

where:
S [mg kg^{-1}] = concentration of the analyte in the solid phase
C [µg L^{-1}] = equilibrium concentration of the analyte in solution
K_f [L g^{-1}] = Freundlich adsorption coefficient
n = Freundlich exponent

Sorption rates (%) were calculated as follows:

$$\frac{HM_{St}}{HM_{At}} \times 100 \tag{2}$$

where:
HM_{St} [µg] = total amount of sorbed heavy metal
HM_{At} [µg] = total amount of applied heavy metal

Sorption isotherms for 2,4-DCP were illustrated by linear regression supporting the earlier described partition hypothesis of nonionic organic substances in soil-water systems (*Chiou*, 1989):

$$S = K_p C_e \tag{3}$$

where:
S [µg g^{-1}] = concentration of the analyte in the solid phase
C_e [µg mL^{-1}] = equilibrium concentration of the analyte in solution
K_p [mL g^{-1}] = partition coefficient

Data of the different heavy metal fractions and the PCB analysis were subjected to ANOVA (P<0.05) to separate spatial variability of pollutant concentrations from variance from tillage treatments. Duncan's multiple range test was used to separate means.

Results and discussion

Sorption experiments

Heavy metals

The influence of tillage on the shape of sorption isotherms is exemplified for Cd in Fig. 1. K_f at a depth of 0-3 cm increased with decreasing tillage intensity in both soils. Soil organic C appeared to have the most dominant influence on K_f at a depth of 0-3 cm (Table 1). At a depth of 10-25 cm, K_f appeared to be more closely related to CEC and soil pH, as only small differences in soil organic C occurred among tillage systems at this depth. The strong dependency of Cd sorption on both soil pH and organic matter content has been previously documented from 159 soil samples (*Schug* et al., 1999b).

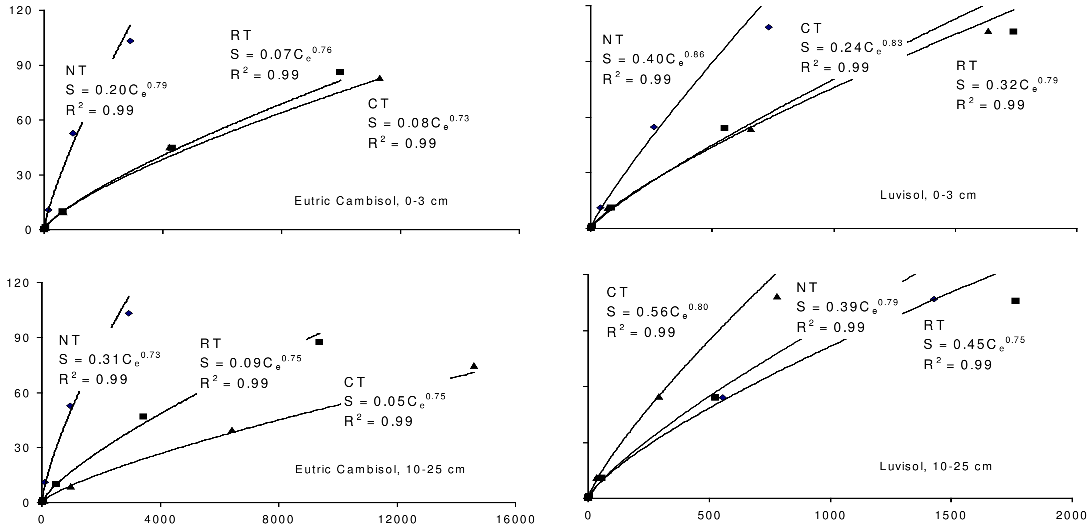

Fig. 1: Freundlich sorption isotherms for Cd in differently tilled (NT = no-tillage, RT = reduced tillage, CT = conventional tillage) soils.

Sorption rates for the different elements were different between soils and depended upon tillage system in the case of the *Eutric Cambisol* (Fig. 2). In some cases there was a large range of variation, especially in sorbed As. This phenomenon indicates initial saturation of the sorption sites of the *Eutric Cambisol* at the highest addition level of 250 mg L^{-1}. Different sorption capacity levels of the two field sites could be related to differences in organic C and soil acidity (Table 1). Capability of soils to buffer the input of heavy metals can be influenced by tillage mainly on sandy substrates with *per se* low sorption capacity. In these soils, the accumulation of organic C primarily in the surface layer due to long-term NT suggests considerable retardation against translocation with water flow.

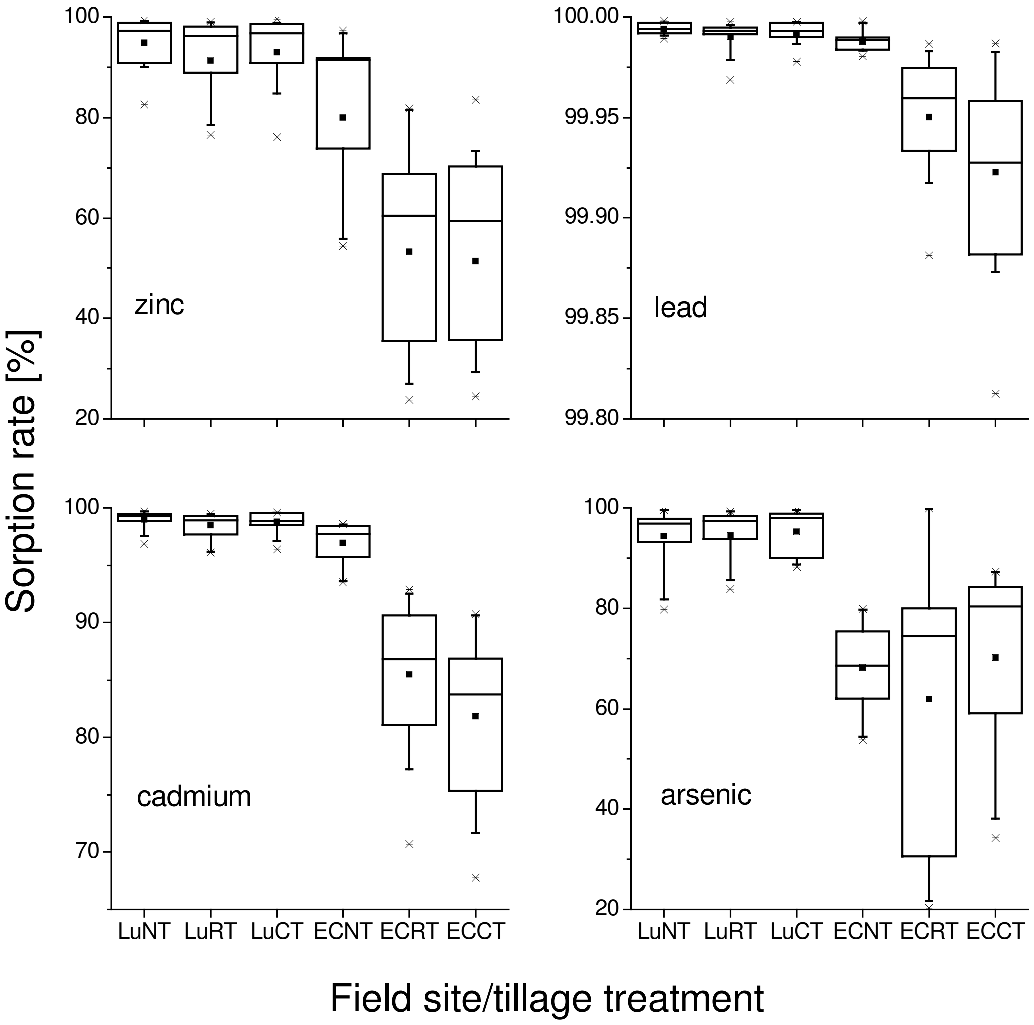

Fig. 2: Sorption rates for the different elements, field sites (*Luvisol* = Lu, *Eutric Cambisol* = EC), and soil treatments including all soil depths (no-tillage = NT, reduced tillage = RT, conventional tillage = CT). Boxes represent 25, 50, and 75 quantiles, whiskers represent 95 and 5% quantiles. Minima and maxima are given as asterisks; ■ = mean values.

2,4-dichlorophenol

Representative results of 2, 4-DCP sorption for the Luvisol are given in Fig. 3. Different stratification of the soils is obvious regarding the slopes of the sorption isotherms depending on tillage treatment and sampling depth. This is in agreement with data on fluometuron, a widely used herbicide, with almost fourfold greater Freundlich partition coefficients in the upper 2 cm of a long-term NT soil compared with plowed soil (*Zablotowicz* et al, 2000). Partition coefficients for fluometuron in NT soils also decreased with increasing depth The higher sorption potential in the surface layer of NT soils should decrease the susceptibility of organic contaminants for vertical translocation into and volatilization from soils.

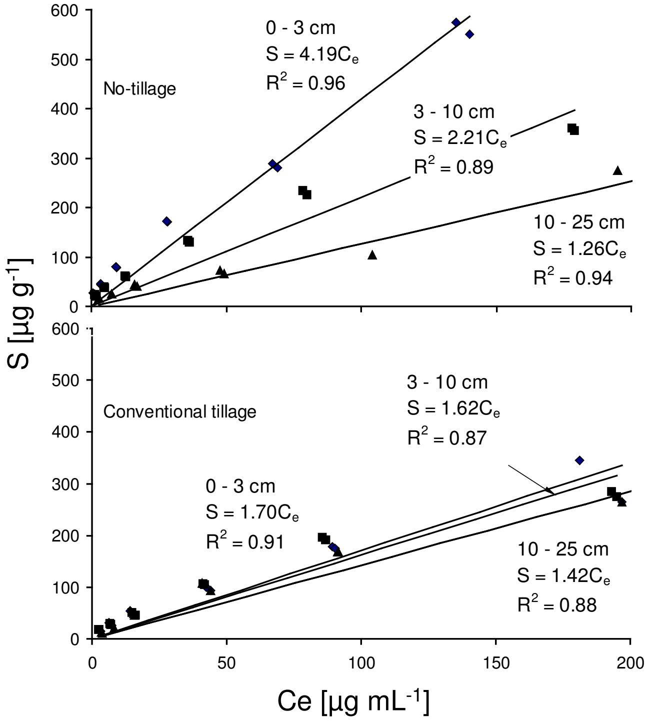

Fig. 3: Linear sorption isotherms for 2,4-DCP in the differently tilled *Luvisol.*

Correlation between the partition coefficient of 2, 4-DCP and the amount of organic C was high (R² = 0.85). The mean organic C partition coefficient (K_{OC}) was 130 mL kg^{-1} with a CV of 17% (n = 17). This K_{OC} is lower than that for 2,4-DCP reported previously by *Schellenberg* et al. (1984) and *Fytianos* et al. (2000) (545 and 774 mL g^{-1}, respectively). Previous values were from aquifer materials and lake and marine sediments which differ from the agricultural soils we investigated.

Heavy metals

Higher concentration of Zn was found in the *Luvisol* in the upper two sampled layers of NT and RT, compared with CT (Table 3). Cu was significantly stratified in the *Luvisol* under NT. This may have been an effect of long-term frequent application of liquid manure on this field site. Organic fertilizers carry heavy metals, i.e. Zn and Cu which are added to swine diet as micronutrients.

The *Eutric Cambisol* was enriched in Cd at all soil depths under NT and RT compared with CT. This may have been due to input of Cd via mineral fertilizing with phosphorus. As demonstrated by the sorption experiments, enhanced sorption capacity for Cd occurred under NT due to soil organic C accumulation in the *Eutric Cambisol*.

In general, total concentrations of heavy metals reflect substrate specific pedogenic amounts and are well below thresholds established by German law. For any permission of sewage sludge application, concentrations of Pb, Cd, and Zn in soil must not exceed 100, 1.5, and 200 mg kg^{-1}, respectively (AbfKlärV, 1992). Anthropogenic effects were obvious for Cu and Zn in the *Luvisol* and cadmium in the *Eutric Cambisol*.

Table 3: Element concentrations in the two different soils [mg kg^{-1}] after digestion with aqua regia and dependent on tillage system, soil, and soil depth[a].

Tillage system	Depth [cm]	Zn	Pb	Cd	As	Cu
Eutric Cambisol						
NT	0-3	27.70 aA	13.41 aB	0.16 aA	2.42 aA	7.32 bB
	3-10	31.10 aA	14.18 aA	0.17 aA	1.97 aA	8.15 aA
	10-25	29.13 aA	13.51 aA	0.16 aA	1.93 aA	7.91 bA
RT	0-3	31.21 aA	14.14 aA	0.14 aA	2.25 aA	8.71 aA
	3-10	29.62 aA	13.39 aA	0.14 aA	2.06 aA	7.92 aA
	10-25	30.73 aA	14.66 aA	0.15 aA	2.05 aA	8.55 aA
CT	0-3	27.24 aA	11.50 aC	0.11 aB	1.86 aA	7.56 aA
	3-10	24.18 aB	10.97 aB	0.11 aB	2.09 aA	7.74 aA
	10-25	27.32 aA	12.01 aB	0.12 aB	2.46 aA	8.68 aA
Luvisol						
NT	0-3	59.20 aA	18.23 aA	0.23 aA	7.89 aA	12.67 aA
	3-10	50.67 bA	19.10 aA	0.23 aA	6.84 aA	10.90 bA
	10-25	44.36 cA	18.29 aA	0.20 aA	7.47 aA	9.10 cA
RT	0-3	46.73 aB	18.13 aA	0.22 aA	5.74 aB	9.74 aB
	3-10	46.11 aA	18.03 aA	0.21 aA	6.06 aA	9.27 aA
	10-25	40.46 bA	16.86 aB	0.19 aA	5.75 aA	9.53 aA
CT	0-3	41.38 aC	17.95 aA	0.21 aA	5.84 aB	10.19 aB
	3-10	41.98 aB	18.17 aA	0.22 aA	6.29 aA	10.46 aA
	10-25	41.66 aA	18.06 aA	0.21 aA	6.15 aA	10.39 aA

[a] NT: no-tillage, RT: reduced tillage, CT: conventional tillage. Different small letters represent significant differences ($p<0.05$) among soil depths within a tillage system. Different capital letters represent significant differences ($p<0.05$) among tillage treatment within a soil depth.

EDTA-derived heavy metal concentrations (Table 4) were lower, but mirrored the concentrations obtained by the digestion with aqua regia. EDTA-extracts represent the potentially bioavailable fraction (*Fergusson*, 1991) which is influenced to a high degree by the organic matter fraction in soil. Correlation between organic C and Zn extracted with EDTA-solution is exemplified in Fig. 4. Hence, there should have been an effect of tillage on the EDTA-extractable heavy metal concentration, reflected by higher organic C in the NT *Luvisol.*

Concentrations of the NH_4NO_3-extractable heavy metal fraction were site-specific, but only little affected by tillage intensity. In the majority of cases, tillage effects were not significant (data not presented). However, related to the total heavy metal amounts determined in the aqua regia extracts, an effect of tillage can be assumed. In the *Eutric Cambisol* with lower sorption capacity the particular tillage treatments induced different proportions of the mobile Zn and Cd fractions (Figure 5). This is in accordance with the data of the sorption experiments which revealed strong influence of tillage treatment on the sorption rates of both zinc and cadmium onto the *Eutric Cambisol* (see Fig. 2). The mobile heavy metal portions in the *Luvisol* were on a lower level indicating slightly higher ratios in the NT soil compared to both other tillage treatments.

Table 4: Element concentrations in EDTA-extracts of the two different soils [mg kg^{-1}] dependent on tillage system, soil, and soil depth[a].

Tillage system	Depth [cm]	Zn	Pb	Cd	Cu
			Eutric Cambisol		
NT	0-3	2.49 aA	2.72 aA	0.050 aA	1.17 aA
	3-10	2.11 aA	2.78 aA	0.051 aA	1.39 aA
	10-25	1.73 aA	2.49 aA	0.042 aA	1.43 aA
RT	0-3	2.50 aA	2.44 aA	0.051 aA	1.54 aA
	3-10	1.89 bB	1.97 aB	0.043 aB	1.26 aB
	10-25	1.75 bA	2.16 aA	0.043 aA	1.43 aA
CT	0-3	0.86 aB	1.32 aB	0.024 aB	0.82 aB
	3-10	0.70 aC	0.98 aC	0.020 aC	0.72 aC
	10-25	0.88 aB	1.07 aB	0.022 aB	0.75 aB
			Luvisol		
NT	0-3	10.88 aA	6.48 aA	0.115 aA	4.26 aA
	3-10	9.02 aA	7.04 aA	0.134 aA	3.92 aA
	10-25	5.94 bA	6.92 aA	0.121 aA	3.40 aB
RT	0-3	5.12 aB	5.56 aA	0.094 aB	3.64 aA
	3-10	4.55 aB	5.17 aC	0.092 aA	3.40 aA
	10-25	3.51 bB	5.14 aC	0.088 aA	3.15 aB
CT	0-3	3.46 aB	6.18 aA	0.127 aA	3.85 aA
	3-10	3.55 aB	5.93 aB	0.084 aA	3.82 aA
	10-25	3.74 aB	5.90 aB	0.086 aA	3.82 aA

[a] NT: no-tillage, RT: reduced tillage, CT: conventional tillage. Different small letters represent significant differences ($p<0.05$) among soil depths within a tillage system. Different capital letters represent significant differences ($p<0.05$) among tillage treatment within a soil depth.

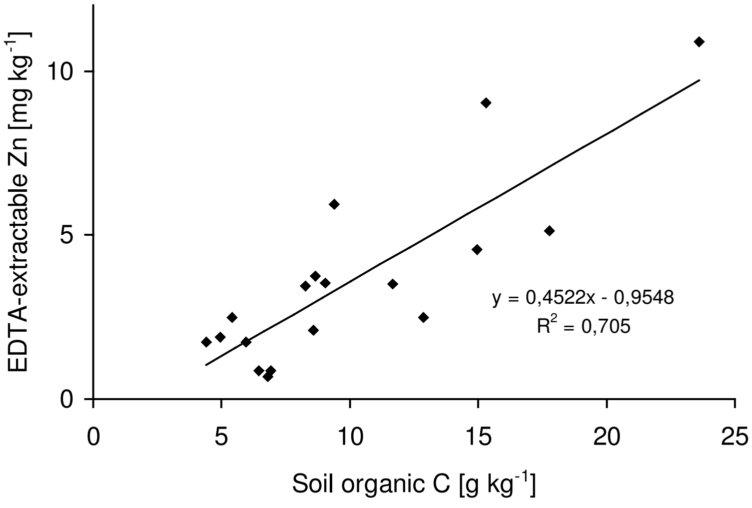

Fig. 4: EDTA-extractable zinc dependent on the amount of soil organic carbon, determined for the differently tilled soils on both field sites.

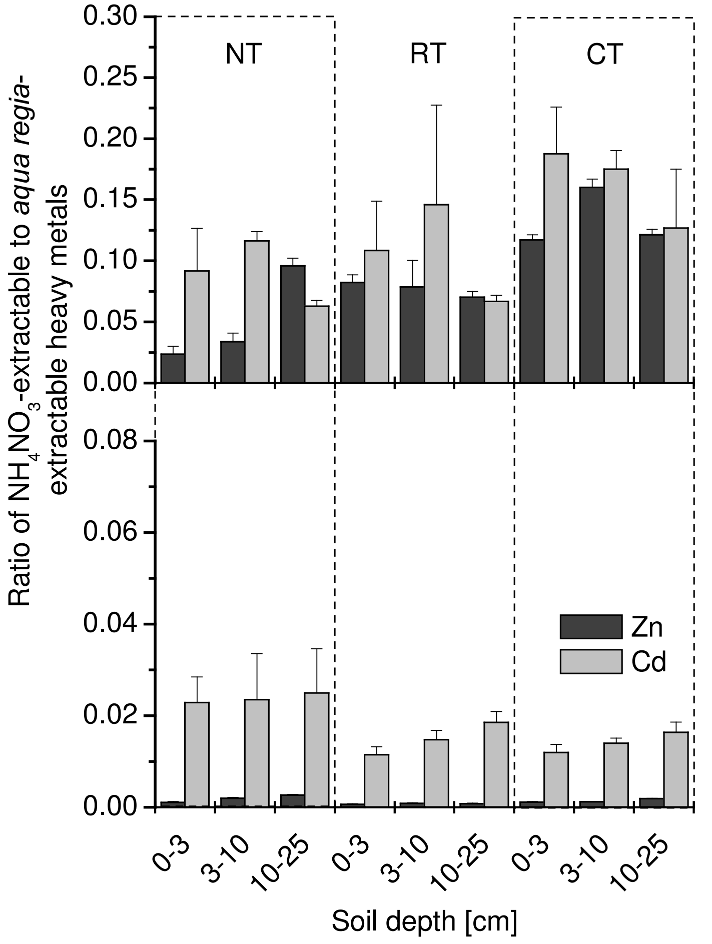

Fig. 5: Ratios of NH_4NO_3-extractable/*aqua regia*-extractable heavy metals in the *Eutric Cambisol* (above) and the *Luvisol* (below), dependent on soil depth and tillage (NT = no-tillage, RT = reduced tillage, CT = conventional tillage); error bars = standard deviations.

Polychlorinated biphenyls (PCB)

Comparison of the sum of the PCBs #28, #52, #101, #153, #138, and #180 (PCB_6) shows a clear effect of tillage in different soil depths (Fig. 6). The *Luvisol* had significantly elevated PCB_6 concentrations under NT compared with RT and CT. Due to large variability, differences in PCB_6 between tillage treatments in the *Eutric Cambisol* were significant only in the 0-3 cm layer. PCBs interact strongly with soil organic matter since calculated and determined K_{OC}-values for the different congeners range from 10^4 to 10^7 (e.g. *Paya-Perez* et al.,1991; *Girvin* and *Scott*, 1997; *Seth* et al., 1999). Hence, only small fractions of freely dissolved PCBs can undergo a soil-water mediated transport and very clear stratification should be likely in long-term NT soils.

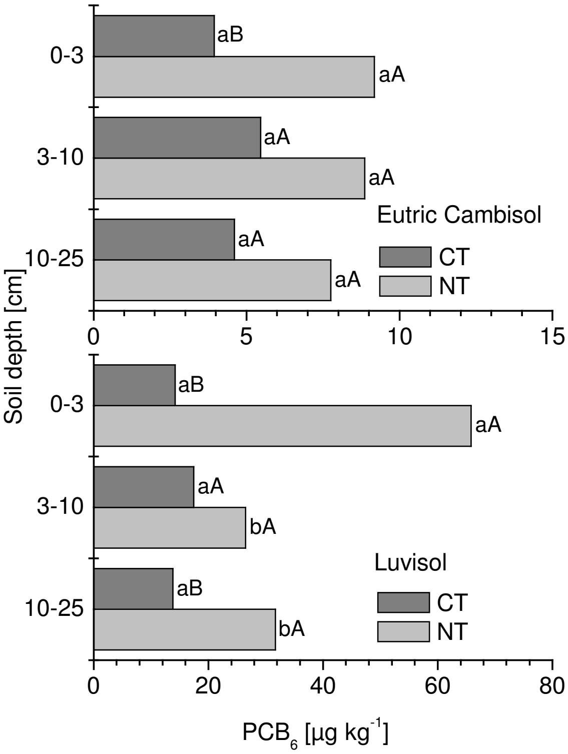

Fig. 6: Concentrations of the sum of six PCB congeners (PCB_6) in the differently tilled soils. NT = no-tillage, CT = conventional tillage, significant differences ($P<0.05$) among soil depths are marked by small letters and significant differences ($P<0.05$) among tillage treatments are marked by capital letters, respectively.

As expected, the mixing effect of plowing resulted in homogeneous distribution of the PCBs in the soils of both field sites. The sampling depth of 3 cm for the surface soil accentuates accumulation of the strongly bound PCBs in the NT soil. PCB concentration in the upper layer of the NT *Luvisol* exceeded the German soil quality criterion of 0.05 mg kg^{-1} for soils with less than 8% humus content (*BBodSchV*, 1999). The total PCB concentration level, especially in the *Luvisol*, was rather high and might have been due to the microwave assisted extraction method we used, which has greater extraction efficiency than the standard extraction method (*Düring* and *Gäth*, 2000). Increased concentrations down to the soil depth of 10–25 cm in NT compared with plowed soils could be attributed to transport processes by bioperturbation, i.e. increased earthworm activity, which has been observed under these same soils under NT (*Tebrügge* and *Düring*, 1999). This non-selective transport by bioperturbation most evident in the *Eutric Cambisol* could be assumed since approximately constant ratios of PCB congeners in the different soil depths occurred (Table 5). Each of the PCB congeners with different properties (i.e. partition behavior) had very similar transport behavior indicating negligible effect of translocation of freely dissolved PCBs via leaching (*Cousins* et al., 1999a). Nevertheless, vertical displacement by leaching in association with dissolved organic matter may have contributed to the distribution pattern of PCBs in the soils. The fate of hydrophobic compounds in soil should be considered as partition within a ternary system. Within this system organic macromolecules in the soil solution can act as carriers to transport the organic contaminants (*Chiou* et al., 1986; *Maxin* and *Kögel-Knabner*, 1995; *Marschner*, 1999).

Table 5: PCB congener distribution dependent on field site, tillage treatment, and soil depth. Numbers in % of PCB_6 concentration[a].

Tillage system	Depth [cm]	Congener#					
		28	52	101	153	138	180
Eutric Cambisol							
NT	0-3	26.0 (22.7)	21.8 (9.8)	28.6 (4.1)	14.3 (3.7)	9.2 (3.8)	n.d.
	3-10	30.5 (27.3)	23.7 (16.7)	26.7 (16.6)	11.4 (7.8)	7.7 (5.4)	n.d.
	10-25	29.2 (25.6)	20.5 (11.7)	26.6 (8.1)	13.3 (2.9)	10.4 (1.5)	n.d.
CT	0-3	13.6 (8.0)	19.8 (4.6)	42.1 (8.4)	15.4 (7.9)	9.1 (6.8)	n.d.
	3-10	13.2 (8.0)	18.3 (5.1)	41.6 (22.7)	14.4 (9.6)	12.6 (7.4)	n.d.
	10-25	8.1 (3.6)	15.6 (4.1)	39.0 (26.8)	20.4 (18.2)	16.9 (16.9)	n.d.
Luvisol							
NT	0-3	7.4 (3.3)	15.7 (1.9)	44.1 (3.1)	17.5 (1.6)	15.3 (2.1)	n.d.
	3-10	10.2 (3.4)	22.9 (7.0)	46.5 (15.7)	13.5 (7.7)	6.9 (0.9)	n.d.
	10-25	8.9 (2.1)	18.3 (2.9)	43.9 (12.7)	17.2 (4.0)	11.7 (3.8)	n.d.
CT	0-3	15.9 (3.6)	21.0 (7.4)	41.7 (21.5)	13.3 (3.7)	8.2 (6.5)	n.d.
	3-10	9.7 (0.7)	21.1 (3.2)	47.1 (7.2)	12.2 (1.5)	9.9 (3.3)	n.d.
	10-25	10.8 (0.8)	16.2 (4.8)	36.9 (8.9)	19.1 (2.2)	14.0 (7.0)	3.0 (2.8)

[a] NT: no-tillage, CT: conventional tillage, n. d.: not detectable.

Congener #101 predominated in both soils, which is different from the congener patterns in organic wastes (i.e. sewage sludge and compost) originating from the same area. In those wastes, accumulation of PCBs was most evident for congener #153 (*Düring* and *Gäth*, 2000). In the Luvisol under NT, congener #28 with high volatility was relatively enriched compared with its concentrations under other tillage systems. This might be due to the soil's higher sorption capacity and slowed heating in spring under NT (*Frede* and *Gäth*, 1993), both of which would reduce volatilization from soil.

With the two different field sites, significant correlation was obtained between PCB concentrations and soil organic C (Fig. 7). This is in agreement with the literature dealing with long-term undisturbed nonagricultural soils (*Cousins* et al., 1999b). Variability in this relationship may not have been only due to spatial variability of the field sites, but also the different climatic conditions (approximately 1 °C difference in average temperature) and higher potential for wet deposition at the *Luvisol* (630 mm per year rainfall when compared to 600 mm per year at the *Eutric Cambisol*). Furthermore, the history of agricultural practice has to be considered. On the *Luvisol*, frequent applications of pig slurry in the last 20 years may have contributed to the relatively high PCB contamination level. As *De la Torre* et al. (2000) stated, swine manure is a source of pollutants when sprayed onto agricultural land. These authors determined a concentration of 430 ppb in this manure for the sum of the investigated PCBs. *Cousins* et al. (1999b) recommended that statistically significant relationships between soil PCB concentrations and soil organic C for site-specific predictions be used to improve accuracy.

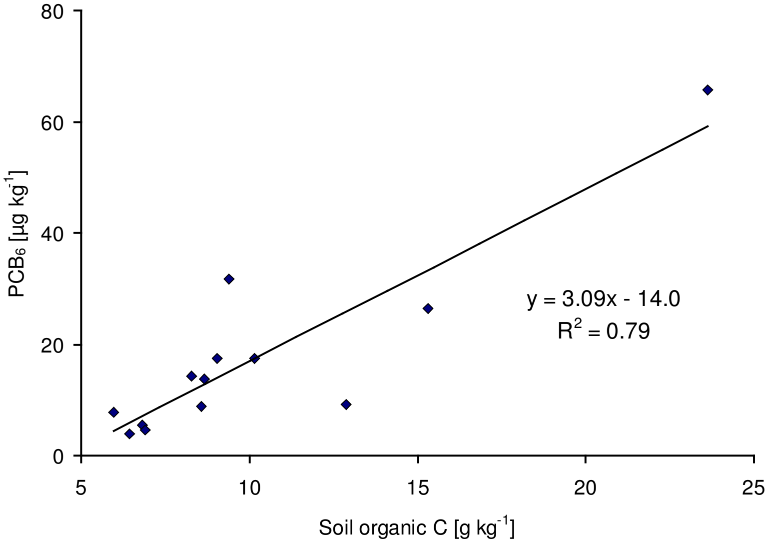

Fig 7: Correlation between concentration of the sum of six PCB congeners (PCB_6) and soil organic carbon concentration in the different depths within the arable layers of both field sites and tillage systems, respectively.

The set up of the side-by-side experimental field plots with different tillage systems for approximately 8–17 years provided experimental conditions nearly *ceteris paribus* for both climate and soil texture. Organic C in soil was clearly tillage-dependent and was the main variable that explained the fate of PCBs. Hence, cross-correlating effects like clay-humus and organic matter-climate could be ruled out to a large extent.

Conclusions

Long-term tillage treatments resulted in characteristic enrichment patterns of soil organic C and some air-borne and fertilizer-carried pollutants. Accumulation of humus in the surface layer of NT soils altered the behavior of reactive substances in soil due to its strong sorption capacity. Elevated pollutant concentrations were found in the surface of NT soils and this could be attributed mainly to higher sorption capacity compared to plowed soils.

Higher sorption rates of heavy metals in the *Eutric Cambisol* under NT were detected by different extractabilities especially of Zn and Cd. This suggests that the availability of those heavy metals for transport should be reduced under NT or RT, which benefit from the supply of organic C from plant residues left on the surface.

Correlation of PCB concentrations with organic C suggests approximation to thermodynamic equilibrium within the investigated field sites. Due to their partition behavior, these compounds are strongly sorbed to the soil matrix and are not suspected to be transported freely dissolved with the water flow. This was also supported by the uniform ratios of different congeners among soil depths. The main route for vertical transport of PCBs in arable soils would be mechanical mixing or, in case of NT, bioperturbation via earthworm activity.

Susceptibility of various pollutants, especially organic contaminants, for movement in and from soil would be directly dependent on the organic C, which may be controlled by tillage intensity.

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Anhang C

Utilization of municipal organic wastes in agriculture: where do we stand, where will we go?

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Journal of Plant Nutrition and Soil Science, 2002, 165, 544-556

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Abstract

Generation of organic waste is increasing worldwide and strategies for its environmentally sound use must be developed and optimized. Regulations in European countries and the USA differ largely with respect to requirements of organic waste quality and the quantities of pollutants which can be added to the soil. Research has shown beneficial effects regarding the improvement of soil fertility. Enrichment of total metals in soil was attributed to long-term sludge application but the effect on bioavailability of metals must be further clarified. A number of organic pollutants, such as hydrophobic persistent organic contaminants and surfactants, are known to accumulate in organic wastes. However, the former interact strongly with organic matter in the sludge-soil-plant system and systemic plant uptake is generally assumed to be minimal. Surfactants may cause adverse environmental impacts when they enter sewage systems in high loads and accumulate in sludge. Surfactants and some of their metabolites are not readily biodegraded in non-aerated environments. Due to their toxicity and estrogenic activity, of nonylphenol for example, more research is needed to optimize analytical techniques and to trace their behavior in soil. Some options to cope with the risks of huge amounts of organic waste and also some benefits are presented: (1) further limitation of standards for pollutants and reduced application rates; (2) improved treatment of sewage sludge to reduce the total and bioavailable portions of both heavy metals and organic pollutants; (3) adaptation of waste application rates to soil properties such as sorption capacity for pollutants; (4) harmonization of analytical protocols for organic contaminants, i.e. surfactants and metabolites, enabling a more thorough monitoring of the wastes which are to be applied onto soils.

J. Plant Nutr. Soil Sci., 2002, 165, 544-556

Introduction

Each year the European Community generates approximately 2 billion Mg of waste and this amount is on the increase. Therefore, the European Union (EU) defined a strategy to avoid waste generation and, if this is impossible, to minimize waste quantities to be deposited (cited in *European Commission, 2000*). Germany was a pioneer in this field of environmental policy by implementing the *"Kreislaufwirtschafts- und Abfallgesetz"* in 1996 and executed it by installing various subsidiary ordinances which pursued the same principle goals as the EU legislation. In 1995 roughly 200 million Mg of municipal solid waste was produced in the European Community with half of this being biodegradable. The huge volume and the corresponding negative effects of biodegradable waste in landfills has forced the creation of EU policies to markedly reduce this deposition, i.e. via composting and anaerobic digestion. Due to the high content of organic matter (OM) in solid waste and certain plant nutrients, especially phosphorus (P), the EU policies have suggested to use the sewage sludge in agriculture. In the USA, the beneficial use of biosolids (stabilized sewage sludge) in terms of soil conditioning and nutrient supply is supported by the Environmental Protection Agency (EPA).

A wide variety of undesired elements are currently found in sludge and compost which could have adverse effects on the environment. The principal impact on the environmental compartments through land spreading of organic and inorganic fertilizer is illustrated in Figure 1. However, we need to keep in mind that soil is a main repository for pollutants which may be introduced via different pathways, including the atmosphere.

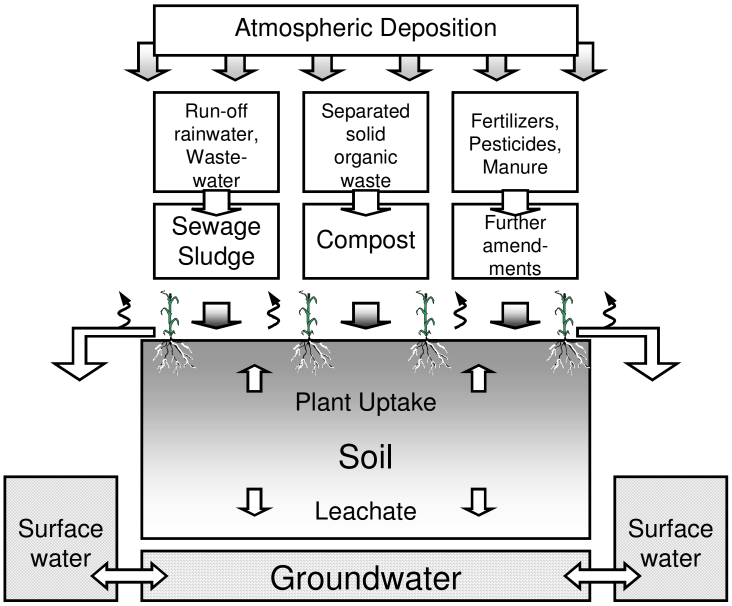

Fig. 1: Paths for pollutants to enter and to leave soil.

According to German law, soils have multiple functions which include buffering the input of hazardous substances for groundwater protection. Consequently, precautionary limit values for pollutant concentrations have been established (*BBodSchV,* 1999). Since the agricultural utilization of organic wastes, especially the use of sewage sludge, is of public concern, some regulations, benefits, and potentially adverse effects have been compiled and are discussed in the following review. The discussion is focused on potential nutrient supply to crops and the introduction and behavior of organic and inorganic pollutants. Numerous publications began to appear in the seventies however, knowledge in this field of research is constantly growing. Since *Smith* gave a thorough review in 1996, this paper is focused on more recently published data.

Generation and use of organic waste

Sludge production and disposal is increasing significantly in the EU and is mainly driven by the EC Urban Waste Water Treatment Directive (*European Commission,* 1991). Currently, sludge disposal to all established outlets has become difficult. This holds especially true for the UK, since approximately 30% of sludge was dumped at sea until 1998 when it was banned by the EU (*Bowler,* 1999). Figure 2 gives an overview of the expected sewage sludge production and its utilization in some European states, the EU and the USA for the year 2005. The USA total annual production of sludge has remained constant or grown very slowly (*Renner,* 2000).

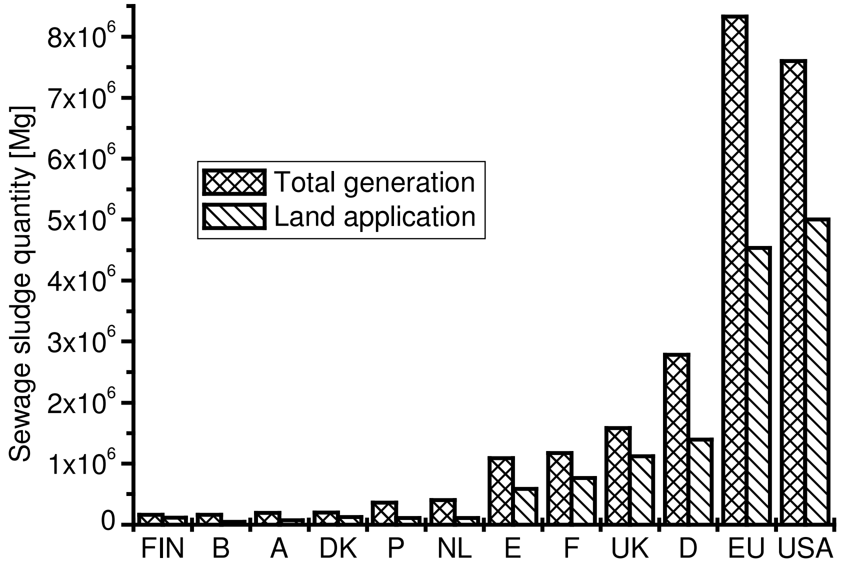

Fig. 2: Expected sewage sludge production and utilization rates of EU member states compared to respective data of the USA in the year 2005 (*European Community, 2001; US EPA, 1999*).

Even though the illustrated data is from developed countries, future sludge production in developing countries must also be considered. For example, China currently produces some 0.4 million tons (dry weight) of sludge resulting from the treatment of only 7% of municipal wastewater in sewage treatment plants. According to national plans, the proportion of municipal wastewater treatment in China will increase up to 50% by 2010 (*Wang,* 1997). If this tendency also holds true for other developing countries, dramatic increases can be expected in the worldwide production of sewage sludge. Environmentally friendly methods must be utilized for the deposition of this waste.

Besides Germany, which currently utilizes approximately 6-7 million Mg d.m. of compost yr^{-1} (*BGK*, 2002), other EU member states are continuing to find and develop strategies to collect biodegradable waste and produce useable compost for agriculture (*European Commission,* 2000).

Legal basis

The different laws in developed countries include specific approaches to limit the load of pollutants via sewage sludge or compost application onto soil. In the EU the Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, regulates sewage sludge application in agriculture (*European Commission,* 1986). This includes limit values for heavy metal concentrations in soil to which sludge is applied, in sludge and maximum annual quantities of heavy metals added to agricultural soils. Organic pollutants are not currently considered. This directive is now under revision (*Working Document on Sludge, 3rd Draft,* 2000*,* unpublished). The proposed and further reduced limit values are therefore given in Tables 1-3. The US EPA developed use and disposal regulations for sewage sludge also including pollutant limits, operational requirements, as well as management practices (*US EPA,* 1993).

Heavy metal input to soils is regulated in the developed countries by at least defining limit concentrations in the sludge to be applied in agriculture. In Germany two directives regulate sewage sludge (*AbfKlärV,* 1992) and compost application *(BioAbfV,* 1998), which include different limits for heavy metals (Table 1).

Table 1: Limit values for concentrations of heavy metals in sewage sludge and compost to be applied onto soil [mg kg^{-1} d. m.] (*European Commission, 2001; US EPA, 1999*).

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
European Union	20-40	-	1,000-1,750	16-25	300-400	750-1,200	2,500-4,000
European Union (proposed)	10	1,000	1,000	10	300	750	2,500
Germany - sewage sludge	10	900	800	8	200	900	2,500
Germany - compost[a]	1.5 (1)	100 (70)	100 (70)	1 (0.7)	50 (35)	150 (100)	400 (300)
France[b]	20	1,000	1,000	10	200	800	3,000
USA ceiling concentrations	85	3,000	4,300	57	420	840	7,500
USA pollutant concentrations	39	1,200	1,500	17	420	300	2,800
Russia[c]	30	1,200	1,500	15	400	1,000	4,000

[a] Values apply for 20 Mg ha^{-1} 3 yr^{-1}, and in brackets, for 30 Mg ha^{-1} 3 yr^{-1}

[b] (*Planquart et al., 1999*)

[c] (*Selivanoskaya, 2002*)

Regarding the standards for metals in sewage sludge ("ceiling concentrations") which at least must be met to allow any application onto agricultural land, the US EPA permits the highest limit values among developed nations (Table 1). However, the US EPA considers ceiling concentrations also for As (75 mg kg^{-1}), Mo (75 mg kg^{-1}), and Se (100 mg kg^{-1}) (based on dry matter = d.m.). Different approaches are behind these standards: (1) a risk assessment on the basis of "no observed adverse effect concentrations" (NOAECs) (US EPA); (2) a precautionary approach to avoid any accumulation of possibly hazardous elements in soil (EU) (*Moolenaar* et al., 1997a). The US EPA also established maximum cumulative pollutant loading rates for eight metals at land application sites. A third set of metals criteria is also considered, known as pollutant concentrations (Table 1). If these concentrations are not exceeded in the biosolids applied to land, the cumulative pollutant loading rates do not need to be tracked. Absolute permissible loads via sewage sludge or compost to be land-applied are given in Table 2. If the ceiling concentration of Cd is put into consideration, the annual whole sludge application rate in the USA may amount to 22 Mg d.m. ha^{-1} yr^{-1}, whereas, for example, the sludge application rate in Germany is limited to 5 Mg d.m. ha^{-1} (3 yr)$^{-1}$. Exceeding the concentration limits of one or more heavy metals in soil (Table 3) will prohibit any use of sewage sludge. Furthermore it has to be ensured that the limit values are not exceeded as a result of sludge use.

Table 2: Limit values for amounts of heavy metals which may be added annually to soil [g ha^{-1} yr^{-1}] (*European Commission, 2001; US EPA, 1999*).

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
EU	150	-	12,000	100	3,000	15,000	30,000
EU proposed)	30	3,000	3,000	30	900	2,250	7,500
Germany - sewage sludge	16.7	1,500	1,333	13.3	333	1,500	4,167
Germany - compost[a]	30 (30)	2,000 (2,100)	2,000 (2,100)	20 (21)	1,000 (1050)	3,000 (3,000)	8,000 (9,000)
USA	1,900	-	75,000	850	21,000	15,000	140,000

[a]Values apply for 20 Mg ha^{-1} 3 yr^{-1}, and in brackets, for 30 Mg ha^{-1} 3 yr^{-1}

Table 3: Heavy metal standards for soils to which sludge will be applied [mg kg^{-1} d. m.] (*European Commission, 2001; US EPA, 1999*).

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
EU (pH 6-7)	1-3	-	50-140	1-1.5	30-75	50-300	150-300
EU (proposed, pH5->7)	0.5-1.5	30-100	20-100	0.1-1	15-70	70-100	60-200
France[a]	2	150	100	1	50	100	300
UK (pH 5->7[b]	3	400	80-200	1	50-110	300	200-300
Germany[c]	1.5	100	60	1	50	100	200 (
USA[d]	20	1500	750	8	210	150	1400

[a](Planquart et al., 1999)

[b](Obbard and Jones, 2000)

[c]Values are for soil pHs >6. At pH 5-6, the Cd and Zn limits are 1.0 and 150 mg kg^{-1}, respectively.

[d]Calculated from maximum cumulative pollutant loading limits mixed into soil plough layer. Soil background concentrations are not taken into account (Renner, 2000).

Germany was the first country which introduced national regulations for organic contaminants in sewage sludge (*AbKlärV,* 1992). Limits were set for some groups of organic pollutants represented by sum parameters: AOX (adsorbable organic halogens), PCBs (polychlorinated biphenyls), and PCDD/F (polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans) (Table 4). With the "Working Document on Sludge, 3rd Draft" (EU, 2000, unpublished), the EU proposed additional limits of concentrations for the following contaminants: linear alkylbenzene sulphonates, NPE as the sum of short-chain nonylphenol polyethoxylates (NPEOs) and nonylphenol (NP), DEHP (di-2-(ethyl-hexyl)-phthalate), and PAHs (polycyclic aromatic hydrocarbons). The LAS and NPE represent surfactants with respective metabolites which enter sewage systems in high amounts and accumulate in sludge, especially when it is anaerobically stabilized. The DEHP (plasticizer) and PAHs are ubiquitous and also accumulate in sewage sludge.

During the 1990s, the US EPA did additional screening of 31 pollutants which were identified for further evaluation (*US EPA*, Dioxin Reassessment, Draft Documents, 2000, unpublished). Resulting from this screening, the EPA proposed a numeric limit of 300 ng toxic equivalency (TEQ) per kg of dry biosolids for polychlorinated dibenzo-p-dioxins/dibenzofurans and dioxin-like coplanar polychlorinated biphenyls (PCBs).

Table 4: Standards for concentrations of organic contaminants in sewage sludge (*European Commission*, 2001; *US EPA*, Dioxin Reassessment, Draft Documents, 2000, unpublished).

	AOX	DEHP	LAS	NP/NPE	PAH	PCB	PCDD/F
EU (proposed)	500	100	2,600	50	6[a]	0.8[b]	100
Denmark	-	50	1,300	10	3[a]	-	-
Sweden	-	-	-	50	3[c]	0.4[b]	-
Lower Austria	500	-	-	-	-	0.2[d]	100
Germany	500	-	-	-	-	0.2[d]	100
USA	-	-	-	-	-	-	300

[a] Sum of acenapthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1, 2, 3-c,d)pyrene

[b] sum of 7 congeners PCB 28, 52, 101, 118, 138,153, 180

[c] sum of 6 compounds

[d] each of the six congeners PCB 28, 52, 101, 138, 153, 180

Benefits from waste application

The OM produced during wastewater treatment or composting can be beneficially added to soil to supply nutrients to crops such as N, P, K and essential micro nutrients (*Jakobsen,* 1995). Intensive agricultural land use, especially in warmer climates, leads to the decomposition of soil organic matter (SOM) and decreased SOM contents which may be replenished by organic waste application (*Navas* et al., 1998). Soil properties, such as texture and water holding capacity which favor root growth and increase drought tolerance of crops, can be improved (e.g. *Joshua* et al., 1998). Beneficial effects on microbial biomass and activity were observed short term after the application of compost (*Leifeld* et al., 2002) and composted sewage sludge (*Selivanovskaya* et al., 2001). The application of waste compost favored the formation of macro-aggregates in soil (*de León-Gonzáles* et al., 2000) which is important for soil conservation. Furthermore, agricultural use of waste can help to preserve global sources of phosphate and potassium. In Germany, the generated sewage sludge contains ca. 36,000 Mg P as a result of biological and chemical P elimination procedures during waste water treatment. This nutrient pool is not always completely available for crops due to strong P sorption by Fe-oxides/hydroxides. Therefore, *Römer* and *Samie* (2002) recommended P elimination from waste water without the use of Fe-salts.

Considerable nutrient inputs will enter the soil if a maximum of 5 Mg d.m. of sewage sludge ha^{-1} $(3\ yr)^{-1}$ or 30 Mg d.m. of compost ha^{-1} $(3\ yr)^{-1}$, is applied. In accordance with the German legislation (*AbfKlärV, 1992, BioAbfV. 1998),* a nutrient balance for a cropping farm without any animal husbandry in Figure 3 shows that P is in surplus when sewage sludge is applied whereas compost application results in a surplus N, P and K (*Beisecker* et al., 1998).

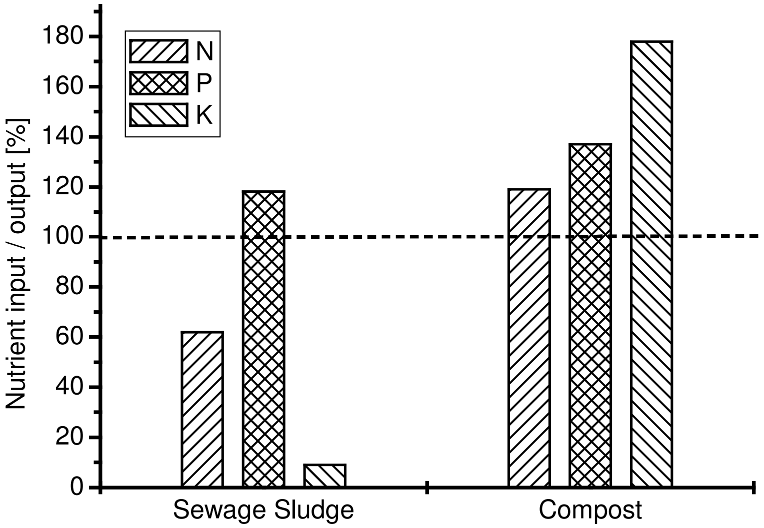

Fig. 3: Nutrient input via application of compost and sewage sludge, respectively, related to the output of a cropping farm in % (according to *Beisecker* et al., 1998).

The use of organic waste should be considered in this nutrient balance as inappropriate application times or rates may lead to poor utilization of nitrogen by the crops and thus, to nitrate leaching and water contamination (e.g. *Joshua* et al., 1998).

Pedreño et al. (1996) and *Debosz* et al. (2002) observed improvements in soil fertility by amendments with sewage sludge or compost. The affected soil composition and increased yields were attributed to an enhanced bioavailability of nutrients. *Bartl et al.* (2002) concluded that compost, applied over the long term, is suitable to re-supply the soil with minerals and nutrients.

The use of sewage sludge for land rehabilitation is increasingly being considered as a technical solution to reverse environmental degradation and to promote the re-establishment of vegetation cover (i.e. *Blechschmidt* et al., 1999; *Delschen,* 1999; *Zier* et al., 1999). In the first 2 years after the application of organic waste materials to mine soils, *Emmerling* et al. (2000) found significantly enhanced microbial activity with increasing application rates of sewage sludge and compost.

According to the US EPA (*US EPA,* 1997), the agricultural use of compost can help to control plant disease and reduce crop losses due to competition by introduced beneficial microorganisms. Compost showed a good ability to suppress Fusarium wilt of tomato in a study by *Cotxarrera* et al. (2002). *Serra-Wittling* et al. (1996) reported on increased soil suppressiveness to fusarium wilt of flax after addition of municipal solid waste compost.

Potential risks from pollutants

Large numbers of toxic elements and chemicals are enriched in sewage sludge. Its use in agriculture disperses the pollutants in the environment via the surface of soils and enables them to enter into the food chain (*Kloepffer,* 1996). Since lipophilic organics and heavy metals are concentrated in OM, compost can also be considered as a sink for pollutants *(Lazzari* et al., 1999). In the following, we focus on the occurrence and behavior of inorganic and organic pollutants and the likelihood of them entering the agricultural food chain through the application of organic municipal waste.

Heavy metals in organic waste

The concentrations of Pb, Cd, and Hg in German sewage sludge decreased slightly from 1992 to 2000 (Figure 4). The concentrations of the other elements monitored remained relatively constant (*Walper,* 2002). By comparison, the mean heavy metal background concentrations in soils from North-western Germany were 0.14 mg Cd kg^{-1}, 6 mg Cr kg^{-1}, 7 mg Cu kg^{-1}, 0.05 mg Hg kg^{-1}, 4 mg Ni kg^{-1}, 11 mg Pb kg^{-1}, and 23 mg Zn kg^{-1} (*Uterman* and *Düwel*, 2000). According to *Beisecker* et al. (1998), mean heavy metal concentrations in German composts were: 0.8 mg Cd kg^{-1}, 35.8 mg Cr kg^{-1}, 46.5 mg Cu kg^{-1}, 0.4 mg Hg kg^{-1}, 20.5 mg Ni kg^{-1}, 83 mg Pb kg^{-1}, and 249.1 mg Zn kg^{-1} (all data on a dry matter basis). The authors found relatively high variations in metal concentrations which may be slightly reduced through optimized collection and processing. Safe agricultural use of compost relies on the separation of organic waste at source offering the opportunity of high-quality input material for composting. Increased total heavy metal contents may occur due to pedogenic composition of the respective catchment area.

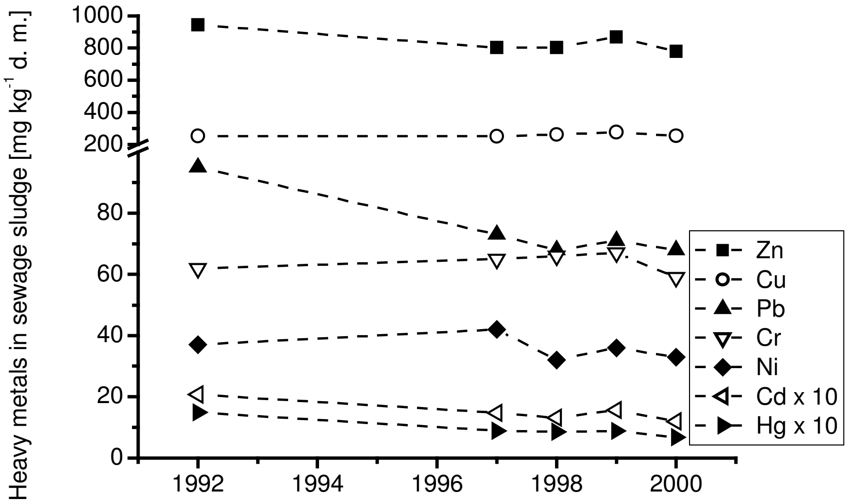

Fig. 4: Mean concentrations of heavy metals in sewage sludge of central Germany (*Walper, 2002*).

Heavy metal impact on soil

The continuous application of municipal organic waste has resulted in heavy metal enrichment in soil when analytically determined as total contents in digests with strong inorganic acids (*Gäth,* 1996). Long term application of sewage sludge and waste compost to reclaimed loess soil led to a significant increase in the concentrations of Pb, Cd, Cu, and Zn (*Delschen,* 1999). Significant differences were observed between metal contents in sludge-amended and untreated soil after the application of 10 – 30 Mg d.m. ha^{-1} to grey forest soils of Tatarstan (*Selivanovskaya* et al., 2001). Fertilization with composted bio-waste for five years significantly increased the total contents of Zn and Pb (*Bartl* et al., *2002*).

Total amounts of heavy metals are not decisive for mobility and bioavailability. The mobile and bioavailable fractions can be assessed by extraction or adsorption experiments (*Esnaola* and *Millán,* 1998; *Maiz* et al., 2000). Bioavailable fractions of heavy metals are commonly extracted using water, neutral salt solutions, and complexing agents such as EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetate). Studies have shown inconsistent results of metal bioavailability in sludge or compost amended soils. *Weissenhorn* et al. (1995) found a high Zn, Cd and Ni availability in plots treated long-term with metal contaminated sludge. *Sadovnikova* et al. (1996) found over time an increasing metal solubility in 1 M NH_4NO_3 solution in sewage sludge amended soils. The application of Cd enriched sewage sludge compost increased the available Cd content of an arid soil and thus, the risk of this heavy metal uptake by plants (*Moreno* et al., 1999).

On the other hand, *Walter* and *Cuevas* (1999) and *Illera* et al. (2000) found increased levels of less soluble heavy metals fractions in sewage sludge-amended soils which were not susceptible to leaching or plant uptake. In another study the contents of DTPA-extracted metals declined with time and it was suggested that the OM applied with biosolids could fix the metals over time (*Walter* et al., 2002). The importance of soil properties was emphasized by *Khan* and *Scullion* (2000): Metal inputs by sewage sludge caused a marked increase in metal availability in slightly acidic sandy loams, a smaller increase in slightly acidic clays and had little effect in an alkaline loam. Contents of EDTA-extracted Zn, Cu, Ni and Pb were significantly increased in sludge-amended soil but a limited water pollution risk through leaching was assumed due to the interaction of the metals with OM at a relatively high soil pH (*Nyamangara* and *Mzezewa, 1999*). Soil contents of all metals of concern were significantly increased by a long term high dose sludge application down to a soil depth of 30 cm. Mass balance calculations of losses ranged from 39% for Cu and Pb to 60% for Ni (*Baveye* et al., 1999). The authors assumed that mobile metal-organic complexes had moved through the subsoil without substantial re-adsorption. *Richards* et al. (1998) found significantly higher metal concentrations in leachates about 20 years after the application of 244 Mg d.m. sludge ha^{-1}. This was explained by preferential flow and metal complexation with soluble OM. Results of *Cornu et al.* (2001) showed an influence of sludge application on water quality, especially at the start of the experiment when Cu, Ni, and Pb were increasingly leached. However, the net impact was reported to be rather low and therefore soil was considered to be an efficient filter for water leaching from the sludge deposit. In investigation of metal concentrations in leachates, *Richards et al.* (2000) found a variable metal mobility dependent on the sludge processing technique with generally low cumulative losses relative to the total amount of metals applied. Increased concentrations of free Zn and soluble Cu were found by *Chaudri* et al. (2000) in soils amended with contaminated sewage sludge over a long term period. The authors criticized that none of the limits in regulations from different countries were based on toxicity thresholds in soil pore water which may be more valid for different soil types and at different pH values than total soil concentrations. *Planquart* et al. (1999) stated that the total heavy metal concentrations in sewage sludge and soil pH were insufficient criteria to control metal accumulation by crops. The authors stressed potential relevant risks that could derive from the mineralization of OM and consequently from the release of heavy metals into more soluble forms.

Once heavy metals become bioavailable, they are known to be toxic to microorganisms (e.g. *Campbell* et al., 1997; *Dahlin* et al., 1997). This led to concerns that soils treated with metal contaminated sludge could adversely affect the mineralization of organic N in the soil sludge-plant system. However, *Chander* et al. (1995) and *Johansson* et al. (1999) concluded that none of the metals investigated in their studies in moderate concentrations showed any adverse effect on soil microbiology. *Munn* et al. (2000) found increased N availability when increased amounts of metal contaminated sewage sludge were added. This indicates that this specific soil amendment did not hinder mineralization of N from legumes. *Khan* and *Scullion* (2000) concluded that variations in soil properties had a major effect on microbial response. The concentrations of $CaCl_2$ and water extractable Cu, Ni, and Zn were closely correlated with microbial indices in sandy loam but not clay soils. Overall, the effect of treatments on microbial and extractable metal indices was greater in loams when compared to soil richer in SOM. Increasing heavy metal concentrations from different sources, including sewage sludge, generally resulted in a decreasing biomass C : soil C ratio and caused a shift in the microbial community structure towards fungi *(Chander* et al., 2001).

A study by *Cole* et al. (2001) indicated adverse effects by a heavy metal contaminated sludge on Collembola. The authors called for further research to determine if current legislation adequately protects the full range of invertebrates in agricultural soils.

Plant uptake of heavy metals

Metal uptake by plants usually was increased when higher concentrations of metals were found in the sludge. Toxic Cd was the most mobile among the investigated heavy metals, resulting in maximum enrichments in plant tissue after sludge application. Thus, Cd is of primary concern in terms of food chain contamination (*McLaughlin* et al., 1999). Uptake of metals by plants growing in sewage sludge-amended soils frequently exhibited a plateau response at high total concentrations resulting from high sludge loads. This was generally attributed to attenuation of metal bioavailability by increased adsorption by sludge constituents at high sludge loads. However, *Hamon* et al. (1999) concluded that plant physiological factors were responsible for the plateau in plant metal concentrations in addition to the attenuation by sludge chemistry. This nonlinear uptake was simulated using Freundlich-type functions (*Krauss* et al. 2002). Metal uptake and concentrations were high in leafy plants and higher in cereal leaves than in cereal grain. Furthermore, a relatively constant or somewhat reduced uptake of metals occurred in successive years after a single application (*Gardiner* et al., 1995; *Miller* et al., 1995). *Gigliotti* et al. (1996) concluded that long-term application of large amounts of urban waste compost to $CaCO_3$ containing soils did not necessarily cause problems to plant, animal, or human health. However, *Richards* et al. (1998) found elevated Cd, Cu, and Ni levels in grass which was growing on sludge-amended soil. *Ramachandran* and *D'Souza* (1998) found a high accumulation of Cd in maize grown in an acidic, sludge/compost-amended soil with low cation exchange capacity. In this study, DTPA extracts were good indicators for the plant availability of Cd, Zn, and Mn. *Oudeh et al.* (2002) described the complexity of soil–plant interactions with regard to metal accumulation after sludge application and concluded that soil variation, including mycorrhizal activity and SOM levels, potentially modify the risks arising from metals in sludge.

Organic contaminants in organic waste

Current legislation has scarcely focused on organic contaminants since the usage of the most important (for example, polychlorinated biphenyls) has decreased and the pretreatment of industrial waste water has improved (*Chaney* et al., 1996). Moreover, hydrophobic toxic organic chemicals rapidly react with the sludge-soil matrix and become less available to crops (*O'Connor,* 1996). The K_{OC}-values of a number of organic compounds (e. g. some pesticides, detergents, dyes) calculated from adsorption experiments with sewage sludge were similar to the K_{OC}-values obtained by experiments with soils (*Kördel* et al., 1997). Dissolved OM originating from organic waste may act as carrier and thus mobilize hydrophobic organic contaminants (*Maxin* and *Kögel-Knabner,* 1995). Numerous organic contaminants with different physicochemical properties enter waste water systems and subsequently accumulate in sewage sludge, and are therefore able to enter the food chain. Attempts were made to prioritize some of those compounds on the basis of toxicity, persistence, physicochemical properties, and quantity in sewage sludge (*Litz* et al., *1998a; Litz* et al., 1998b). In Canada, *Webber* et al. (1996) concluded based on the monitoring of numerous organic contaminants in sludge that these compounds represented no significant contamination risk to agriculture and the environment. *Duarte-Davidson* and *Jones* (1996) identified some chlorinated benzenes and phenols, PCBs, and PCDD/Fs as potentially accumulating in livestock after sludge application to pasture. *Schnaak* et al. (1997) assessed, after monitoring a number of organic contaminants in sewage sludge from the north-east of Germany, some solvents (dichloromethane and toluol) and surfactants, as well as their degradation products, (LAS and NP) as being critical.

Alcock et al. (1999) identified "new" hazardous chemicals as the following compounds and groups of compounds probably present in sewage sludge: chlorinated paraffins, quintozene, brominated diphenyl ethers, polychlorinated naphthalenes, polydimethylsiloxanes, chloronitrobenzenes, and a range of biologically active and pharmaceutical compounds. Determinations of 14 major PAHs in sewage sludge from Poland indicated that sludge from rural regions could be applied to soil whereas sludge from industrial regions was unsuitable (*Bodzek* and *Janoszka,* 1999). The PCB concentrations in composted sewage sludge from Poland were similar to those in Germany but the lower chlorinated congeners were relatively more abundant in this Polish organic waste when compared to the German sewage sludge (*Düring* and *Gäth,* 2000). Due to the amended regulation on the agricultural use of sewage sludge (*AbfKlärV,* 1992), PCBs were frequently determined in the routine monitoring of sewage sludge in Germany (Figure 5). Accumulation of PCBs was also observed to be lower by 50% in composts than in sewage sludge of the same origin. Losses of PCB #28 were attributed to volatilization during composting (*Düring* and *Gäth,* 2000).

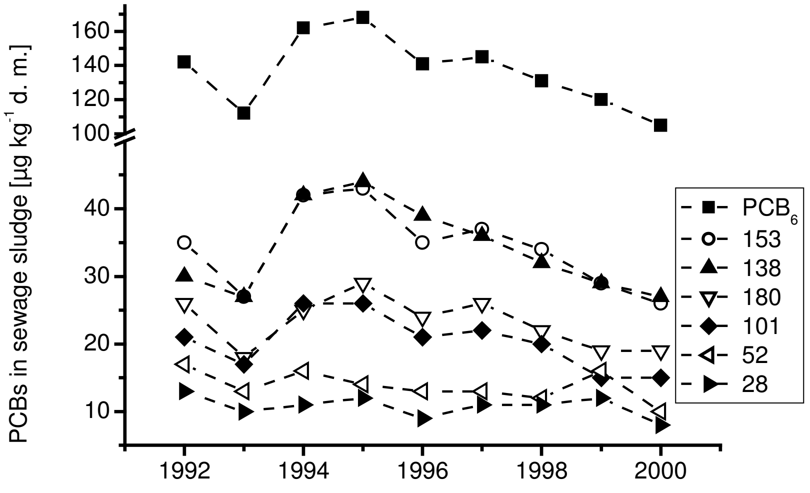

Fig. 5: Mean concentrations of PCBs in sewage sludge of central Germany (*Walper, 2002*).

Studies in Catalonia, Spain showed that PCDD/F concentrations in sewage sludge have declined since the 1980s *(Eljarrat* et al. 1999). In Brazil, *Grossi* et al. (1998) found increased concentrations of PAHs, PCBs, and PCDD/Fs in composted unsorted municipal solid waste from metropolitan areas. Compost from a separate collection of organic waste had pollutant concentrations well below reference values in Germany. *Berset* et al. (2000) found ubiquitous nitro musk compounds, mainly as their monoamino metabolites, in sewage sludge. These metabolites were probably more toxic than their parent compounds. This generally confirms the necessity of considering the degradation products in analytical protocols and in future standards.

Hale et al. (2001) found high concentrations of brominated diphenyl ethers (BDEs) in sewage sludge from four different regions of the United States. Due to their widespread use as flame retardants and their occurrence in organic waste, the authors suggested further investigation into the environmental consequences of application of sewage sludge onto agricultural land.

Abnormal sexual development in wildlife and various symptoms in humans which may be attributed to a disruption of the endocrine system, were suggested to be related to environmental chemicals (e.g. *Safe,* 1998). The increasing list of chemicals showing estrogenic activity now includes compounds like DDT, certain phthalate esters, non-coplanar PCBs and metabolites, bisphenol-A and alkylphenols. Organotin compounds which have also shown a potential to affect the hormonal system, have been found to be enriched in sewage sludge *(Fent,* 1996). *Bolz* et al. (2001) determined six phenolic xenoestrogens (i.e. different alkylphenols, bisphenol-A, hydroxylated biphenyls) in sewage sludge in a concentration range from the µg kg^{-1} to the low mg kg^{-1} level. A relatively low concentration of nonylphenol was attributed to the fact that the respective sludge was not anaerobically stabilized. It is well known that NP accumulates in anaerobic stabilized sludge as an intermediate degradation product of NPEOs (e. g. *Johnson* and *Sumpter,* 2001). In a study of *La Guardia* et al. (2002), biosolids derived from 11 USA wastewater treatment plants contained detectable levels of octylphenol, nonylphenol, and short-chain nonylphenol ethoxylates. NP was found to be the major component and its concentration ranged from 5.4 to 887 mg kg^{-1} d. m. The authors stated that alkylphenol ethoxylate degradates in USA biosolids may cause adverse environmental impacts due to their toxic and estrogenic properties.

Between 10 and 100 µg of natural and synthetic estrogen is excreted daily by cycling women. Pregnant women may secrete up to 30 mg of estrogen daily. Effective removal within sewage treatment plants was attributed mainly to biodegradation and not to adsorption on particulate matter (*Baronti* et al., 2000). *Vader* et al. (2000) confirmed these results and identified nitrifying bacteria capable of rapidly degrading ethinyl estradiol. Possible eco-toxicological and human health risks cannot be explained simply on the basis of the toxicity of natural and synthetic estrogenic compounds (*Kortenkamp* and *Altenburger,* 1998). However in organic municipal wastes, mixtures of natural and synthetic estrogens along with phytoestrogens and xenoestrogens can accumulate and therefore, it is conceivable that those substances might interact with each other. The research on additive and synergistic effects is just beginning, and up until now, effects have been difficult to prove. *Körner* et al. (1999) made a promising attempt to quantitatively determine the estrogenic activity of sewage treatment plant effluents.

They optimized a simplified proliferation test using human estrogen receptor-positive breast cancer cells and thus adapted the so-called E-screen assay which could show some additive effects. Since this test was suitable also for untreated sewage, it may be possible to apply it to sludge. Recently, drug residues were detected in the aquatic environment and many pharmaceuticals (e. g. antibiotics) were frequently found in sewage treatment plant effluents. However, concentrations of tetracyclines and penicillins could not be detected at higher concentration levels (*Hirsch* et al., 1999). The question remains as to which way those drugs are to be eliminated in sewage treatment plants. Since tetracyclines and many other pharmacologically active compounds easily form stable complexes (*Hirsch* et al., 1999), or interact with biological membranes (*Schreier* et al., 2000), they tend to accumulate in sewage sludge. However, there is a lack of research on the partition behavior of pharmaceuticals in soil/sediment-water systems. The first data on the partition behavior of antibiotics with varying physicochemical properties in the system soil-water were recently presented by *Thiele* and *Beck* (2001).

Impact of organic contaminants on soil

Some experiments with increased sewage sludge application rates demonstrated an accumulation of PCBs in treated soils (*Folch* et al., 1996*; Alcock* et al., 1996*; Eljarrat* et al., 1997; *Delschen,* 1999). In the short-term however no significant PCB increase could be determined on soils amended with compost and sewage sludge, respectively. PCB content was related to soil OM content providing sorption sites for PCBs which were mainly introduced by atmospheric input (*Düring and Gäth, in press*). This concentration-dependence on soil organic carbon was recently confirmed by *Ribes* and *Grimalt* (2002).

It is evident that only part of the total concentration of hydrophobic organic contaminants in soil are available for the partitioning between soil and solution and therefore, a subsequent uptake by biota or microbial degradation which was introduced by *Krauss* et al. (2000). They stressed that availability decreases with increased residence time ("aging") of the compounds in soil or sediment and differs between compound classes. *Alexander* (2000) argued that exposure to persistent compounds was generally overestimated by currently used chemical methods since aging appeared to occur in most contaminated soils. To assess bioavailable concentrations, different extraction methods and approaches using solid adsorbents were applied (e.g. *Krauss* and *Wilcke,* 2001). Semipermeable membrane devices (SPMDs) were applied to assess total and bioavailable concentrations of persistent organochlorine contaminants in composts by *Strandberg* et al. (1997). The contaminant levels in the composts ranged between 0.2 and 444 ng g^{-1} d. m. Furthermore, this analysis revealed that the considered pollutants were evaporating from the compost surface.

Mineralization of 14-C-labeled nonylphenol in homogenized and non-homogenized soil-sludge mixtures was investigated by *Hesselsøe* et al. (2001). NP was degraded within 38 days in aerobic homogenized mixtures. In non-homogeneous mixtures containing sludge aggregates, the degradation of NP was retarded and was generally not completed within 3 months. Their data suggested that more than 1 year was required to obtain fully aerobic conditions in a 2 cm sludge aggregate. Since NP is scarcely degraded in the absence of oxygen, residual amounts of NP may be present in the anaerobic center of aggregates for prolonged periods. However, these valuable data are limited to the degradation behavior of the linear isomer of NP which does not occur in sewage sludge as a degradation product of different NPEOs. Nevertheless, anaerobic soils may not be appropriate sites for amendment with sewage sludge which contains high amounts of surfactants and respective degradation products such as NP (*Scott* and *Jones,* 2000). *Ibanez* et al. (2000) demonstrated accumulative effects of steroids in soils treated with manure and different doses of sewage sludge.

Enhanced transport of pesticides in sludge-amended fields was attributed to the development of preferential flow pathways around hydrophobic clods of sludge and the development of complexes with dissolved OM derived from sludge degradation (*Graber et al., 2001*).

Plant uptake of organic contaminants

After revision of data on the uptake of organic compounds by crops grown in sludge-amended soils, *O'Connor* (1996) concluded that contamination of crop plants with known toxic organic contaminants is negligible.

A sensitive bioassay detected low concentrations of dioxin-like compounds in all carrot, zucchini and cucumber samples grown in soil amended with sewage sludge. However, whether or not sludge application results in the accumulation of dioxin-like compounds in the soil, thereby increasing the risk of plant uptake, remains to be investigated (*Engwall* and *Hjelm,* 2000). *Smith* et al. (2001) pointed out that persistent organic contaminants may be introduced into the grazing animal food chain if sewage sludge is applied to pasture land.

Conclusions and perspectives

Land application of organic waste such as sewage sludge and compost may be a practical way to recycle organic municipal solid waste as long as the materials are quality controlled. Organic wastes have been shown to return valuable nutrients to the soil and enhance conditions for vegetative growth. For developing countries, which are not highly industrialized and have rapidly increasing amounts of organic waste, this option would be practical for both economical and ecological reasons.

However, in industrialized countries with a high population density, public concern has grown with regard to the unforeseeable hazardous impacts from known and unknown toxic substances which might enter the agricultural food chain through the utilization of organic wastes. Furthermore, an inevitable accumulation of persistent pollutants occurs in soils since the output via plant uptake is small. The potentially adverse effects, especially from the agricultural use of sewage sludge, have been intensively discussed (*Bannick*, 2001) and may result in the land application of sewage sludge being forbidden in Germany. The best strategy to cope with the benefits and risks of huge amounts of organic waste would be to use a range of options which should include waste minimization.

At first the accumulation of persistent contaminants in agricultural soil can be prevented by inputs smaller than, or equal to, the outputs. This "balance approach", should not only consider pollutants, but should include the effects of soil amendments on soil composition which in turn determines soil bulk density (*Moolenaar* et al., 1997b).

Without doubt there is a potential to improve the quality of organic waste which will be applied to agricultural land. Composting will play a bigger role in the sewage sludge treatment in the future (*Wei* et al., 2000*; Nissen* et al., 2000). Synthetic zeolite, as an amendment for sewage sludge-based compost or liming, significantly reduces the soluble and extractable metal contents in sludge (*Fang* and *Wong,* 1999*; Nissen* et al., 2000).

Heavy metals can be removed from sewage sludge by biological and chemical measures (*Xiang* et al., 2000*; Yoshizaki* and *Tomida,* 2000). Organic contaminants may be degraded during sewage treatment and improved processes. Dewatered activated sludge has a high potential for the mineralization of pyrene (*Klinge* et al., 2001). PCBs can be dechlorinated under anaerobic conditions (*Chang* et al., 1999) but they can not be significantly degraded during composting of sewage sludge (*Lazzari* et al., 1999; *Lazzari* et al., 2000). However, composting matrices are rich sources of xenobiotic-degrading microorganisms which can mineralize or biotransform pollutants into less toxic substances and/or lock up pollutants within the organic matrix (*Semple* et al., 2001). PAHs can be significantly degraded during composting (*Lazzari* et al., 1999*; Potter* et al., 1999; *Lazzari* et al., 2000). The aerobic treatment of contaminated sewage sludge is promising regarding the degradation of DEHP, NPEOs, and NP (*Jones* and *Westmoreland,* 1998; *Banat* et al., *1999; Banat* et al., *2000*). Following the upcoming regulations of the EU, only sludge that has undergone advanced treatment can be applied to agricultural land.

Not only must waste quality be controlled but the ability of the soils to cope with the nutrients and pollutants introduced must also be considered. Hence, the application rate of organic wastes should be adapted to the soil properties. Heavy metal concentrations vary considerably between soil types. Thus, in relative terms, the change in concentrations in topsoil after the application of a specific amount of sludge can differ noticeably between different soil types (e.g. *Swedish Environmental Protection Agency,* 2001). Furthermore, soils exhibit different retention capacities for trace elements. Therefore, important soil properties which influence sorption capacities should be examined. By a multiple linear regression approach, soil properties can be weighed in terms of influencing sorption capacity for heavy metals and, with that knowledge, sorption capacities of soils in other regions can be assessed by using available data (*Schug* et al., 1999). Application of organic wastes onto pasture land should be banned due to evident contamination of plants and metal uptake by grazing animals.

Heavy metals should be analyzed with regard to their bioavailability to be determined by standardized procedures. For this, chemical sequential extraction is a precious operational tool (*Prudent* et al., 1996; *Álvarez* et al., 2002). Analytical methods for the determination of endocrine disrupting compounds and surfactants in sewage sludge have to be optimized and standardized. One attempt to fill this gap was the development by *Petrović* and *Barceló* (2000) of a comprehensive analytical method based on liquid chromatography and mass spectrometry for the simultaneous determination of the above mentioned compounds in sewage sludge. *Arnold* et al. (1998) described ASE (accelerated solvent extraction, a relatively new and highly efficient extraction technique) as very adequate for compounds covering a broad range of hydrophobicity and polarity. Another option would be the application of further developed bioassays to assess toxicity and endocrine potential. Research on the environmental behavior of surfactants and their degradation products must be intensified to assess their impact on human health via transfer from sludge to the agricultural food chain. Declining concentrations of dioxins (PCDD/F) do not justify their routine monitoring in Europe for the future, but for sludge of specific origin it may be necessary to determine PCDD/F´s. The US EPA however will include a dioxin standard in their upcoming biosolid regulations as a result of a comprehensive risk assessment. Furthermore, the situation differs to Europe with regard to high sludge contamination with BDEs and NPEs. Such findings of contamination with "new" organic pollutants further stresses the need for intensive monitoring of organic wastes such as sewage sludge and compost with standardized methodologies.

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Anhang D

Microwave assisted methodology for the determination of organic pollutants in organic municipal wastes and soils: Extraction of polychlorinated biphenyls using heat transformer disks

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Abstract

Known benefits of microwave assisted extraction (MAE) of polychlorinated biphenyls (PCB) from solid matrices could be proven by the described approach using n-heptane as solely applied extraction solvent. Heat transfer within the extraction vessels was achieved by heat transformer disks which absorb microwave energy and transform it into heat rapidly and independently of the temperature present in the sample-solvent system. Disadvantageous co-extraction of polar substances could be ruled out and thus clean-up of the samples was simplified and sufficient for subsequent GC-MC analysis. Comparison with other extraction techniques confirmed the efficiency of this method also for aged samples.

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Introduction

The agricultural utilization rather than disposal of sewage sludge and compost is mandated by German law (*KrW-/AbfG*, 1994). Nutrients in those materials make them desirable for plant production and can substitute mineral fertilizers. Carbonates derived from stabilized sewage sludge contribute to desirable neutral soil reaction. However, inorganic and organic pollutants can end up in these two media, and thus accumulate and deteriorate the quality of soils. Consequently, some pollutants must be monitored in organic wastes considering established threshold values (*AbfKlärV*, 1992; *BioAbfV*, 1998). In the analysis of sewage sludge six representative congeners of the PCB have to be considered.

Assuming an increasing rate of land application of organic wastes, not only in Germany but also in other European countries, there is a need for efficient procedures to analyze such complex matrices like compost and sewage sludge for different organic pollutants. A challenge for analytical laboratories is still to perform efficient and selective extraction and clean-up with as low as possible consumption of time and material inputs.

Extraction of lipophilic organic pollutants like PCB from solid matrices has long been accomplished by Soxhlet or sonication extraction techniques. Those techniques separate the analytes from the matrix with high efficiency, but they require large volumes of solvents and long extraction times (*Rahman* et al., 1998). With technological progress faster extraction techniques arise in the field of residue analysis: The Accelerated Solvent Extraction (ASE™) as a relatively new technique employs elevated temperature and pressure to yield recoveries comparable to or higher than the traditional Soxhlet method with a considerable saving of both solvent volume and extraction time (*Wenzel* et al., 1998; *Pörschmann* and *Plugge*, 1999). However, this automatically operating method is limited by the considerable investment cost for the ASE apparatus and is profitable only with high sample through-puts.

Benefits of microwave assisted extraction (MAE) of different organic pollutants from solid matrices have already been published (*Ganzler* et al., 1990; *Dupont* et al., 1999; *Kodba* and *Marsel*, 1999; *Letellier* and *Budzinski*, 1999). Nevertheless, for any heating effect, a polar solvent which is miscible with the non-polar extraction solvent must be added, taking into account the disadvantageous co-extraction of undesired substances.

The approach presented here is a strictly hydrophobic and therefore more selective microwave assisted extraction of PCB using specially designed transformer disks followed by chromatographic clean-up and determination via GC-MS. Suitability of this method had to be proven by application to real samples of sewage sludge and compost of different origin and to a reference material with certified content of the technical PCB mixture Aroclor 1242.

Experimental

Materials

Solid matrices

Recovery studies were carried out using dried samples of 2 different top soils (soil A: 115 g sand kg^{-1}, 756 g silt kg^{-1}, 129 g clay kg^{-1}, 17,6 g C_{org} kg^{-1}; soil B: 181 g sand kg^{-1}; 582 g silt kg^{-1}; 237 g clay kg^{-1}, 21,6 g C_{org} kg^{-1}) and organic-free sand. A reference material (CRM910-050, Promochem GmbH, Wesel, Germany) with a certified concentration of Aroclor 1242 served as a standard for the evaluation of the extraction efficiency for the PCB in soil. Samples derived from municipal sewage sludge and compost were freeze dried and ground (0.1 mm particle size) prior to the experiments for making the matrix more accessible for the extraction solvent and diminishing volatilization losses of the analytes.

Chemicals

For recovery studies, the samples were spiked with Aroclor 1242 in acetone (Pestanal™) at different concentrations. The spiked samples were allowed to sit (assuring complete volatilization of the solvent) either for 24 h or 14 d in the dark at room temperature. As extraction solvent n-heptane (Pestanal™), mixed with 1% (v/v) n-decane (p. a.) was used. In the analysis of real samples a blend of Aroclor 1242 and Aroclor 1254 (Sigma-Aldrich, Steinheim, Germany) served for elucidation of the PCB pattern. PCB congeners [IUPAC numbering is given in *Fischer* and *Ballschmiter*, (1988)] # 28; 52; 101; 138; 151; 180 (Restek Corp., Bellefonte, PA, USA) were used as calibrants. 1,2,3,4,-tetrachloronaphthalene (Promochem, Wesel, Germany) was the internal standard. Pre-dried Na_2SO_4 (Merck, Darmstadt, Germany) was mixed with the ground samples before extraction. For clean-up of the extracts solid-phase extraction on Florisil® cartridges (Bakerbond SPE, Baker Inc., Phillipsburg, NJ, USA) was carried out.

Extraction techniques

MAE was performed with a 1200 MEGA microwave oven from MLS Corp. (Leutkirch, Germany) operating at 2.45 GHz and a maximum power of 1000 W. For method development, both a temperature and pressure sensor provided control of experimental conditions. Closed extraction vessels consisting of Teflon allowed enhanced pressure and temperature. Depending on the matrix, 1 g (organic wastes) or 2 g (soils) of sample were thoroughly mixed with an equivalent amount of Na_2SO_4 and weighed into the vessels. To each sample one Weflon® disk (MLS Corp., Leutkirch, Germany), consisting of a synthetic material on a Teflon basis mixed with carbon, and 15 mL of extraction solvent were added. The Weflon®-disks absorb the microwave energy and allow a rapid convective heating of the non-polar solvent. With this set-up, conditions with extraction temperatures far above the boiling point of n-heptane could be achieved.

After cooling to room temperature, the extracts within the extraction vessels were centrifuged (approx. 2000g) to remove the matrix. In case of compost samples, an additional membrane filtration step (0.45 µm) was necessary. The supernatants and filtrates were each concentrated to approximately 2 mL.

Soxhlet extractions were carried out according to (DIN, 1996), using n-hexane (pestanal™) as solvent. Extracts were concentrated to approximately 2 mL using a rotary evaporator at 40°C and 350 mbar. After rinsing the flasks with up to 5 mL of solvent and adding this amount to the extracts, the samples were concentrated under a gentle stream of nitrogen again to approximately 2 mL.

ASE was performed using stainless steel vessels of a Dionex ASE 200 apparatus (Dionex GmbH, Idstein, Germany). Samples (1 g of organic waste material or 2 g of soil) were subjected to the following conditions with n-heptane as extraction solvent: 12 MPa, 120°C, with a static and heat time of 10 min. Crude extracts were concentrated under a gentle stream of nitrogen to approximately 2 mL.

Clean-up

To separate the analytes from lipids and fats, a convenient clean-up procedure was performed with disposable Florisil® solid-phase extraction cartridges as described by *Folch* et al. (1996) and *Dupont* et al. (1999). In case of clear and colorless soil extract concentrates the clean-up step can be omitted for further GC-MS analysis.

GC-MS analysis

Concentrated and, if needed, purified extracts were analyzed on a Hewlett-Packard (Palo Alto, CA, USA) GC-MS system (GC: HP 5890 Series II, directly coupled to a MS engine HP 5989A). A cold injection system (Gerstel Muehlheim, Germany, KAS 2) allowed temperature programming of the injection port and selective removing the solvent. Acquisition was performed with the G1034C$^{©}$ software running on a personal computer. The GC oven was equipped with a low polar DB-XLB column (J&W Scientific, Folsom, CA, USA) of 30 m length, 0.25 mm I.D., and film thickness of 0.25 µm. Helium was used as a carrier gas at a linear velocity of 38 cm s^{-1} for 100°C. Depending on the type of sample, an injection volume was chosen in a range of 0.5 µL to 5 µL. For eliminating the solvent, the cold injection system was programmed as follows: initial temperature 60°C, initial hold 0 s, first heating rate 5°C s^{-1} to 70°C and 100 s hold, second heating rate 10°C s^{-1} to 300°C and 360 s hold. The column temperature was held at 80°C for 1.7 min and then increased at 5°C min^{-1} to 170°C, 1 min held, programmed to achieve 250°C at a rate of 2°C min^{-1}. This temperature was held for 13 min. The final temperature of 280°C was achieved with a rate of 10°C min^{-1} and held for 1 min. Total analysis time was 77.7 min. In preliminary recovery tests with soil samples spiked with Aroclor 1242 an analysis time of 38 min (using higher temperature rates) was sufficient to resolve the relevant PCBs (up to tetrachloro biphenyls) from the matrix and from each other. Both the temperatures of the transfer line interfacing the GC with the MS and of the ion source were set to 300°C. The temperature of the quadrupole was set to 110°C. The electron impact operated at 70 eV. Using the selected ion monitoring mode (SIM) the following m/z values within distinct time windows were monitored for quantification and for qualitative confirmation: 254, 256 for PCB 28; 290, 292 for PCB 52; 194, 264, 266 for TCN (1,2,3,4-tetrachloronaphthalene as internal standard); 254, 326, 328 for PCB 101; 290, 360, 362 for PCB 153 and 138; and 324, 394, 396 for PCB 180. The MS was tuned manually biweekly with the masses 100, 219, 414.

Results and discussion

Recovery rates from spiked materials

Preliminary MAE experiments on extraction conditions yielded highest extraction efficiency under the following settings: 1 min microwave power set at 250 W followed by 14 min under microwave power of 500 W, resulting in temperatures of up to 150°C using n-heptane as an exclusive extraction agent. For the spiked materials, the overall recoveries for the PCB #28 and #52 ranged for the three different matrices from 72 to 99% with a mean of 86% (n = 32) 24 h after the application of Aroclor 1242. Results for the different materials and the two mentioned congeners are given in Fig. 1. Lower recovery rates for PCB #28 were obvious for each considered material. Losses of this slightly volatile congener can be explained by volatilization after spiking the sample and during following concentration steps within sample clean-up *Lopez-Avila* et al. (1995). Therefore, evaporation to dryness was avoided using a small amount of a keeper (75 µL *n*-decane per sample). The vapor pressure of *n*-decane (130 Pa) was found to be different enough from that of the analytes (Aroclor 1242: 0.05-0.13 Pa). This allowed depreciating n-decane sufficiently by the cold injection system for the subsequent GC-MS analysis. However, concentration steps should be reduced to the really unavoidable degree. In our experiments, nitrogen blowdown evaporation at a temperature of 40°C within the extraction vessels (controlled by weighing) was the most suitable. Thus, contamination and losses due to a frequent transfer from one to another vessel and due to the evaporation of large solvent volumes could be diminished to a low extent within this concentration step. However, for compost samples, a filtration step was necessary due to particles in the supernatant which could not be separated by centrifugation. These filtered extracts were evaporated to a defined volume in appropriate glassware. Recoveries from the two soils for the congeners #28 and #52 after an incubation time of 24 h and 14 d, respectively, are given in Fig. 2. Lower recovery rates for the congener #28 in particular after 14 d of incubation were again attributed to volatility losses of this compound.

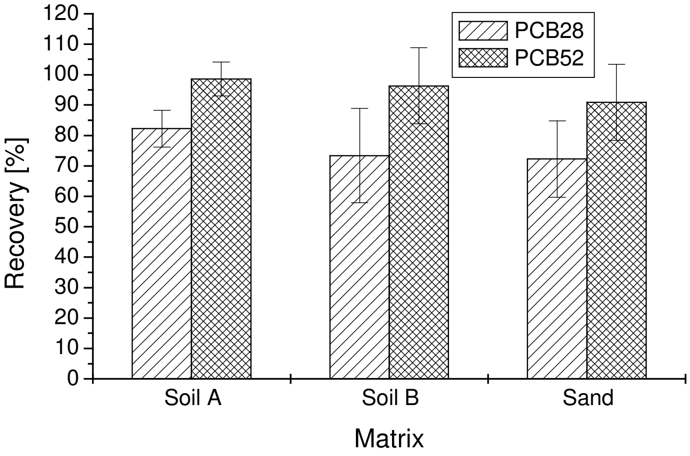

Fig. 1: Recovery of PCB congeners #28 and #52 after MAE of soils and sand spiked with Aroclor 1242.

Volatility of analytes must be considered when assessing the cooling time after the extraction step. Even though extraction times are very short, the cooling phase (in an ice bath) must take at least 30 min.

Besides volatilization losses considerable cross-contamination was recognized in preliminary tests (data not presented here). To diminish this cross-contamination of the extraction vessels, a thorough rinse step had to be introduced: Successive rinsing with distilled water, acetone, and n-heptane was followed by a treatment with nitric acid (60%) in the microwave oven (500 W, 10 min). After this, the vessels were rinsed again with distilled water and acetone. Due to the invention of the fluorinated polymer PFA with preferable surface porosity (*Ortner* et al., 1996), memory effects could be diminished when the described washing procedure was considered. The results presented here were obtained by using the PFA-material.

The Weflon® disks were subsequently treated with the same solvents in an ultrasonic bath. However, to assure the quality of this treatment, frequent measurements of basic noise were necessary.

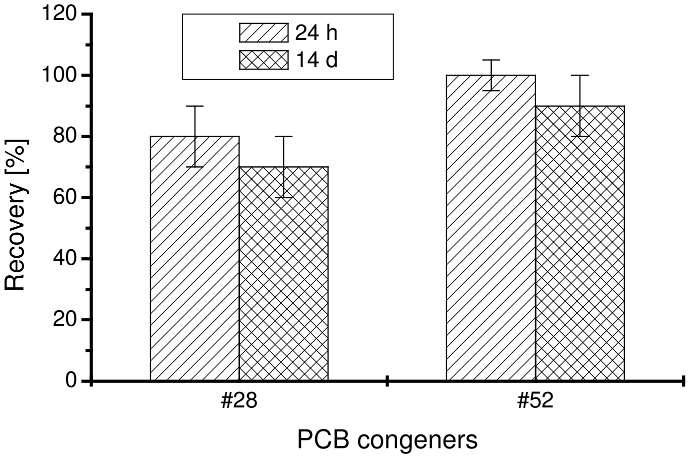

Fig. 2: Recovery of PCB congeners #28 and #52 after MAE of soils spiked with Aroclor 1242 which were incubated for 24 h and 14 d, respectively.

Real sample analysis

MAE of certified reference material (CRM910-050, Lot No: D910) resulted in a mean recovery of 111% (min = 98%, max = 123%, n = 3) of the reference value of 39.4 mg Aroclor kg^{-1}. Soxhlet extraction and ASE yielded 97% (min = 89%, max = 109%, n = 3) and 98% (min = 86%, max = 111%, n = 3) respectively, of the referenced concentration. The reference value of this soil is based on the EPA method 3540A/8081, using Soxhlet extraction. The results may indicate a slight systematic underestimation of the real PCB content in aged samples by the traditional Soxhlet extraction. Further research is needed to validate this tendency.

Figure 3 illustrates a typical PCB pattern in a sample of a German sewage sludge after MAE and clean-up compared to a chromatogram of a 50 : 50 blend of Aroclor 1242 and 1254.

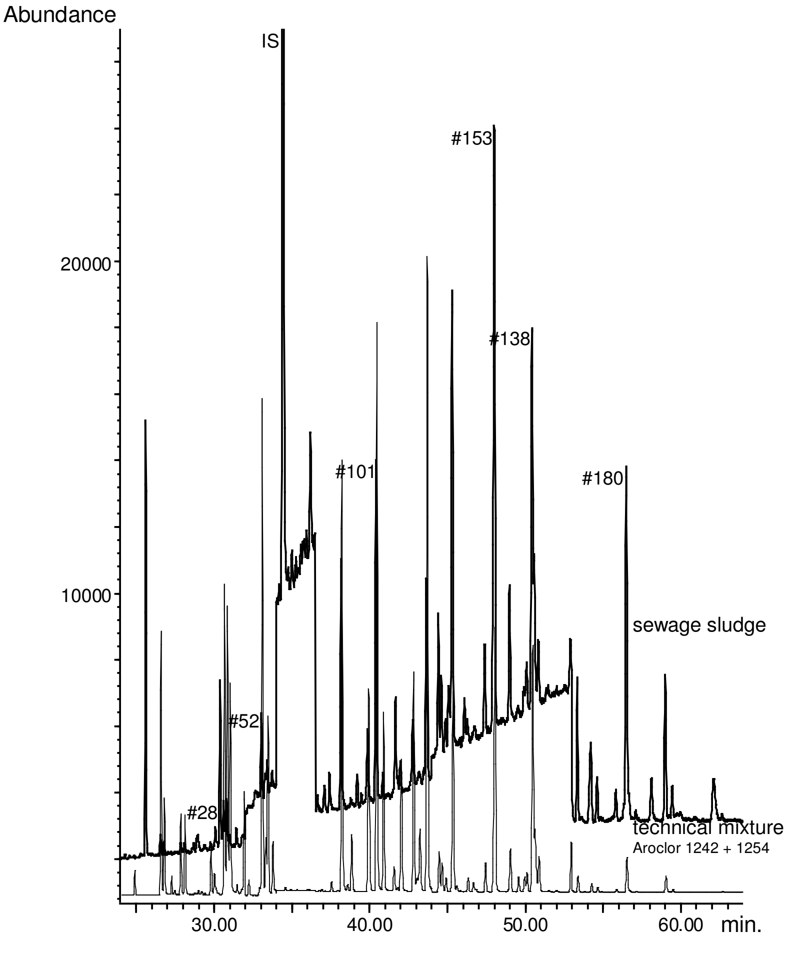

Fig. 3: PCB pattern in a sewage sludge sample compared to a blend of Aroclor 1242 and 1254. The numbers identify standard PCB samples, IS = internal standard (TCN). Bold curve: sewage sludge sample, thin curve: technical mixture.

Quantitative results of an application of the MAE methodology to real organic waste samples and compared to results from the Soxhlet method are given in Table 1. Analysis of municipal waste from Poland revealed a slight shift within the PCB pattern towards lower chlorinated biphenyls when compared to German wastes. As shown in Table 1, accumulation of PCB can be assumed also in compost materials. The distribution of the individual PCB congeners in compost samples is similar to the respective sludge samples of the same origin (Fig. 4). However, PCB #28 was not detected in German compost. This is explained by volatilization losses during the microbiological process of composting under elevated temperatures of up to 70°C.

Table 1: PCB concentrations [µg kg^{-1} d.m.] found in organic municipal wastes of different origin after MAE (for comparison: Soxhlet extraction of German wastes).

PCB congener No.	#28	#52	#101	#153	#138	#180
German compost MAE (n=6)						
mean	n.d.*	9.09	16.79	33.26	24.95	28.12
min	n.d.	n.d.	15.06	22.33	20.97	19.00
max	n.d.	15.18	17.96	40.32	30.89	36.71
Soxhlet (n = 2)						
mean	n.d.	n.d.	21.15	18.53	17.01	13.10
German sewage sludge (n=6)						
mean	14.82	20.54	40.19	67.18	53.34	42.65
min	11.72	13.09	32.17	49.84	38.42	26.89
max	18.86	31.36	49.61	80.28	65.29	54.55
Soxhlet (n = 2)						
mean	15.34	12.61	53.37	49.29	40.77	23.00
Polish sewage sludge/compost mixture (n=3)						
mean	11.98	20.63	54.43	43.04	25.91	8.63
min	8.93	17.46	49.49	38.90	24.35	5.79
max	16.17	24.32	59.58	47.88	29.00	13.69
Polish sewage sludge (n=3)						
mean	17.82	31.51	74.41	49.12	35.14	11.49
min	10.95	22.76	65.76	39.40	29.08	9.28
max	26.47	37.13	86.35	59.48	39.17	14.50

* n.d. = not detected

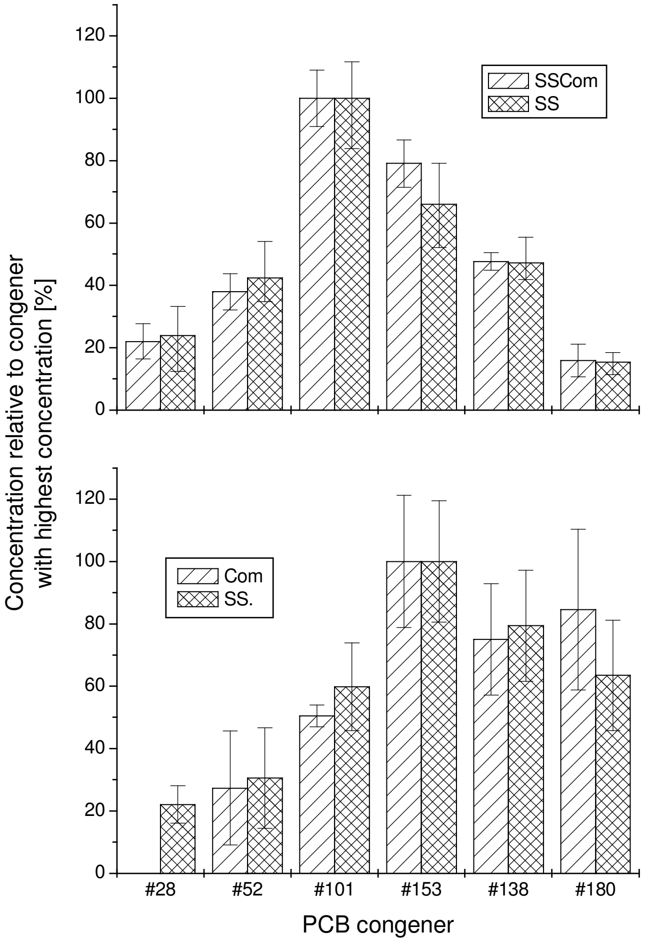

Fig. 4: Relative distribution of the determined PCB congeners in organic wastes (Polish wastes above, German wastes below). SS = sewage sludge, Com = compost, SSCom = 50 : 50 sewage sludge/compost mixture.

Conclusions

MAE as a closed vessel system using specially designed Weflon® heat transformer disks yields at least the same extraction efficiency as the Soxhlet method and the Accelerated Solvent Extraction (ASE), respectively. Using *n*-heptane as solely applied extraction solvent, high temperatures above the boiling point can be achieved and coextraction of undesired compounds should be diminished. Therefore, extracts are easily purified before being subjected to GC-MS analysis.

Volatility of the analytes must be considered when assessing the cooling time after the extraction step. Even though extraction times are very low, the cooling phase (in an ice bath) must take at least 30 min.

A limiting factor in residue analysis of organic compounds, even if MAE is used, is the material of the extraction vessels which can cause cross-contamination. From our experience, PFA with preferable surface porosity is suitable for residue analysis of PCB.

Regarding the results, the described methodology offers high efficiency and simplicity when appropriate measures to avoid cross-contamination are taken. This high efficiency and more rapid GC-MS techniques (i. e. with low pressure gas chromatography) may open up opportunities for better monitoring organic pollutants in municipal wastes which should be utilized in crop production. Since many analytical laboratories are equipped with a microwave oven mostly purchased for digestions in metal analysis, the application of this technique in the analysis of organic pollutants is cost effective and should be expanded to other classes of organic compounds.

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Anhang E

Microwave-assisted steam distillation with simultaneous liquid/liquid extraction of pentachlorophenol from organic wastes and soils

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Abstract

An efficient method for extracting pentachlorophenol (PCP) from organic solid matrices and soils using direct excitation of the fresh samples by microwave energy is presented. Steam-volatile PCP partitioned into the organic solvent *n*-hexane within the closed extraction vessel, resulting in recovery rates of 85–92% from aged samples. Condensed water provided a boundary layer between extract and sample thus preventing any contact of PCP with and re-partitioning into the sample. Duration of the microwave-assisted process was 35 min. Crude extracts were derivatized by heptafluorobutyric anhydride (HFBA) to improve selectivity and sensitivity resulting in detection limits of 1–2 μg kg^{-1}. GC–MS/MS analyses proved that suitable extracts with only minor impurities were obtained. Common sample treatment steps like drying, thorough grinding, frequent transferring, and tedious clean-up, and concentration procedures which all can cause certain losses of analyte were minimized. The efficiency of the method was verified by comparison with an established ultrasonic extraction procedure. This microwave-assisted pressurized steam distillation with simultaneous partition into an organic phase thus provides a streamlined and efficient strategy which requires no additional investment in standard equipment for microwave-assisted extractions (MAE). Degradation of analytes at longer extraction times must be taken into account.

Introduction

The US Environmental Protection Agency considers pentachlorophenol (PCP) a priority pollutant (*Keith* and *Telliard*, 1979) owing to its toxicity to humans and aquatic organisms. PCP and other chlorophenols are frequently applied as biocides to preserve wood, and this results in contamination of soil and water in the vicinity of wood-treatment plants (*Mikesel* and *Boyd*, 1988; *Laine* et al., 1997; *Lyytikäinen* et al., 2001). Mobility of the comparatively persistent PCP in the environment can be attributed to its steam-volatility and pH-dependent water solubility. Thus, contamination of indoor and outdoor air, soils, waters, and organic wastes was frequently detected (*Alcock* and *Jones*, 1997; *Khodadoust* et al., 1999; *Schnelle-Kreis* et al., 2000). Furthermore, PCP may be transformed into more toxic and even more objectionable compounds, such as polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) (*Öberg* and *Rappe*, 1992). Due to the environmental fate and (eco)toxicology of PCP and other chlorinated or alkylated phenols, their monitoring in and their removal from the environment is indispensable. Moreover, for environmentally sound recycling of organic wastes like waste wood or sewage sludge an efficient analytical procedure for determining those phenolic contaminants is necessary. Their quantitative extraction from different solid environmental matrices can be difficult due to strong fixation to the matrix. To extract residues of phenolic contaminants, different methods like Soxhlet extraction, ultrasonication, shaking, including their combination, supercritical fluid extraction, microwave-assisted extraction, and pressurized liquid extraction exist (*Khodadoust* et al., 1999; *Llompart* et al., 1997; *Egizabal* et al., 1998; *Polese* and *Ribeiro*, 1998; *Buhr* et al., 2000; *Ferguson* et al., 2000; *Fitzpatrick* et al., 2000). Under most environmental conditions, the acidic property of PCP ($pKa = 4.8$) results in the establishment of the respective phenolates (e.g., sodium pentachlorophenolate). Thus, PCP should be extracted in its molecular form under acidic conditions and an alkaline extraction should yield PCP as the respective salt. However, for GC analysis, the aqueous extract must be acidified to transfer the phenolate into PCP and subsequently to partition it into an appropriate organic phase. Usually, to improve chromatographic behavior, derivatization of PCP follows extraction. The different steps within PCP analysis are – more or less – characterized by difficulties emerging from the already mentioned physicochemical properties of the molecule. Expensive procedures were used to handle those PCP-specific analytical problems resulting in wide ranges of recoveries and detection limits.

Microwave-assisted extraction (MAE) is a strong competitor to other modern sample preparation techniques (*Eskilsson* and *Björklund*, 2000) and provides appropriate treatment to analyze phenolic substances originating from solid matrices. A review by *Camel* (2000) points to a different suitability of MAE for phenolic substances which are more or less stable under microwave conditions. However, in a systematic study on MAE of phenols, degradation of some analytes was assumed and resulted in recoveries as low as 10% in the case of certain nitrophenols (*Lopez-Avila* et al., 1994). The microwave-assisted process (MAP) exploits the ability of microwaves to selectively heat certain chemicals (*Paré* et al.,

1994) and may be an approach to extract organic contaminants like PCP out of heterogeneous matrices (i.e., soils and wastes mediated by the highly excitable intrinsic water of the sample). By taking advantage of the rapid MAP, it is the aim of this paper to examine the extraction efficiency of a microwave-assisted method utilizing a steam distillation effect with simultaneous partitioning into a small amount of organic solvent. Different environmental media like soils and wastes, in which considerable PCP contamination can occur, were spiked to optimize extraction conditions. By means of contaminated soil with certified PCP content and a waste wood sample, this method was further validated.

Experimental

Materials

Chemicals

Pentachlorophenol (PCP) and 2,4,6-tribromophenol (TBP), each of 99.5% purity, *n*-hexane (Pestanal® grade), heptafluorobutyric-acid anhydride, acetic anhydride, potassium carbonate, sodium chloride, and sodium sulfate, all of p. a. quality, were purchased from Sigma-Aldrich Chemie GmbH (Seelze-Hannover, Germany). Water was prepared (deionized and membrane filtrated) by a MilliQ plus water purification system.

Solid matrices

Recovery studies were carried out using sieved samples (2 mm mesh) of 2 different soils (Soil A silt loam 27 g C_{org} kg^{-1}; Soil B sandy loam 9 g C_{org} kg^{-1}), one ground sample (2 mm mesh) of wood (untreated softwood), and one sample of sewage sludge (organic matter 510 g kg^{-1}, 30% dry mass).

With a waste wood sample (ground, 2 mm mesh) the procedure was tested. Ground reference soil with a certified PCP content of 2.9 mg kg^{-1} (BAM-U009, Bundesanstalt für Materialforschung, Berlin, Germany) served for validation of the method.

Spiking of samples

The materials were spiked with PCP (210 µg mL^{-1} methanol stock solution) and diluted in n-pentane to achieve 8.4 and 2.1 µg g^{-1} sample, respectively. After 1 h gently shaking the sample/solvent suspension was homogenized. Complete evaporation of the solvents in the dark and at room temperature was established 12 h after application by weighing. Within that time, instantaneous sorption to the matrix was assumed. Spiked samples were aged at least for one and up to six weeks at 4°C and in the dark. Untreated material served as a control of PCP background levels.

Simultaneous microwave-assisted distillation/extraction

Each matrix (0.3 - 1.0 g) was weighed into PFA (perfluoroalkoxy resin) extraction vessels and 8 mL of water (pH 2; 9% NaCl) was added. This mixture was allowed to stand for 1 h at 4°C (to ensure equilibration of proton activity between both phases) and then 4 mL of *n*-hexane (Pestanal) was added. The closed vessels then were exposed to 1 min of 250 W followed by up to 14 min of 500 W of electrical power in a microwave oven operating at 2.45 GHz (1200 MEGA, MLS Corp. Leutkirch, Germany). In preliminary experiments, we used options of higher power with decreased irradiation time (4 min of 1,000 W) and vice versa, lower power with longer irradiation time (up to 40 min of 250 W). The initial low-energy step was selected on purpose to avoid a hazardous extremely rapid rise in temperature. After cooling to ambient temperature (30 - 60 min in an ice bath), the *n*-hexane extract was removed carefully with a Pasteur pipette, and after the addition of the internal standard (80 µL of a 30 µg L^{-1} TBP-solution) was adjusted to a defined volume. During method optimization actual conditions in the system were controlled by means of a reference vessel equipped with both a temperature and pressure sensor. The profiles of temperature and pressure inside the vessels are given in Fig. 1.

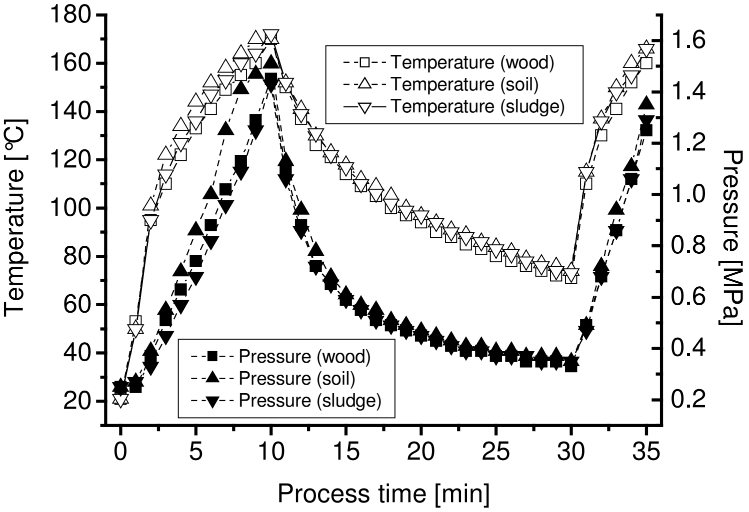

Fig. 1: Temperature and pressure profiles during extraction of different matrices which were irradiated between 0 - 1 min at 250 W, between 1 - 9 min at 500 W, and subsequently between 30 – 35 min at 500 W.

An ultrasonic extraction with acetone and hexane (1:1 mixture) (*Polese* and *Ribeiro*, 1998) served for comparison of methods.

Further sample treatment

A clean-up step could be omitted due to selectivity of the steam distillation approach. Derivatization of the MAE-derived extracts according to a method of *Heemken* et al. (2001) provided further selectivity and sensitivity of the method: PCP was transferred into its ester by the reaction of its phenolic group with heptafluoro-butyric acid anhydride (HFBA). Therefore, 300 µL of K_2CO_3 solution (20% w/w) was added to 500 µL of the *n*-hexane extracts, followed by 50 µL HFBA. The organic phase was separated after two shaking periods of 35-min 25-min duration at 60°C. The resulting aqueous phase was extracted twice with a total of 800 µL *n*-hexane. Adjusted to a defined volume, the pooled extracts were prepared for quantitative analysis.

GC-MS/MS analysis

Quantitative determination of PCP was performed on a Varian (Walnut Creek, CA, USA) GC-MS system (GC: CP 3800, directly coupled to an ion trap MS/MS system: Saturn 2000). The GC oven was equipped with a low polarity column of the DB-5 type of 30-m length, 0.25-mm I.D., and film thickness of 0.25 µm. Helium was used as a carrier gas at 1 mL min^{-1} in the constant flow mode.

The injection volume was 1 µL. The programmable temperature vaporizer (PTV) system was adjusted to an initial temperature of 60°C, initial hold 0.5 min; eventually an injection temperature of 260°C was reached with a rate of 200°C min^{-1}. The oven temperature was held at 50°C for 3 min and then increased at 17°C min^{-1} to 300°C. This temperature was held for 2.40 min. Total analysis time was 20.11 min.

The temperature of the transfer line interfacing the GC with the MS was 285°C and the ion trap was set to 245°C. The electron impact operated at 70 eV. Using the MS/MS mode, parent ions with following *m/e* values were selected: 447 (TBP derivative), 462 (PCP derivative), 332 (TBP), and 266 (PCP). Daughter ions with the following *m/e* values were monitored for quantification and for qualitative confirmation: 328; 305; 307 (TBP-derivative), 432; 265; 237 (PCP-derivative), 330; 250; 223 (TBP), and 264; 228; 202; 167 (PCP). The collision-induced dissociation resonant amplitude was 2 V for each analyte.

Results and discussion

Recoveries of pentachlorophenol from organic wastes and soils as a function of irradiation time are given in Fig. 2.

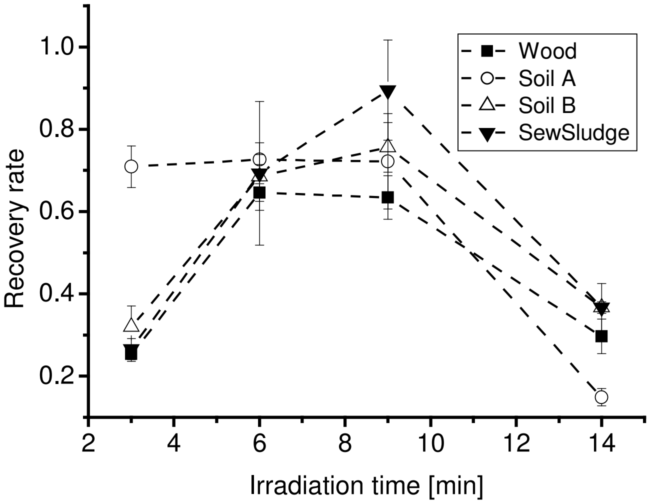

Fig. 2: Recovery rates of pentachlorophenol from spiked organic wastes and soils depending on the microwave irradiation time (experimental conditions: 1 min 250 W, followed by 500 W for different lengths of time).

For all samples, recoveries of more than 60% were obtained after six minutes of extraction time. This must be due to the intrinsic moisture of the fresh and swelled samples superheating spontaneously under microwave irradiation which facilitates loosening the analytes from the matrix (*Paré* et al., 1994). However, with further increasing irradiation time, PCP concentration decreased. At least two main kinetic processes occur in this closed vessel microwave irradiated system: steam distillation with simultaneous partitioning into the organic phase and, counteracting it, any dissipation process of the analyte. Matching of our data to a function of appearance-disappearance kinetics (Bateman function) was not successful, thus we cannot consider our approach of steam distillation and simultaneous liquid/liquid extraction of pentachlorophenol a simple one-compartment model. Besides an instantaneous transfer from the sample into the aqueous phase, the partition from the aqueous phase into the cold hexane solvent is an additional time-dependent equilibration process. During those processes, degradation of the analyte may take place. A specific microwave effect can be attributed to heating of the solvent above its boiling point (within our system up to 170°C) and the production of hot spots in heterogeneous systems (*Caddick*, 1995). According to previous work (*Lopez-Avila* et al., 1994; *Alonso* et al., 1998), this loss of analyte can be related to catalytic matrix effects on irregular surfaces supported by the introduced microwave energy. *Alonso* et al. (2002) demonstrated the degradation of tributyltin into dibutyltin and monobutyltin under conditions of microwave-assisted extraction. Microwave-hydrothermal decomposition of PCP was described by *Park* et al. (2000): however, the molecule was destroyed by substitution of chlorine atoms by hydroxyl groups under alkaline conditions. In their study, 88% of PCP was decomposed after 10 min with the microwave-assisted, alkaline hydrothermal treatment. *Abramovitch* et al. (1998) utilized microwave energy in the presence of Cu_2O and aqueous alkali to remedy PCP-contaminated soil and recovered only minute amounts of analyte in final extracts.

The applied 500 W of electrical power is a result of a pulsed mode consisting of equivalent proportions alternating between 1,000 W and 0 W, while the 250 W level is specified by the manufacturer as a permanent low-energy mode. To verify if there is any effect due to this regime, we applied this low-energy 250-W mode for 19, 30, and 40 min, respectively. In comparison to the pulsed mode, no improvement could be observed with highest recovery rates of 70% for sewage sludge at 30 min irradiation time and 58% and 14% recovery rates for 19 min and 40 min, respectively.

However, the recoveries given in Fig. 2 were not quantitative, and we re-extracted the remaining samples with fresh solvent under the same conditions. Depending on the matrix, an additional amount of 10 – 16% of the spiked analytes was recovered. Consequently, the extraction program was prolonged as follows: Samples were irradiated at 250 W for 1 min followed by 9 min at 500 W, then the closed vessels were allowed to cool down to approximately 70°C, and from 30 min onward the samples were irradiated again at a power of 500 W for 5 min. The resulting conditions inside the vessels are given in Fig. 1.

Comparison of the optimized microwave-assisted approach with a high efficient ultrasonic-based extraction (*Polese* and *Ribeiro*, 1998) confirmed the accuracy of the method (Table 1).

Table 1: Comparison of time and solvent need and recovery rates of PCP extracted from different matrices obtained by the microwave-assisted approach and an established ultrasonic method, respectively (n = 6; SD = standard deviation).

	ultrasonic				microwave			
	Recovery [%]	SD	Extraction time [min]	Solvent need [mL]	Recovery [%]	SD	Extraction time [min]	Solvent need [mL]
Soil A	88	5.3	40	30	92	11.2	35	4
Soil B	68	1.3	40	30	85	11.7	35	4
Sewage sludge	91	11.0	40	60	87	7.4	35	4
Wood	71	6.9	40	60	92	11.2	35	4

In Table 2, PCP concentrations in contaminated waste wood and the reference soil are given. The results indicate comparable recovery rates for both methods. However, in terms of solvent need, the microwave-assisted procedure should be preferred over the ultrasonic extraction method. Regarding the microwave-assisted approach, a 1-h equilibration of the sample suspension before extraction and another 30 min for cooling the samples to ambient temperature in an ice bath should be considered and included into the process time.

Table 2: Time and solvent need and concentrations of PCP in different samples obtained by the microwave-assisted approach and an established ultrasonic method, respectively ($n = 3$).

	ultrasonic				microwave			
	[mg kg^{-1}]	SD	Extraction time [min]	Solvent need [mL]	[mg kg^{-1}]	SD	Extraction time [min]	Solvent need [mL]
BAM-U009	2.94	0.32	40	30	2.72	0.07	35	4
Waste wood	2.82	0.43	40	60	3.61	0.59	35	4

Derivatization with heptafluorobutyric acid anhydride resulted in the corresponding esters of both TBP and PCP and significantly enhanced chromatographic behavior of the analytes and sensitivity of determination. A comparison of the chromatograms from microwave-assisted extracts with and without derivatization is given in Fig. 3. With that derivatization procedure detection limits of 1 - 2 µg kg^{-1} sample were achieved. The extracts obtained from the ultrasonic procedure were not suitable for this derivatization step, apparently due to high levels of impurities. Clear evidence for these impurities could be obtained by scanning the background of the GC-MS signal after 16 min (data not presented). In the extracts derived by the ultrasonic procedure this background was approximately 10 times higher than the background from the microwave approach.

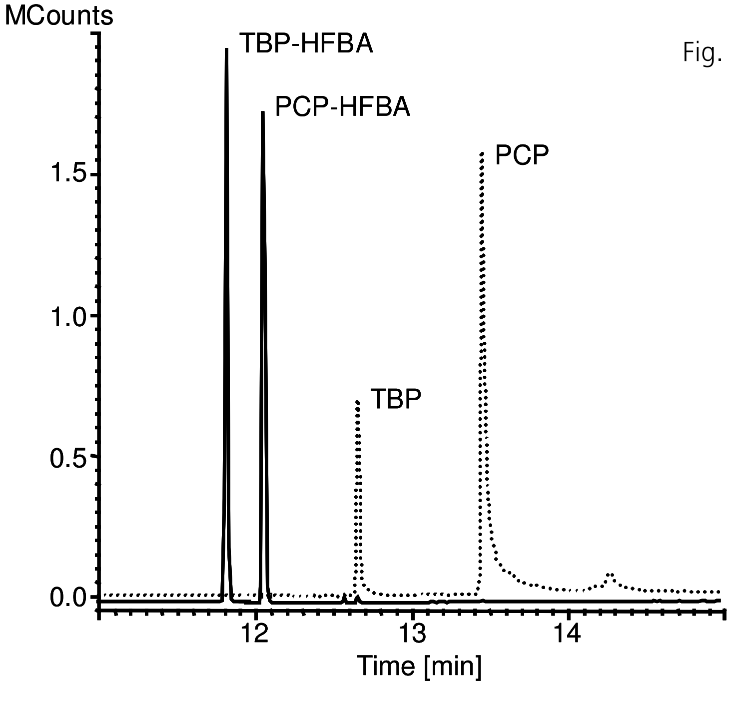

Fig. 3: GC-MS/MS chromatograms of an extract of spiked sewage sludge derived by microwave-assisted steam distillation and liquid/liquid extraction. Untreated extract (*dotted line*) showing 2,4,6-tribromophenol (TBP) and pentachlorophenol (PCP) versus extract after derivatization with heptafluoro butyric acid anhydride (HFBA). MS/MS quantification with the following *m/e* values of daughter ions: 328; 305; 307 (TBP derivative), 432; 265; 237 (PCP derivative), 330; 250; 223 (TBP), and 264; 228; 202;167 (PCP).

The results indicate for the investigated sample types that the microwave-assisted steam distillation with simultaneous liquid/liquid extraction of PCP is competitive when compared to existing methodologies. The extraction can be accomplished very easily favoring this method when compared to other microwave-assisted extraction procedures. Existing methodologies also using water as an extractant need more complex set-ups of the extraction device (*Conte* et al., 1996; *Luque-Garcia* et al., 2002) when compared to the described approach. The sample-dependent destructive effect of microwave irradiation must be considered especially in the case of labile analytes.

Conclusions

The described method using water and a small amount of an energy-transparent solvent (hexane) results in efficient extraction of pentachlorophenol from soils and organic samples. With this approach, dissociation of PCP in different media can be easily diminished by adjusting the pH of the applied water and equilibrating this sample suspension. Thus, phenolate in the samples is converted into the steam-volatile phenol and extraction losses due to formation of the hexane-insoluble phenolate can be ruled out. Spontaneous superheating of the intrinsic moisture of the fresh and swelled samples under microwave irradiation facilitates loosening the analytes from the matrix. The evolving steam transports PCP from the matrix to the surrounding solvent. After irradiation, the condensed water presumably provides a boundary layer between extract and matrix avoiding any further contact of PCP with and re-partitioning into the sample.

The obtained extracts showed relatively low amounts of impurities, as could be proven by GC-MS. By uing the GC-MS/MS technique, matrix effects can be minimized and thus the selectivity of the whole procedure which includes derivatization is further enhanced. The time requirement of 35 min is justified, since the simultaneous elaboration of six samples with the employed system allows for improved statistical significance of the results.

With this efficient and environmentally friendly procedure, analyte losses due to sorption and volatilization are extensively ruled out by excluding or minimizing steps of transferring, filtering, and concentrating. Sample pre-treatment like drying and grinding may be skipped to further save labor costs. The described procedure requires a minimum of only one particular organic solvent. Moreover, potential for miniaturization merits further investigations. The extracts obtained are compatible with GC-MS very commonly used in many laboratories. For all investigated sample types, this method provides satisfactory recovery rates for PCP. Analyte losses occurring during longer irradiation times must be considered. The approach is currently tested for other steam-volatile compounds.

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Anhang F

Sorption behavior of nonylphenol in terrestrial soils

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Abstract

Nonylphenol (NP) as an intermediate from anaerobic degradation of widely used nonionic surfactants occurs widespread in the environment. Partition behavior of this toxic and endocrine disrupting chemical between soil and water was not examined until yet. The objective of this investigation was to quantify sorption and desorption behavior of 4-nonyl-[^{14}C]-phenol in a set of 51 soils using the batch equilibrium approach. Kinetic studies indicated apparent equilibrium within 20 h. Sorption was influenced by sorbate structure as could be shown with branched 4-nonyl-[^{14}C]-phenol and the linear 4-*n*-NP, respectively. Linear 4-*n*-NP behaves differently from the branched isomers of 4-NP. Sorption of 4-nonyl-[^{14}C]-phenol tested with five different initial concentrations resulted in linearly fitted isotherms which provided calculation of sorption partition coefficients (K_P). Desorption partition coefficients ($K_{P\text{-des}}$) revealed hysteresis independent of soil properties but decreasing with decreasing initial NP concentrations. K_P were correlated with organic carbon content of the soils yielding a log K_{OC} of 3.97.

Environ. Sci. Technol., 2002, 36, 4052-4057

Introduction

The environmental occurrence of alkylphenols (AP) such as nonylphenols (NP) is proven since the late seventies (*Sheldon* and *Hites, 1978*), and its aquatic toxicity and potential to disrupt the endocrine system was determined several times in the last two decades (*Mc Leese* et al., 1980*; Soto* et al., 1991*; Jobling* and *Sumpter,* 1993). Different environmental media like waters, sediments, sludge, biota, and air were analyzed (*Giger* et al., 1984; *Ahel* et al., 1994a; *Dachs* et al., 1999; *Sekela* et al., 1999; *van Ry* et al., 2000; *Solé* et al., 2000; *Isobe* et al., 2001; *Heemken* et al., 2001).

Within waste-water treatment the degradation of nonylphenolethoxylates (NPEO) results in an emission of NP. NP accumulates mainly in anaerobically digested sewage sludge (*Giger* et al., 1984; *Ahel* et al., 1994b; Metcalfe et al., 2001). It is widespread distributed via the application of sludge and, to a smaller extent, pesticide formulations (*Mc Leese* et al., 1980) onto agricultural land. Furthermore, NP can be introduced by atmospheric deposition onto soils (*Dachs* et al., 1999; *Vikelsøe* et al., 1999).

Partition of NP in the environment is assessed to be more than 60% in sediment, >10% in soil, and aprox. 25% in the water phase (*Nordic Council of Ministers,* 1996). Recent results on the distribution and behavior of NP in different waters and sediments revealed approx. 20% of NP was found in the particulate phase (*Isobe et al.,* 2001). However, besides the results from the monitoring of NP in different environmental media no fundamental laboratory data exist on its sorption behavior in soils or sediments.

To assess the environmental fate of any pollutant, the investigation of its sorption/partition behavior is essential. Sorptive and desorptive behavior of nonylphenol should be quantified since its enrichment in sediments and sewage sludge provides pools to release NP into the environment (*Hesselsøe* et al., 2001). Furthermore, uptake of NP by plants from sludge-amended soil depends on its bioavailability which is determined by sorptive behavior.

Nonylphenol is known to be lipophilic with reported octanol-water partition coefficients (P_{OW}) in a range of $\log P_{OW} = 3.01$ to 4.48 (*BUA,* 1988*; Ahel* and *Giger*, 1993). Regarding different $\log P_{OW} - \log K_{OC}$ (organic carbon normalized partition coefficient) correlations existing for a set of organic pollutants, moderate to high adsorption potential of this compound to the soil matrix can be expected (*Wild* and *Jones,* 1992). Nonylphenol behaves as a weak acid with a pK_a of 10.7 (*Maguire,* 1999) and ionisation under neutral to alkaline conditions probably influences its solubility and sorption to solid matrices as already determined for chlorinated phenols (*Schellenberg* et al., 1984).

Nonylphenol consists of a number of isomers with differently branched nonyl chains. Nonetheless, there are still no published data on distinctive estrogenic activity of each isomer which can be postulated to be effectuated to a large extent by different branching. Significant estrogenic activity was found for the branched octylphenol and nonylphenol isomers whereas no significant induction was seen with the two linear isomers (*Pedersen* et al., 1999).

In a work on the environmental fate of NP a group of NP isomers was assumed to degrade more slowly than other isomers (*Hawrelak* et al., 1999). Different logK_{OC} for the linear and the branched isomers, respectively, were recently expected (*Hesselsøe* et al., 2001). Differing estimated log P_{OW}-values differing from 4.78 to 5.72 for singular proposed structures of some distinct isomers of 4-nonylphenol indicate that bioconcentration of isomers will likely differ (*Gundersen,* 2001).

The present paper reports the sorption behavior of 4-nonyl-[^{14}C]-phenol considering adsorption and desorption kinetics at different concentration levels. Some isomer-specific phenomena are also illustrated. Partition coefficients for the ad- and desorption of 4-nonyl-[^{14}C]-phenol were obtained for a large set of soils.

Experimental Section

Sorbents

Soil material was taken from field sites located in different parts of Germany. This pool of soils included mainly agricultural soils exhibiting pH values from 5.2 to 7.8. In addition, some "extreme" soils with lower pH derived from forests were considered (Figure 1). Organic matter content was determined as follows: Carbonate-free ground soil samples where weighed (approx. 20 mg) into tin capsules. The samples were burned and detected with a thermal conductivity detector by a carbon/nitrogen analyser (Carlo-Erba, NA 1500, Milan, Italy). Soil pH was measured in a 1:2.5 (w/w) mixture of soil with $CaCl_2$ solution (0.01 mol L^{-1}).

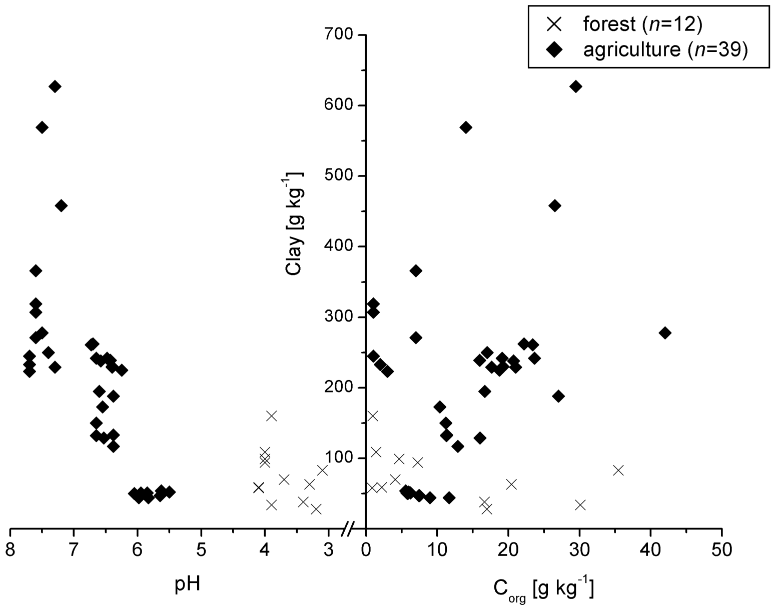

Fig. 1: Properties of examined soil samples (*n*=51), C_{org}=organic carbon.

Sorbates and Chemicals

Due to the relatively low water solubility and high surface affinity of alkylphenols (*Jobst,* 1987*; Johnson* et al., 1998) and thus limited suitability of classical analytical techniques, experiments were carried out with radio labeled, branched 4-nonylphenol. The substance was synthesized according to a method of *Ekelund* et al. (1990): A mixture of isomers of nonene was added to phenol which was spiked with uniformly ^{14}C-labeled phenol (12.2 mCi mmol^{-1}, International Isotopes Munich, Germany) in a ratio of 25 : 1 under acidic conditions to produce labeled 4-nonylphenol. Non labeled linear 4-*n*-NP (Riedel de Haën, Seelze, Germany) was added within this synthesis. The product was purified by preparative normal-phase HPLC (mobile phase: dichloromethane/methanol 95%/5%; column: LiChroSphere, Si60, 10 µm particle size, 20 mm I. D., 250 mm length; MZ-Analysentechnik, Mainz, Germany) to separate remaining phenol and other reaction products. That mixture should provide to assess sorption behavior of the different isomers by means of GC-MS analysis. Specific radioactivity of the product 4-nonyl-[^{14}C]-phenol was 594 µCi mmol^{-1}.

NP solutions were prepared as follows: 1-5 µL of the labeled NP-mixture was dissolved in 5 mL acetone (Riedel de Haën, Pestanal®). This NP-solution was filled up to 1,000 mL with 0.01 M $CaCl_2$ (Riedel de Haën, p.a.)-aqueous solution, resulting in 5 concentration levels given in Table 1.

Table 1: Concentrations of 4-nonylphenol [mg L^{-1}] in 0.01 M $CaCl_2$-solution applied within the sorption experiments.

4-nonyl-[^{14}C]-phenol	4-nonyl-[^{12}C]-phenol	4-*n*-nonyl-[^{12}C]-phenol
0.15	3.75	0.29
0.30	7.5	0.59
0.45	11.25	0.88
0.60	15.0	1.17
0.75	18.75	1.46

Octanol/water partition coefficient

To further characterize the test substance, $\log P_{OW}$ was determined by the shake flask method according to OECD guideline 107 (*OECD,* 1995). After the experiments, activity in both of the separated phases was quantified by liquid scintillation counting (see below).

Sorption experiments

Sorption experiments were carried out in conformity to OECD Guideline 106 (*OECD,* 1999). 3 g of air dried and sieved (<2 mm particle size) soil material was filled in 30 mL Pyrex® glass vessels and 15 mL NP-solution was added to result in a soil : liquid phase ratio of 1 : 5 (w/w). The vessels were closed with PTFE-lined plastic caps. Equilibrium conditions were established by shaking on a laboratory shaker (175 rpm, Bühler KS 15, Hechingen, Germany). Assuming equilibration, the two phases were separated by centrifugation of the glass vessels at approx. 1,500x g for 20 minutes.

Sorption kinetics were studied by a parallel approach. After shaking over distinctive different periods of time (from 1 min up to 6 d) three vessels of 45 replicates were centrifuged and their supernatants quantified for ^{14}C activity. The time periods were: 1; 3; 10; 30; 45 min; 1; 2; 5; 10; 20; 30; 50; 75; 100; 150 h. For comparison, the kinetic experiment was performed without shaking the soil suspensions simulating a static system.

To assess the influence of degradation on decreasing solute concentrations within the long-term kinetic experiment, two soils were chosen to be sterilized by χ-irradiation (1.03 Mrad).

Sorption isotherms were determined with the above described method by shaking until apparent equilibrium was reached. Each soil was treated with five solutions differing in the NP concentration level (Table 1).

Subsequently to adsorption experiments, desorption was examined. Thereupon, 80% of the liquid phase was replaced by NP-free 0.01 M $CaCl_2$-solution. The glass vessels were shaken for 22 h, allowing sorbed NP to move from the solid to the liquid phase. Likewise with the adsorption kinetic experiment, desorption kinetic was studied with the parallel approach.

Desorption isotherms providing $K_{P\text{-des}}$ were obtained by including all five different concentration levels of NP used within the adsorption experiments.

To examine exhaustive desorption, up to three desorption steps were employed.

All sorption experiments were carried out with at least three replicates.

Radio analysis

Aliquots of the liquid supernatants remaining after centrifugation were mixed with scintillation cocktail (Rothiszint ecoplus®). The activity of ^{14}C of the liquid sample was measured by liquid scintillation analysis (Packard Tri-Carb 2700TR, Downers Grove, USA). 2 minutes of scintillation counting were sufficient to minimize statistical error (RSD < 5%) and provided sensitivity of 0.2 µg L^{-1}.

Chemical analysis

GC-MS (HP 5890 series II, directly coupled to MS engine HP 5989A, Palo Alto, CA, USA, equipped with a DB-XLB capillary column, J & W Scientific, Folsom CA, USA) analyses were used to confirm the quality of the used synthesized product 4-nonyl-[^{14}C]-phenol and provided qualitative information on the liquid samples of the sorption experiments.

The GC oven program was as follows: Initial temperature 80°C, increased at 30°C min^{-1} to 130°C, up to 180°C at 10°C min^{-1}, final temperature of 240°C achieved with a rate of 3°C min^{-1} and held for 5 min, total analysis time: 32 min). Masses of characteristic molecular fragments were determined in distinct time windows given in Figure 2. A qualitative comparison of the used mixture of synthesized 4-nonyl-[^{14}C]-phenol and the supplemented 4-*n*-nonylphenol is given in Figure 2.

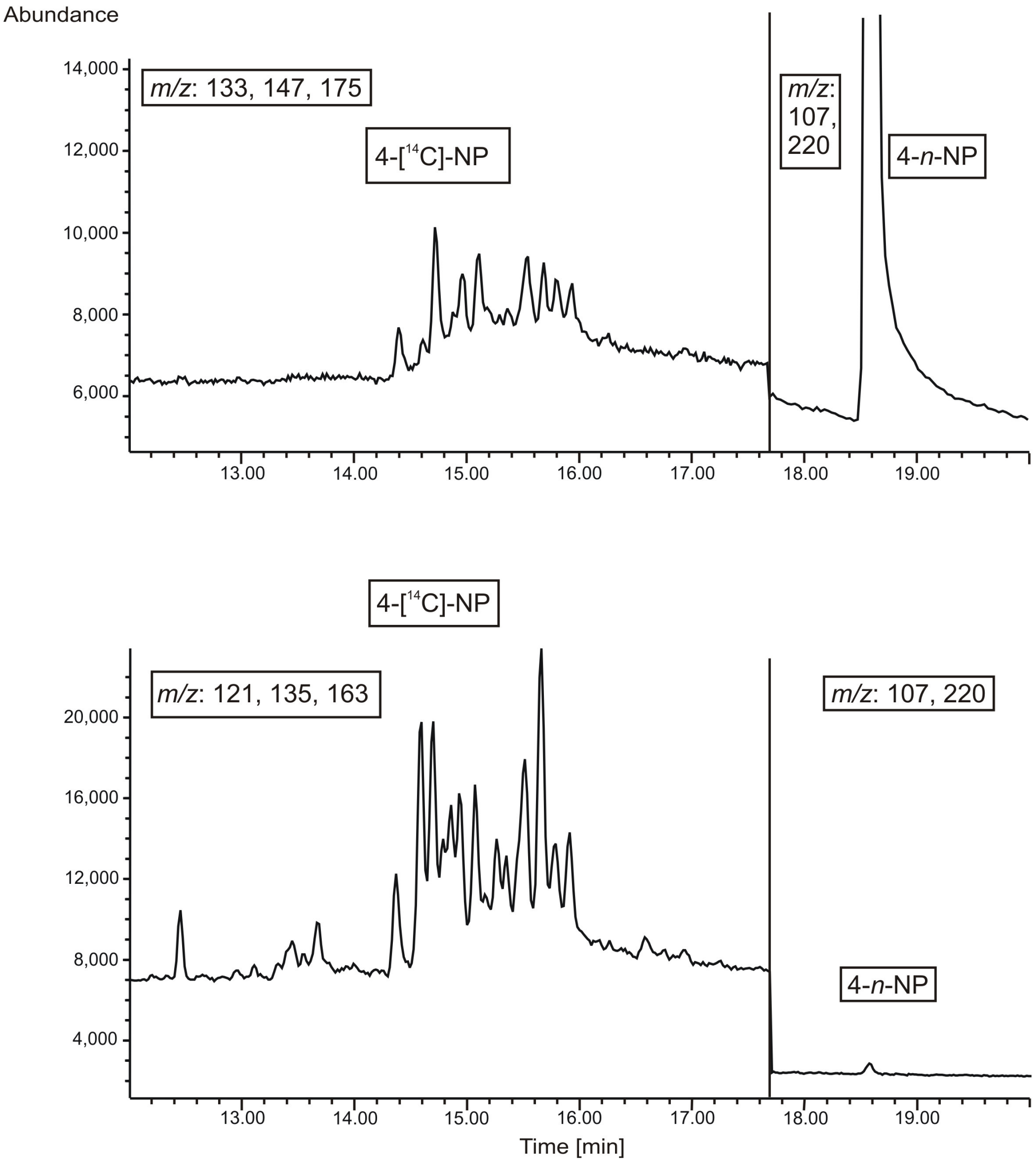

Fig. 2: GC-MS chromatograms of nonylphenol compounds. Total ion current (*m/z:* 133; 147; 175 and 107; 220) of 4-nonyl-[^{14}C]-phenol and 4-*n*-nonylphenol, respectively (top), compared to total ion current (*m/z:* 121; 135; 163 and 107; 220) of commercially available standard of 4-nonylphenol (bottom).

By means of solid phase microextraction (SPME®), NP was extracted solventless from the aqueous phase. The SPME® fiber coatings were polyacrylate of 85 µm film thickness (Supelco, Bellefonte, PA, USA). After conditioning and verifying procedure blanks, 5 mL aliquots of the supernatants and NP-solution were extracted by immersing the fiber for 10 min without stirring at room temperature. Fibers were thermally desorbed (4 min, 310°C) within the GC injection port.

Data analysis

The dimensionless octanol/water partition coefficient (P_{OW}) was calculated by the ratio of the equilibrium concentrations of 4-nonylphenol in both phases:

$$P_{OW} = \frac{C_O}{C_W} \tag{1}$$

where C_O is the 4-nonylphenol concentration in n-octanol [µg L^{-1}], and C_W is the concentration of 4-nonylphenol in water [µg L^{-1}].

Losses of nonylphenol mass from the aqueous solution during partitioning NP between soil and solution was assumed to be sorbed to the soil matrix:

$$q_S = (C_0 - C_t) \cdot \frac{V_A}{W_S} \tag{2}$$

where q_S is the mass of NP sorbed to soil [µg g^{-1}], C_0 is the initial concentration of NP [µg mL^{-1}], C_t is the aqueous phase concentration of NP at the end of the sorption experiment [µg mL^{-1}], V_A is the volume of the aqueous phase [mL], and W_S is the mass of soil [g].

Linear isotherms were assumed to model sorption of NP to soil, with the following equilibrium expression:

$$q_S = K_P \cdot C_t \tag{3}$$

where K_P is the equilibrium partition coefficient [mL g^{-1}].

Desorption from the solid phase during the *i*th desorption step is expressed by the following equation (*Kan* et al., 1994):

$$\Delta q^{i}_{desorbed} = \left[C_i - C_{i-1} \cdot (1 - r)\right] \cdot \frac{V_A}{W_S} \tag{4}$$

where $\Delta q^{i}_{desorbed}$ is the change in the solid phase concentration [µg g^{-1}] during the *i*th desorption step, $C_i - C_{i-1}$ are the solution phase solute concentrations at the end of the *i*th and (i – 1)th desorption steps, and *r* (0.8) is the fraction of the supernatant replaced at each dilution.

The linear model (eq. 3) was applied for the desorption isotherms resulting in the partition coefficient $K_{P\text{-}des}$ after each desorption step.

Desorption hysteresis coefficient was determined via the ratio between desorption and sorption partition coefficients, modified after *Xiangke* et al. (2000):

$$H = \frac{K_{P-des} - K_P}{K_{P-des}} \tag{5}$$

Assuming soil organic carbon is the most important factor determining interaction of NP with soil, the individual partition coefficients for each soil were related to the organic carbon content of the respective soils by the equation given by (*Karickhoff* et al., 1979):

$$K_p = f_{OC} \cdot K_{OC} \tag{6}$$

where f_{OC} is the weight fraction of organic carbon in soil.

Results and discussion

Kinetic studies

Under the batch equilibrium conditions, fast initial sorption from the liquid to the solid phase was observed within the first hour of equilibration (Figure 3). The following slow increase in sorbed concentration can be ascribed to the movement of the chemical from external sites to internal sites on the insoluble organic matter by intra-organic matter diffusion. This intra-organic matter diffusion was assumed to be the rate limiting process and is already described in the literature (*Wu* and *Gschwend,* 1986).

Much slower sorption rates were found in unshaken soil, supporting that sorption of organic pollutants is limited by diffusion. Under these conditions, less soil surface is available for sorption processes in comparison to a shaken soil. Considering this static model, the partition coefficients obtained by the batch equilibrium method can hardly be achieved under natural conditions where additional processes like degradation take place, i. e. in soil/water and sediment-river water systems. However, the analyte will degrade to some extent within longer time periods and under aerobic conditions (*Marcomini* et al., 1989). Thus, increasing differences between sterilized and non sterilized soil after 75 h may account for microbial degradation. As recognizable in Figure 3, sorption equilibrium for NP under batch equilibrium conditions apparently was approximated after 20 h of elapsed time. Therefore, assuming equilibrium-near conditions with merely little losses due to degradation, and for laboratory convenience, 22 h of equilibration time was fixed for generating partition coefficients.

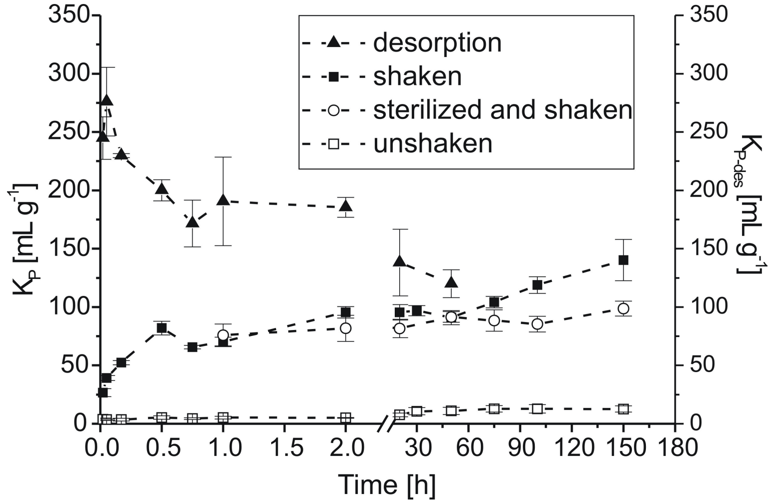

Fig. 3: Example of sorption/desorption kinetics of 4-nonyl-[^{14}C]-phenol in soil 27. Error bars represent standard deviations (*n*=3).

Desorption kinetics illustrated in Figure 3, imply that sorption and desorption of NP consists of a labile desorption compartment and an entrapped compartment as proposed for neutral hydrocarbons (*Kan* et al., 1998). It is obvious that sorption was not completely reversible and the build up of more stable chemical bonding to the organic matter of the soil may be a reason for this observation.

Equilibrium partition coefficients and their relation to soil properties

Octanol-water partition coefficient

Partition of NP between octanol and water resulted in a P_{OW} of 9312.2 (coefficient of variation 12.81%). The log P_{OW} of 3.97 is within a range given in the literature obtained by the shake flask method (*BUA, 1988; Ahel* and *Giger,* 1993) and by a high performance liquid chromatography (HPLC) method (*Mc Leese* et al., 1981), respectively.

Soil-water partition coefficients

Sorption experiments resulted in sorption isotherms which are exemplarily illustrated in Figure 4. The results fitted to the linear regression model given in Table 2, representing partitioning of NP between soil and water. Considering NP as hydrophobic substance in a sufficiently dilute system the linear fit should describe its partition behavior appropriately (*Karickhoff,* 1981).

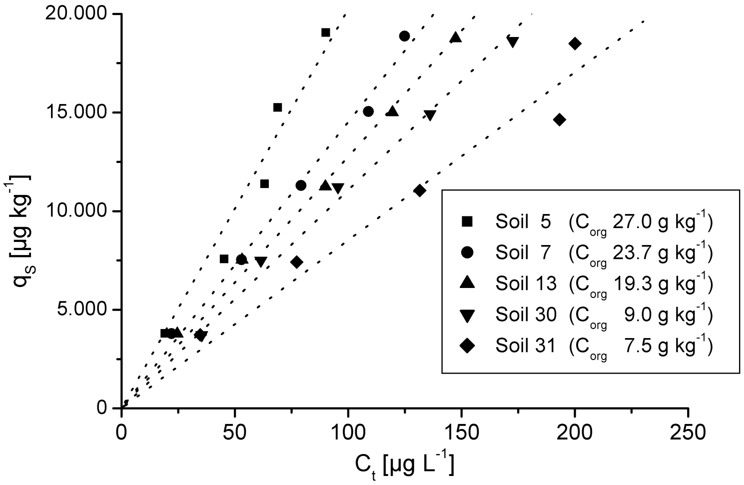

Fig. 4: Sorption isotherms for 4-nonyl-[^{14}C]-phenol and selected soils.

The desorption partition coefficients ($K_{P\text{-des}}$) were almost always higher than the sorption coefficients, indicating more or less hysteresis (H). With Figure 5, the degree of hysteresis can be estimated exemplarily. The extent of hysteresis was greater as the equilibrium starting point concentration was higher; this phenomenon was already observed in sorption experiments with the herbicide imazamethabenz (*Cartón* et al., 1997).

Table 2: Parameters of the sorption experiments obtained from linearly fitted sorption isotherms for the different soils (K_P: partition coefficient; $K_{P\text{-des}}$: desorption partition coefficient; r^2: coefficient of determination; H: hysteresis factor).

Sample	**K_P**	**r^2**	**$K_{P\text{-des}}$**	**r^2**	**H**
Soil1	215.65	1.00	266.27	1.00	0.19
Soil2	321.78	1.00	856.51	0.99	0.62
Soil3	279.48	0.99	627.28	0.86	0.55
Soil4	138.74	0.91	255.50	0.99	0.46
Soil5	202.17	0.96	293.83	0.95	0.31
Soil6	182.26	0.99	61.93	0.24	-1.94*
Soil7	145.62	0.99	276.60	0.97	0.47
Soil8	156.26	0.99	225.69	0.96	0.31
Soil9	141.62	0.98	287.73	0.94	0.51
Soil10	137.84	0.86	237.27	0.93	0.42
Soil11	158.79	1.00	251.66	0.94	0.37
Soil12	205.98	1.00	466.06	0.99	0.56
Soil13	127.68	1.00	215.76	0.95	0.41
Soil14	133.36	1.00	134.46	0.18	0.01*
Soil15	134.75	0.96	279.89	0.95	0.52
Soil16	122.01	0.97	115.40	0.74	-0.06*
Soil17	49.61	0.98	82.45	0.96	0.40
Soil18	178.77	0.90	68.77	0.16	-1.60*
Soil19	136.30	0.92	246.49	0.98	0.45
Soil20	153.59	0.99	313.73	0.97	0.51
Soil21	141.43	0.98	241.48	0.97	0.41
Soil22	112.90	0.99	191.48	0.93	0.41
Soil23	91.07	0.99	134.06	0.89	0.32
Soil24	141.30	0.96	207.60	0.94	0.32
Soil25	124.28	0.99	190.58	0.99	0.35
Soil26	117.90	0.98	160.48	0.93	0.27
Soil27	104.22	0.97	147.21	0.89	0.29
Soil28	71.32	0.90	130.70	0.94	0.45
Soil29	77.15	0.93	123.25	0.88	0.37
Soil30	110.59	0.99	123.26	0.96	0.10
Soil31	85.86	0.96	146.88	0.99	0.42
Soil32	76.16	0.95	134.55	0.98	0.43
Soil33	70.28	0.99	181.91	0.91	0.61
Soil34	56.72	0.99	101.06	0.94	0.44
Soil35	39.24	0.98	69.23	0.96	0.43
Soil36	62.15	0.96	116.04	0.97	0.46
Soil37	59.07	0.84	111.76	0.87	0.47
Soil38	54.64	0.81	96.85	0.99	0.44
Soil39	58.49	0.90	110.00	0.88	0.47
Soil40	50.52	0.85	103.94	0.69	0.51
Soil41	38.45	0.97	89.32	1.00	0.57
Soil42	42.52	0.98	101.52	1.00	0.58
Soil43	16.25	0.99	28.39	0.93	0.43
Soil44	15.67	0.97	22.53	0.81	0.30
Soil45	29.14	0.86	137.73	0.84	0.79
Soil46	15.88	0.97	29.64	0.74	0.46
Soil47	21.96	0.96	42.37	0.97	0.48
Soil48	17.24	0.94	30.25	0.89	0.43
Soil49	24.80	1.00	40.56	0.92	0.39
Soil50	13.05	0.95	78.46	0.85	0.83*
Soil51	8.52	0.96	16.23	0.98	0.48

* Outlier defined as value deviating more than 3s from mean.

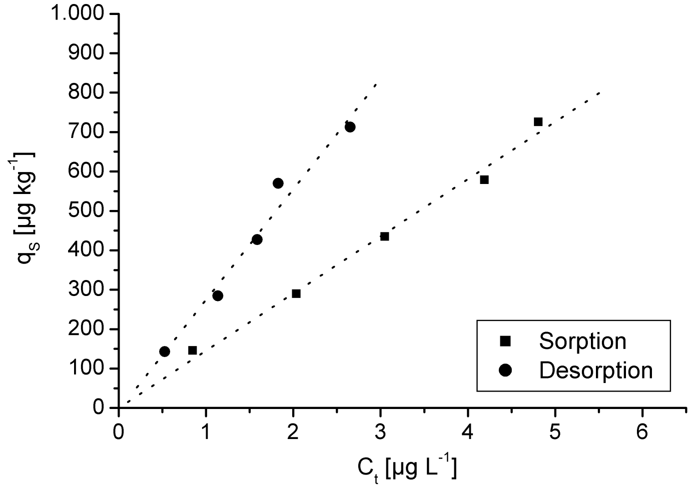

Fig. 5: Example of sorption/desorption isotherms of 4-nonyl-$[^{14}C]$-phenol in soil 7.

In Figure 6, adsorption and desorption of 4-NP for one distinctive soil/suspension system in the three-step desorption experiment are plotted. The desorption paths are clearly different from the adsorption path, signifying again hysteresis. However, part of the initially sorbed NP was released under the given experimental conditions, indicating availability of NP for transport processes.

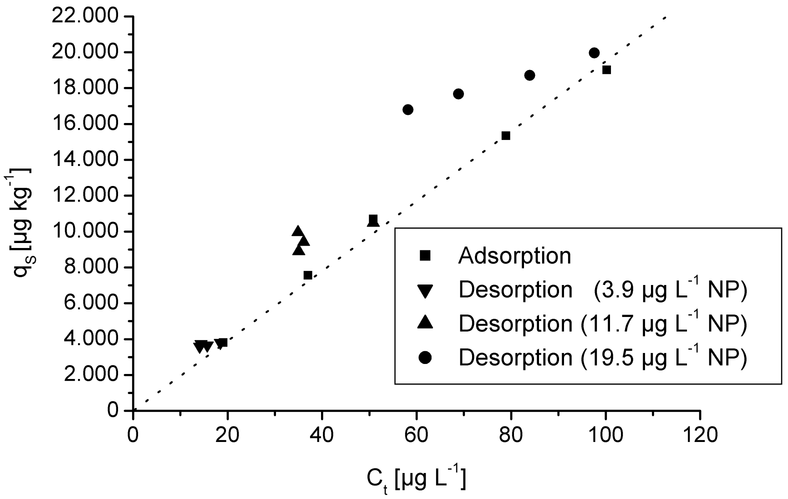

Fig. 6: Example of sorption/desorption isotherms of 4-nonyl-$[^{14}C]$-phenol in soil 5 after three consecutive desorption steps.

Figure 7 illustrates the relation of NP partition coefficients to the content of organic carbon in soil with an r^2 of 0.82. Standardization of NP-partitioning to the organic carbon fraction (see eq 6) seems to be applicable here for the soil samples included in the experiments (n=51) and resulted in a mean K_{OC} of 9285.4 (CV=41.8%). The calculated log K_{OC} of 3.97 differs from partition coefficients reported in the literature. Those log K_{OC} are "in situ" partition coefficients obtained from aquatic systems considering sediment and suspended particles as solid phase of the system, and ranging from 4.7 to 5.9 (*Sekela* et al., 1999; *Isobe* et al., 2001; *Heemken* et al., 2001; *Ferguson* et al., 2001). The "in situ" coefficients are hardly to compare with our laboratory data: Concentrations of sorbate and the ratio between solid to liquid phase in our study were completely different compared to those in the literature. The mean log K_{OC} obtained in the study presented here was derived by minimizing other processes like volatilization, degradation, and chemical bonding, summarized as "aging" which should influence significantly the "in situ" partition coefficients. Furthermore, qualitative differences of the organic matter between river sediments and soil may exert great influence on the sorption strength.

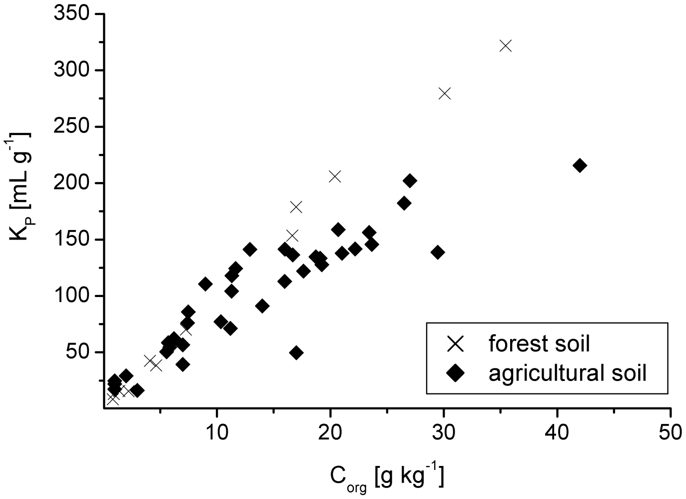

Fig. 7: Relation of NP partition coefficients to the content of organic carbon in the investigated soils.

Figure 7 shows some variation within K_P/C_{org} relation: Deviating data points may have been resulted from differing proton activity in some soil samples. As given in Figure 1, we performed experiments with soil material of both relatively high and low pH, respectively. In the investigated natural soils whose pH-values are well below the pK_a of 10.7 for NP (*Maguire,* 1999), contribution of the sorption of the deprotonated specie should be neglected as (*Schellenberg* et al., 1984) already determined for chlorinated phenols with lower pK_a-values. Nevertheless, the degree of deprotonation of NP can take place to some extent in the soils with higher pH, and sorption of the respective phenolates is expected to be significantly lower as already shown for chlorinated phenols (*Lagas,* 1988).

However, pH seems to be a factor influencing NP's affinity to soil material and may be influenced by land use and soil management. Nevertheless, in agricultural soils and depending on texture, pH should be adjusted to optimize plant nutrition.

Apart from the soil parameters pH and soil organic carbon, the concentration of dissolved organic carbon (DOC) may influence the partition behavior of NP. DOC can act as a carrier and cosolvent for hydrophobic substances (*Chiou* et al., 1986) and is applied via municipal wastes i. e. sewage sludge.

Isomer-specific considerations

Figure 8 shows chromatograms of 4-nonyl-[^{14}C]-phenol and 4-*n*-nonylphenol in the liquid phase applied to soil changed due to sorption.

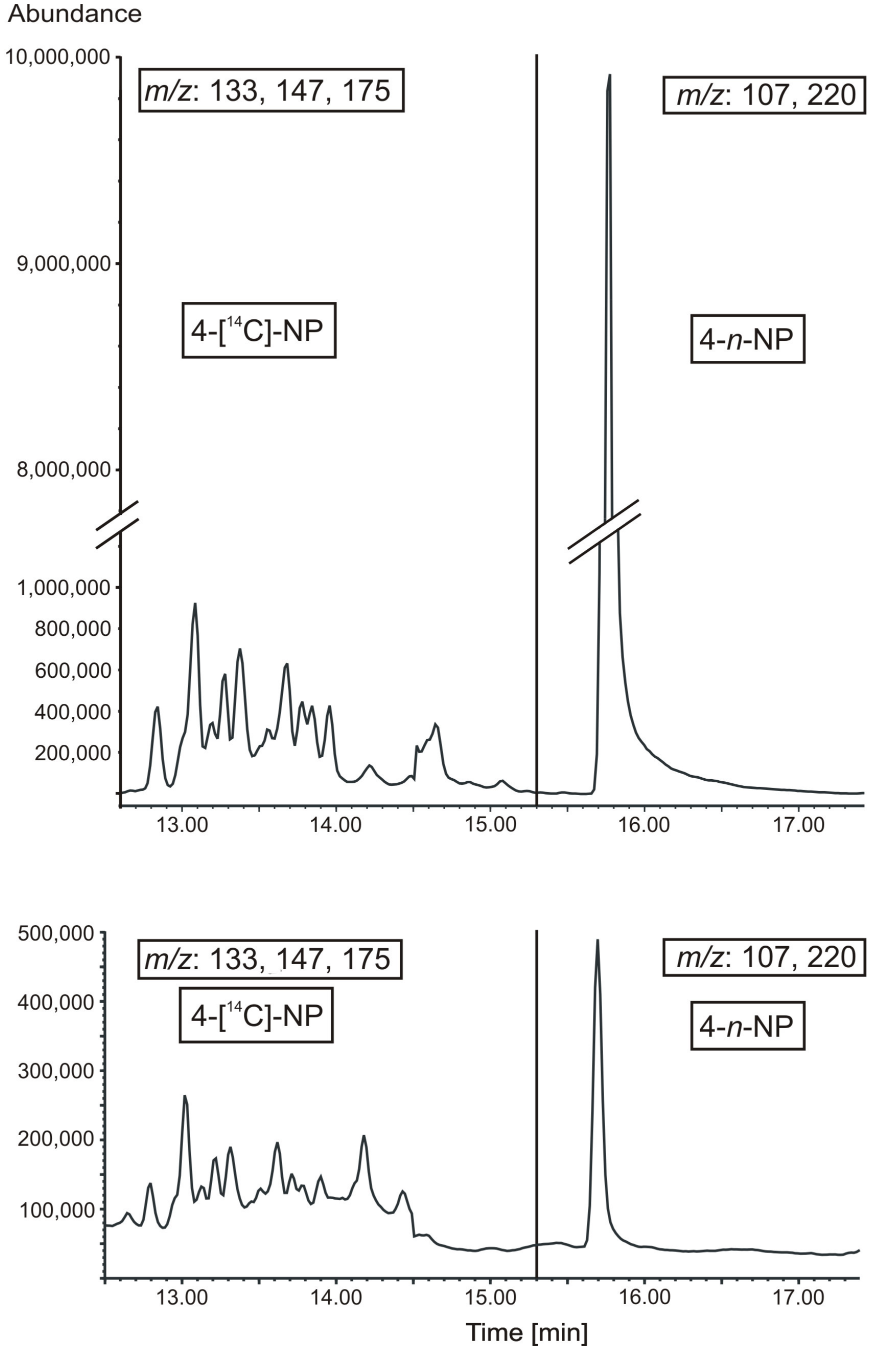

Fig. 8: GC-MS chromatograms of nonylphenol compounds extracted by SPME from the liquid phase before (top) and after 1 h shaking with a sandy soil 39 (bottom). Total ion current (*m/z:* 133; 147; 175 and 107; 220) of 4-nonyl-[^{14}C]-phenol and 4-*n*-nonylphenol, respectively.

Sorption was different for the branched 4-nonyl-[^{14}C]-phenol isomers and the linear 4-*n*-NP, respectively. With the kinetic experiment (Figure 9), differing behavior of the isomers became evident: The initial ratio between peak areas of 4-nonyl-[^{14}C]-phenol and 4-*n*-NP in the liquid phase was 0.6. This ratio increased to a value of approximately 6 after 50 h in the case of soil 25, indicating stronger partitioning into the organic phase of 4-*n*-NP when compared to 4-nonyl-[^{14}C]-phenol. After 75 h, the ratios decreased to values of approx. 6 and 1 for soil 25 and soil 39, respectively.

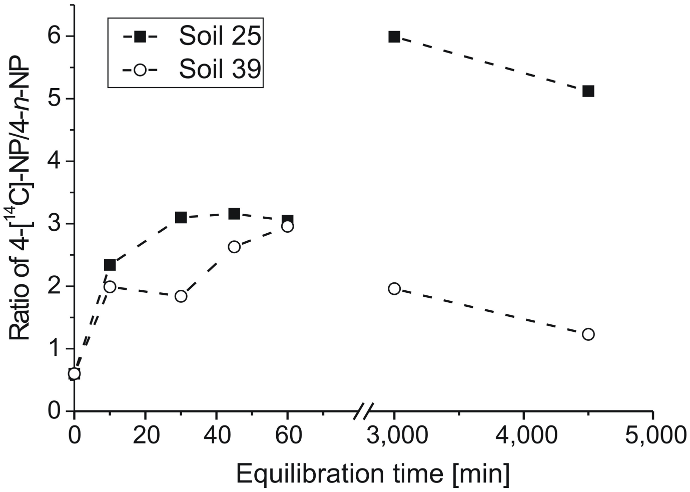

Fig. 9: Ratios of peak areas of 4-nonyl-[^{14}C]-phenol and 4-*n*-NP after SPME-GC-MS of the liquid phase, depending on the duration of shaking, for two selected soils.

The resulting mean logK_{OC} determined with the two soils after 50 h shaking were 4.0 and 4.9 for 4-nonyl-[^{14}C]-phenol and 4-*n*-NP, respectively.

The different isomers of 4-NP behave differently in soil, as could be demonstrated under non equilibrium conditions by different partition behavior of 4-nonyl-[^{14}C]-phenol and 4-*n*-NP, respectively. Thus, data obtained from experiments with the linear NP must be critically reconsidered when it was used as a "model" simulating the behavior of the branched isomers of 4-NP which in fact occurs in the environment. Branching of the isomers of 4-NP probably hinders diffusion within aggregates and organic matter and limits specific interaction with the soil matrix. This will result in lower partition coefficients when compared to them of 4-*n*-NP. To elucidate the environmental fate of NP, the differing behavior of its various isomers should be respected.

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Anhang G

Estrogenic activity of different nonylphenol-fractions assessed by the E-Screen-Assay

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Chemosphere, eingereicht

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Abstract

Industrial chemicals are ubiquitous in the environment. For a number of these chemicals, e.g. nonylphenol (NP), an estrogenic activity could be shown. NP is a mixture of several isomers, but little is known about the estrogenic activity of the single isomers. Differences in their activity as well as in their environmental behavior are likely.

To determine the estrogenic activity of different fractions of nonylphenol which were obtained by preparative GC, the E-Screen-Assay was used. The endpoint of this in vitro assay is the estrogen-dependent increase of proliferation of the human breast cancer cell line MCF-7 in comparison to the hormone-free control.

Six fractions of technical nonylphenol plus the technical mixture were screened in the E-Screen-Assay. Slight but not statistically significant differences in the estrogenic activity between the individual fractions in comparison to the technical mixture were detected.

Chemosphere, eingereicht

Introduction

Alkylphenols such as nonylphenol (NP) are toxic for aquatic organisms and disrupt the endocrine system (*Soto* et al., 1991; *Jobling* and *Sumpter*, 1993). Recently, NP was found to be ubiquitous in food (*Günther* et al., 2002).

Technical NP generally is produced by the alkylation of phenol with propylene. This reaction produces many isomers due to possible *ortho* or *para* positions of the hydrocarbon chain joined to the phenol ring and various possible positions of the double bond of propylene along the hydrocarbon chain. Some attempts were made to analytically separate the different isomers by sophisticated separation techniques and tentative structures were obtained by means of spectroscopic methods including GC-MS and NMR (*Bhatt* et al., 1992; *He* and *Lee*, 1996; *Wheeler* et al., 1997). Presently, individual standards are not available to confirm the proposed structures.

To assess the estrogenic activity of natural and synthetic substances, the E-Screen Assay has proven successful several times (i. e. *Soto* et al., 1995; *Blom* et. al., 1998). This cell culture bioassay measuring the cell proliferation of human breast cancer MCF-7 cells in response to estrogen, gives quantitative estimates of test samples and is applicable for environmental samples (*Körner* et al., 1999).

The comparison of some alkylphenols exhibiting different structural features with estrogen suggested that some isomers may be more effective endocrine disruptors than others: *Routledge* and *Sumpter* (1997) determined that optimal estrogenic activity requires a single tertiary branched alkyl group of six to eight carbons located at the *para* position on an otherwise unhindered phenol ring. Significant estrogenic activity was found in an *in-vivo* experiment for the branched octylphenol and technical nonylphenol whereas no significant induction was seen with the two linear isomers 4-*n*-octylphenol and 4-*n*-nonylphenol (Pedersen et al., 1999). Furthermore, different environmental behaviour such as bioconcentration, adsorption to soil and degradation, for the different isomers is assumed (*Hawrelak* et al., 1999; *Bennett* and *Metcalfe*, 2000; *Gundersen*, 2001; *Düring* et al., 2002). *Lalah* et al. (2001) performed synthesis of one pure nonylphenol isomer, 4-(3’, 6’-dimethyl-3’-heptyl)phenol: Its physicochemical properties were found to differ considerably from those of the technical mixture. Nevertheless, both toxicity and estrogenic activity of technical NP usually was determined considering it as a single compound.

Yamashita et al. (1999) fractionated technical NP into six fractions using capillary GC with repeated large-volume injections and found, based on luciferase activity, different estrogenic potency for the considered fractions. However, single individual isomers of NP have not been separated by nondestructive methods until now.

Detailed studies of the different isomers are needed in terms of both industrial production and environmental protection. With the present paper, an approach is given to fractionate technical NP by means of preparative GC and to quantify estrogenic activity of the fractions with the E-Screen-Assay.

Materials and Methods

Chemicals

Unless otherwise noted, all chemicals were obtained from Merck, Darmstadt, Germany, and Sigma, Taufkirchen, Germany. Cell culture materials were from Biochrom, Berlin, Germany or Sigma, Taufkirchen, unless otherwise noted.

Technical NP kindly was provided by Sasol (Marl, Germany).

Fractionation of Nonylphenol

Preparative separation was performed on a Carlo Erba Fractovap 2450 GC (column: I. D. 6 mm, 2 m length, 5% OV-101, VolaSpher A2, 60-80 mesh; carrier gas: helium at 60 mL min^{-1}; fraction collector: Carlo Erba Mod. 210, cooled). Technical NP was dissolved in *n*-hexane to 0.7 g mL^{-1} and an aliquot of 70 µL (equal to 50 mg of technical NP) was injected. GC oven temperature was programmed from 150-220°C with a rate of 2°C min^{-1}. Aliquots of the six fractions were characterized by means of capillary GC/MS (GC: HP 5890 Series II, directly coupled to a MS engine HP 5989A), equipped with a cold injection system (KAS 3, Gerstel, Muehlheim, Germany) and a DB-XLB (Agilent, Palo Alto, USA) column of 30 m length, 0.25 mm I. D., and 25 µm film thickness. The analytes were determined on the basis of masses of characteristic molecular fragments (*m/e* 121, 135, 163).

All nonylphenol-fractions and technical NP were diluted in ethanol p.a. (Merck).

E-Screen-Assay

Details of the E-Screen-Assay including evaluation (SRB-Assay) and coincubation are described elsewhere (*Skehan* et al. 1990, *Soto* et al. 1995, *Körner* et al. 1998, *Bitsch* et al. 2001). Before beginning the assay the stock solutions of the NP-fractions were diluted with experimental medium. In brief, MCF-7 cells were cultivated in an incubator at 37°C, 5% CO_2 and 95% relative humidity.

Cells were passaged and seeded with culture medium in 24-well-plates at a density of 10.000 cells per well. The following day, medium was removed and experimental medium containing the test substances at equal concentrations was added. The maximal tested concentration of each fraction was 0.0012 g L^{-1}. Each fraction was tested in five concentrations following a dilution row of 1:10. Each concentration was tested in 4 wells per plate. Additionally, each plate contained 4 wells with ethanol 0.1% (v/v) as the negative control. In each assay, one plate containing 17β-estradiol serving as the positive control was tested in five different concentrations (10^{-13} to 10^{-9} Mol L^{-1}). The cells were incubated for the following 5 days. Then the assay was stopped by removing the medium.

Consecutively, cells were fixed in 10% (w/v) trichloroacetic acid and subsequently stained with 250 µl of a 0.4% (w/v) sulforhodamine B-solution (dissolved in 1% acetic acid) per well. After 10 minutes of incubation at room temperature the cells were washed and dried. The dye was then removed from the cells with 500 µL 0.01 molar TRIS buffer (pH 10.5) per well.

Photometric determination of the total protein content was performed at a wavelength of 550 nm using a microtiter photometer (Anthos, Krefeld, Germany). For technical reasons, a reference wavelength of 620 nm was used rather than 630 nm as used by *Körner* et al. (1998).

To test for the receptor-mediated increase of the rate of proliferation, cells were coincubated with 1 µMol L^{-1} of the anti-estrogen tamoxifen. The experimental conditions of coincubation were the same as those used in the normal E-Screen assay.

Evaluation of the assays

Endpoint of the E-Screen Assay is the increase of the rate of proliferation in comparison to the hormone free control. Determination of efficacy compared to 17β-estradiol (E2) was calculated according to the literature (*Soto* et al. 1995; *Körner* et al. 1998). The following parameters were calculated:

Proliferative Effect PE:

The PE is the ratio of the largest mean cell number that was obtained with the test substance or E2 to that of the negative control

$$\mathrm{PE} = \frac{\text{cell number (test substance, or E2)}}{\text{cell number (negative control)}}, \qquad (1)$$

therefore the negative control always has a PE-value of 1.

Relative Proliferative Effect RPE:

The RPE is a comparison of the maximal proliferation with the test substance to that of E2.

The RPE indicates whether a substance is a full or partial agonist to the estrogen receptor. For the sake of clarity it is expressed in percent.

$$\mathrm{RPE}(\%) = \frac{\mathrm{PE} - 1\left(\text{test substance}\right)}{\mathrm{PE} - 1\left(\mathrm{E2}\right)} \times 100, \qquad (2)$$

whereby the “1” is derived from the negative control (see above).

Statistical analysis

For statistical analyses, SPSS 10.0 for Windows 98 was used. To determine significant deviations from the negative control, a one-way ANOVA, followed by a paired t-test was used. A p-value < 0,01 was regarded as statistically significant. To determine differences between coincubation and single incubation, a F-test (Microsoft Excel 97) following a t-test (Microsoft Excel 97) was performed. A p-value < 0,05 was regarded as statistically significant.

Results and Discussion

Chromatographic characterization of the NP fractions is given in Figure 1.

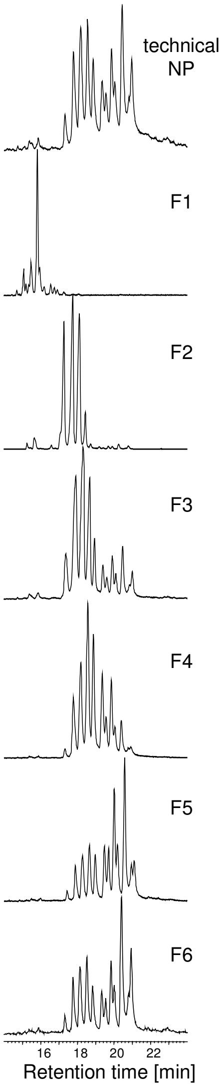

Fig. 1: Technical NP (top) and the six fractions (F1 – F6) presented as total ion chromatograms (*m/e:* 121; 135; 163).

A significant separation of F1 from the other fractions was achieved, as F1 exhibits a distinct group of peaks which do not significantly occur in the other fractions. The considerable shorter retention times of those peaks may indicate that this group consists of *ortho* isomers which are also present in technical NP (*Günther* et al., 2001). However, the main contribution in this technical mixture is derived from the *para* isomers which should be presented by the following fractions. Also F2 showed only minor impurities derived by the remaining fractions. However, there was considerable overlapping of peaks occurring in F3-F6, whereas the less volatile were somewhat increased in the latter two fractions.

Figure 2 shows the increase in the rate of proliferation of the six tested NP-fractions and technical NP in comparison to the negative control and to 17β-estradiol.

F1, which is assumed to consist of *ortho* isomers, exhibited the same proliferative effect as technical NP. This is contrary to *Sonnenschein* and *Soto* (1998), who stated that only the para isomers are estrogenic. Coincubation with tamoxifen showed that the increase in the rate of proliferation was significant for all fractions including the technical mixture.

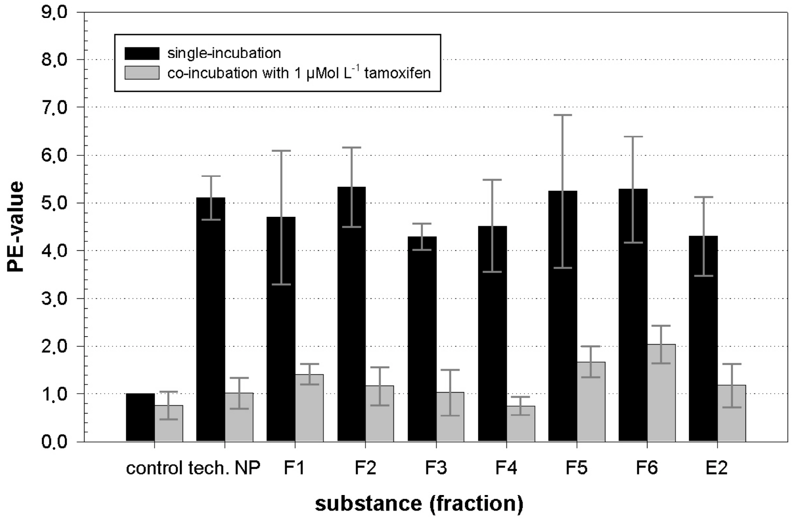

Fig. 2: Increase in the rate of proliferation of six NP-fractions and technical NP (each of 0.00012 g L^{-1}) in comparison to the negative control and 17β-estradiol (E2, 0.1 nMol L^{-1}). The values are presented as mean +/- standard deviation SD. Each sample was tested in three individual assays (*n*=3).

However, comparison of the rate of proliferation increase of all single fractions and the technical mixture showed only slight but no significant differences.

Table 1 shows the RPE-values of all NP-fractions tested, including the technical mixture.

The mean PE-value of technical nonylphenol was 5.1. The average mean of the six fractions of technical nonylphenol was 4.9. The average of the RPE-values of the six NP-fractions was 111.3, the RPE-value for technical NP was 115.5 (see table 1).

Table 1: RPE- and RPP-values of the test substances in comparison to 17β-estradiol

Substance	Test concentration [Mol L^{-1}]	RPE (%)
17β-estradiol	$1*10^{-10}$	100.0
technical NP	$5{,}45 * 10^{-7}$	115.5
F1	$5{,}45 * 10^{-7}$	103.7
F2	$5{,}45 * 10^{-7}$	121.9
F3	$5{,}45 * 10^{-7}$	92.5
F4	$5{,}45 * 10^{-7}$	98.9
F5	$5{,}45 * 10^{-7}$	130.1
F6	$5{,}45 * 10^{-7}$	120.5

The data agree with the results of *Schuller* (1998), who determined for technical NP in the E-Screen Assay a RPE value of 104.8% with approximately the same concentration (1 µMol L^{-1}) as in the present paper.

Figure 3 shows the dose-response-curves for all tested NP-fractions and for technical NP. All fractions and technical NP showed almost the same dose-response, except fraction F3. This fraction exhibited a lower estrogenic potency, i.e. a higher EC_{50}-value than the other ones. At the highest concentrations tested, all fractions including technical NP, showed a cytotoxic effect, except F3 (see Figure 3). Furthermore, the RPE-value for F3 was the lowest of all tested fractions, including the technical mixture (see table 1). It can be assumed that this fraction has the lowest estrogenic potency in comparison to the other fractions and technical NP.

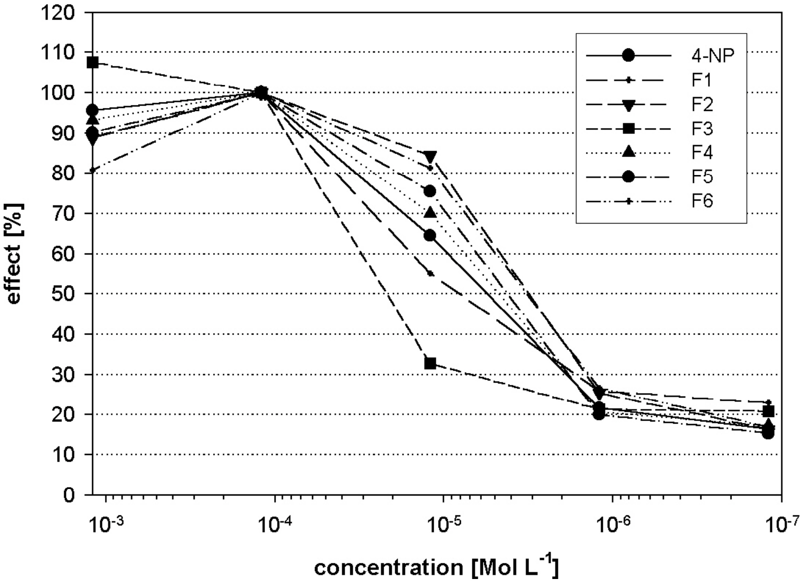

Fig. 3: Dose-response of technical NP and the six tested NP-fractions.

Differences in the estrogenic activity of individual nonylphenol fractions separated by gas chromatography also could show *Yamashita* et al. (1999) by means of a gene expression assay with MCF-7-cells. Here, the so-called „F3"-fraction exhibited the highest luciferase activity. However, *Yamashita* et al. (1999) also could not clarify the exact composition of the individual GC-peaks. Other authors described isomer-specific differences in estrogenic activity. *Soto* et al. (1995) could determine for the DDT-position-isomers *o,p'*-DDT and *p,p'*-DDT in the E-Screen assay at the same concentration RPE-values of 86.1 and 71.0, respectively. *Körner* et al. (1999) showed differences in the estrogenic activity for the α-, β- and γ-isomers of hexachlorocyclohexane (HCH).

In conclusion, the single fractions of technical NP displayed slight differences of estrogenic activity in the E-Screen-Assay but these differences were not significant. For a clarification of these slight differences, an exact chromatographic separation of the NP-isomers and synthesis of distinct isomers, respectively, subsequently to be analyzed in the E-Screen-Assay is necessary. In this way, significant differences in the estrogenic activity of single isomers of technical NP can possibly be shown.

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Anhang H

Tillage effects on the accumulation of polychlorinated biphenyls in biosolid-amended soils

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Abstract

Soil tillage along with the application of organic waste probably affect the concentrations of organic carbon and the enrichment of introduced polychlorinated biphenyls (PCBs). In a three year experiment the PCB status of soils from three different field sites (silty clay loam, silt loam, sandy loam) which were long-term differently tilled (NT = no-tillage, CT = conventional plough tillage) and amended with two different organic wastes such as sewage sludge and compost (biosolids) was examined. No significant alteration in soil-PCB quality and quantity with biosolid application could be proven within the course of the experiments. This indicates soil-air exchange of PCBs dominates their concentrations in soil. Organic carbon in soil was significantly tillage-dependent and determined the fate of PCBs resulting in a generally elevated PCB-level in the non tilled soils. Linear regression of PCB load and organic matter content of all investigated untreated soils was highly significant ($R^2 = 0.73$). Due to already elevated PCB levels in non tilled soils with a maximum of 65 µg kg^{-1} in the superficial layer of the silt loam control plot, any additional potential input, i. e. through the amendment with organic wastes, should therefore be avoided.

Introduction

Sewage sludge and compost materials accumulate a wide range of organic contaminants. This may restrict the beneficial use of organic waste for soil amendment. In Germany, the ordinance on sewage sludge (*AbfKlärV,* 1992) regulates some toxic organics such as polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) in this organic waste material to be applied onto agricultural soil. Limits for those substances in soil are not considered within this ordinance.

The persistent and lipophilic PCBs were used worldwide in large quantities over decades resulting in widespread environmental occurrence (*Lang,* 1992). Due to their physicochemical properties, they are transported globally and may accumulate in food chains. Therefore, enrichment of PCBs in sewage sludge was demonstrated several times (i. e. *Keding* et al., 1989; *Alcock* and *Jones,* 1993*; Eljarrat* et al., 1997).

In the past, some experiments (starting in the early seventies and lasting until the middle of the nineties) with increased sewage sludge application rates showed accumulation of PCBs in treated soils (*Kampe,* 1987*; Keding* et al., 1989; *Folch* et al., 1996; *Alcock* et al., 1996; *Eljarrat* et al., 1997). Since that time, the PCB concentrations in sewage sludge decreased significantly due to the ban of production and use of PCBs, improved industrial pretreatment of waste water, and strict regulations within water management legislation (*Chaney* et al., 1996). However, continuing leaks from PCB-filled equipment remaining in use, along with the persistence of the PCBs, means that they still maintain a significant environmental presence *(Currado* and *Harrad,* 2000*)*. As PCBs concentrate on organic-rich material, compost also should be considered as a sink for PCBs *(Lazzari* et al., 1999) and, when applied onto agricultural land, as a source to burden soils with those and other contaminants. The limited legal application rates for both sewage sludge and compost should prevent soils from excessive enrichment of contaminants (*AbfKlärV,* 1992*; BioAbfV,* 1998). However, any enrichment of PCBs in soil hardly can be proven analytically: The attenuating effect due to tillage within the arable layer of approximately 15 - 35 cm thickness makes it difficult to detect any residues of the introduced contaminants.

With appropriate management, conservation tillage including no-tillage presents economically competitive systems in crop production. Inherent to them, the accumulation of soil organic carbon as a result of remaining plant residues at the soil surface positively affects soil quality (*Karlen* et al., 1994; *Franzluebbers* et al., 1999). This organic carbon enrichment may promote fixation of introduced PCBs in soils building up an accumulation layer of those contaminants at the surface.

The purpose of this study was to assess the impact of sludge and compost derived PCBs on differently tilled soils. Detection of any effect should be facilitated in case of non tilled surface soil which was left undisturbed preventing the dispersion of substances within the entire arable layer.

Materials and methods

Soils

The field experiments were carried out on three long-term differently tilled (NT = no-tillage, CT = conventional plough tillage) soils with differing genesis and texture. With respect to the World reference base for soil resources (*ISSS-ISRIC-FAO, 1998)*, the soils belong to the major soil groups Cambisol, Luvisol, and Fluvisol. According to clay contents from 57 to 310 g kg^{-1} the soils were classified as sandy loam, silt loam, and silty clay loam. The tillage systems had been applied repeatedly to the same plots for several years (sandy loam: 17 yr, silt loam: 9 yr, silty clay loam: 11 yr) until the first biosolid application. The average rainfall and the mean temperatures were 600 mm yr^{-1} and 9°C (sandy loam), 630 mm yr^{-1} and 8°C (silt loam), and 600 mm yr^{-1} and 8°C (silty clay loam). Further characteristics of the field sites were described in *Tebrügge* and *Düring* (1999).

Biosolids

We used digested municipal sewage sludge mainly influenced by domestic sewage and small amounts of industrial waste water, and finished compost derived from a mixture of yard wastes (garden litter, loppings) and separately collected organic domestic waste. The mean total organic carbon (TOC) and total nitrogen (N_t) concentrations were 225 and 31 g kg^{-1} d. m. and 185 and 15 g kg^{-1} d. m. for sewage sludge and compost, respectively.

The application (rates according to *AbfKlärV* (1992) and *BioAbfV* (1998), respectively) of the biosolids on 36 m^2 plots was started in 1997 and lasted over three growing seasons. Compost application was repeated each year at a rate of ≈ 10 Mg ha^{-1}. Sewage sludge was added once at the beginning of the experiments at a maximum rate of ≈ 5 Mg ha^{-1}. In addition to legally allowed application rates a high dose sewage sludge treatment (threefold application rate) was carried out on 36 m^2 plots for each field site and tillage system. All treatments were conducted in duplicate.

Soil sampling

Soil sampling, according to the working depths (0-3 cm, 3-10 cm, and 10-25 cm) of the distinctive tillage systems, was carried out on 5/9/00 (sandy loam), 9/15/99 (silt loam), and 4/26/00 (silty clay loam). The differently treated soils were each sampled on two replicated field plots. Each plot provided two subsamples. Both subsamples were represented by composite samples pooled from at least 10 randomized cores. Surface soil (0 – 3 cm) was sampled carefully with at least 10 randomized soil cores of 8 cm diameter which were also subsequently pooled. The samples were frozen at –18°C immediately after transfer to the laboratory.

Analysis of total organic carbon (TOC) and total nitrogen (Nt)

Carbonate-free ground soil samples where weighed (approx. 20 mg) into tin capsules. The samples were burned and detected with a thermal conductivity detector by a carbon/nitrogen analyser (Carlo-Erba, NA 1500, Milan, Italy).

Analysis of polychlorinated biphenyls (PCB)

Microwave assisted extraction and GC/MS analysis for the congeners #28; #52; #101; #138; #153; and #180 provided detection limits of approx. 0.5 µg kg^{-1} d. m. for each congener. Recovery rates were proven to be at least as high as for the reference method which is based on a soxhlet extraction. Further details on this analytical method were described in *Düring* and *Gäth* (2000).

Statistics

All data of soil analysis were subjected to ANOVA followed by Tukey's test to separate means.

Results and discussion

PCB-load in biosolids

PCB burden of the applied organic waste materials and exploitation of German PCB limit values with resulting loads are given in Table 1.

Table 1: Concentrations of PCBs in biosolids, limit exploitations according to *AbfKlärV* (1992), and resulting loads.

	Mean concentration [mg kg^{-1}]		Limit exploitation [%]		Mean load [g ha^{-1} $3a^{-1}$]	
	Compost	Sewage sludge	Compost	Sewage sludge	Compost	Sewage sludge
Congener						
#28	n.d.*	0.015	n. a.**	7.4	n.d.*	0.075/0.225***
#52	0.009	0.021	n. a.**	10.3	0.270	0.105/0.315***
#101	0.017	0.040	n. a.**	20.0	0.510	0.200/0.600***
#138	0.025	0.053	n. a.**	26.7	0.750	0.265/0.795***
#153	0.033	0.067	n. a.**	33.6	0.990	0.335/1.005***
#180	0.028	0.043	n. a.**	21.3	0.840	0.215/0.645***

* not detected
** not applicable
*** high dose treatment with threefold application rate of sewage sludge

Given Tab. 1, the mean PCB load via compost application was higher when compared to legally allowed sludge application. Although PCB #28 was not detected in compost, the distribution of the determined individual PCB congeners in compost samples was similar to the sludge samples. The mean loads of PCBs result from the mean concentrations given in Tab. 1 and the described application rates.

Total organic carbon (TOC) and total nitrogen (Nt) in soil

Concentrations of TOC and N_t in the control plots (Tab. 2) were significantly different in both TOC and N_t between CT and NT in the silt loam and the sandy loam. This confirms the general statement that long-term no-tillage treatment accumulates humus especially at the soil surface (*Franzluebbers,* 1999). However, in the silty clay loam organic matter accumulation in the NT treatments was weakened due to frequent removal of the plant residue cover even on the NT plots.

Table 2: Total organic carbon (TOC) [g kg^{-1}] and total nitrogen (N_t)[g kg^{-1}] in three long-term differently tilled soils.

Soil depth	Tillage	sandy loam		silt loam		silty clay loam	
[cm]	system	N_t	TOC	N_t	TOC	N_t	TOC
0-3	NT	1.5**	13.1**	2.1**	23.7**	2.2*	24.0*
	CT	0.8	6.7	0.7	8.3	1.7	18.4
3-10	NT	1.1**	8.8*	1.6**	15.5**	1.9	21.9
	CT	0.8	7.0	0.7	9.1	1.7	19.5
10-25	NT	0.7	5.9	1.1*	9.4	1.6	17.1
	CT	0.7	6.7	0.7	9.3	1.7	19.3

* and ** represent significant differences ($P<0.05$ and $P<0.01$, resp.) among tillage treatments within a soil depth. NT = no-tillage, CT = conventional tillage, N_t = total nitrogen, TOC = total organic carbon.

Influence on both TOC and N_t due to biosolid amendments was observed only for the compost treated silt loam which was sampled four weeks after application (data not presented here). For those samples, time for mineralization was too short to considerably decrease TOC concentrations to tillage specific equilibrium.

PCB-load in soils

In Fig. 1, the comparison of the sum of the PCBs #28, #52, #101, #153, #138, and #180 (PCB_6) in the soil samples shows the PCB burden was site-specific. A clear effect of tillage is obvious, whereas the influence of fertilization with biosolids seems to be small. The mixing effect of ploughing resulted in homogeneous distribution of the PCBs in the soils. The sampling depth of 3 cm for the surface soil accentuates accumulation of the strongly bound PCBs in the NT soil. The silt loam showed significantly elevated PCB_6 concentrations under NT compared to CT among all fertilization treatments. Due to large variability at low concentrations of the distinct congeners, differences in PCB_6 concentrations between tillage treatments in the sandy loam were less significant. In the silty clay loam, influence of tillage was – according to the results for organic matter content – significant for some soil samples but less pronounced.

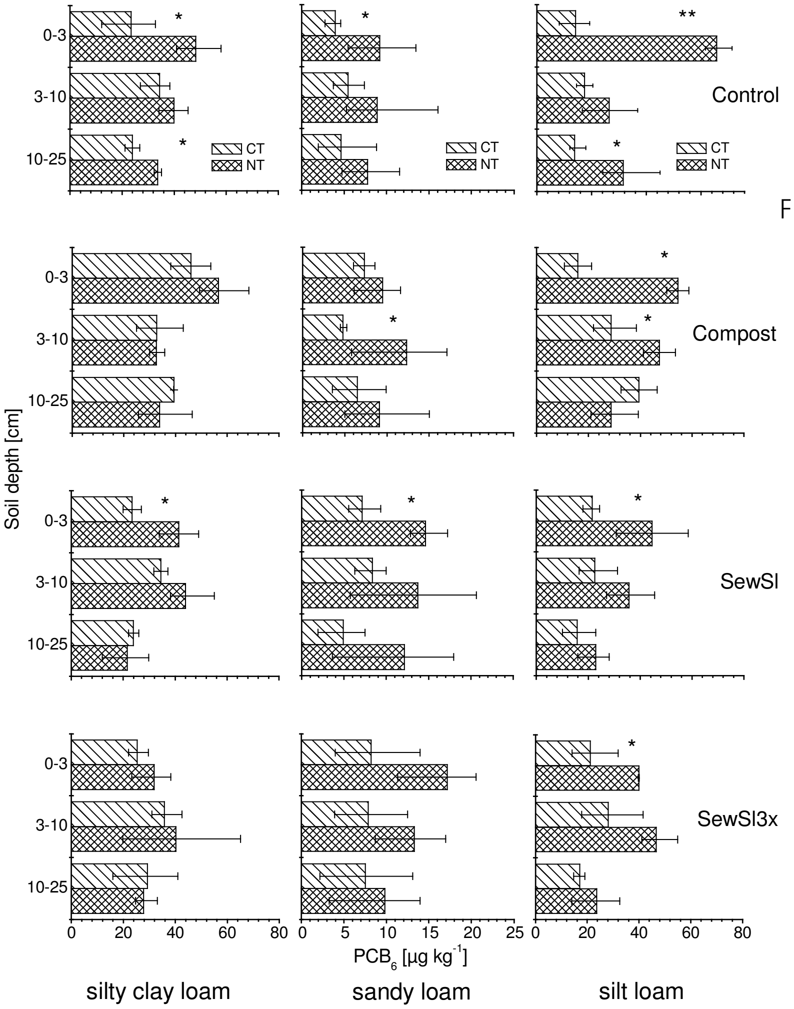

Fig. 1: Concentrations of the sum of six PCB congeners (PCB_6) in the long-term differently treated soils from three field sites. CT = conventional tillage, NT = no-tillage. Biosolid treatments are: control (first line), compost application (second line), sewage sludge application (third line: SewSl), threefold sewage sludge application (fourth line: SewSl3x). * and ** represent significant differences ($P<0.05$ and $P<0.01$, resp.) among tillage treatments within a soil depth, error bars reflect minima and maxima.

Increasing PCB concentration due to biosolid application can be supposed only in the sandy loam. This soil exhibits the lowest background concentration of all three soils and an influence by the additional input of PCBs via biosolid application is most likely.

In the case of three soil samples, PCB_6 concentration in the upper layer of the NT exceeded the German soil quality criterion of 0.05 mg kg^{-1} for soils with less than 8% humus content (*BBodSchV,* 1999). This reflects the typical stratification pattern of substance concentrations in non tilled soils (*Lavado* et al., 1999; *Franzluebbers* et al., 1999) and cannot be transferred to the mentioned soil quality criterion which refers to a soil sampling depth of 0 – 30 cm. However, the PCB_6 concentration level, both in the silt loam and the silty clay loam, was rather high and can partly be attributed to the applied microwave assisted extraction method with high extraction efficiency (*Düring* and *Gäth,* 2000). In a study on the fate of PCBs in sewage sludge-amended soils the PCB_6 concentration in two control soils ranged between 10 and 15 µg kg^{-1} d. m. in a soil layer of 0 – 15 cm (*Alcock* et al., 1996). Another study on heavily sludge-amended soils comprising six field sites in Germany, reported on a mean value of 14 µg kg^{-1} d. m. in the arable soil layer of the control plots (*Kampe,* 1987).

Considering the soil masses per hectare as a result of their tillage-dependent soil densities and the volumes sampled in the distinct soil depths, loads of PCBs and amounts of organic carbon correlated strongly in the investigated soils (Fig. 2). The scatter diagram of PCB_6 load in soil vs. soil organic carbon content indicates there was no significant increase in PCB_6 load due to the amendment with organic wastes. Most of the data points which were obtained from the biosolid treated soils fell into the confidence belt ($\alpha = 0.95$) of the untreated soils.

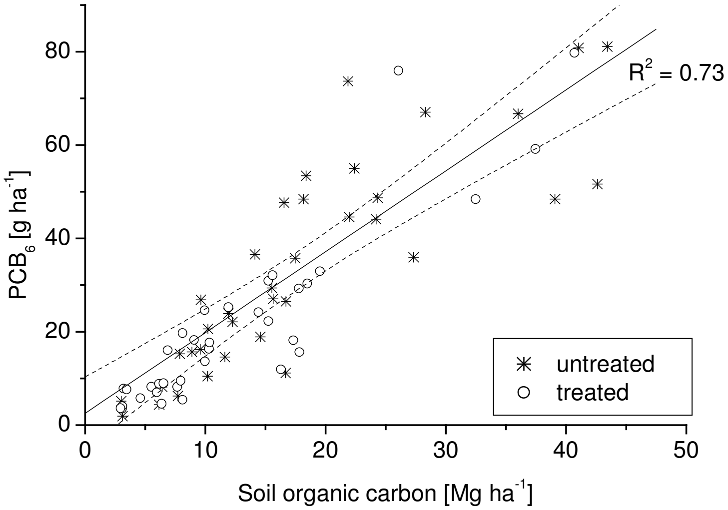

Fig. 2: Relationship between PCB_6 load and organic carbon content in soil samples of 0 – 3, 3 –10, and 10 – 25 cm depth. Regression line and confidence belt given for soil samples which were not amended with biosolids.

Single congener proportions of the total PCB burden in untreated and in fertilizer treated soils are given for the congeners #52, #153, and #138 in Figure 3. Only slight influence by the fertilization with the organic wastes can be expected due to small and insignificant differences between the congener patterns. The higher chlorinated congeners such as #153, #138, and #180 predominated in the waste materials (Tab. 1) whereas in the untreated soils lighter congeners as the fivefold chlorinated (#101) or fourfold chlorinated (#52) were pronounced (*Düring* et al., 2002). However, the slight increase in the percentage of both congeners #153 and #138 (#180 was detected only in a few samples) due to biosolid amendment and the differences of all the rest of them were not important.

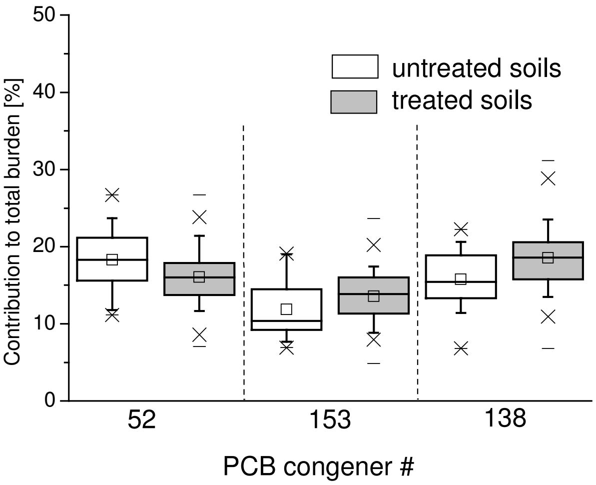

Fig. 3: Relative proportions of selected PCB congeners in untreated and in soils treated with biosolids. Boxes represent 25, 50, and 75 quantiles, whiskers and crosses represent 95 and 5% and 99 and 1% quantiles, respectively. Minima and maxima are given as lines; □ = mean values.

Consequently, the effect of any of the considered fertilizer treatments both on PCB pattern and quantity in the investigated soils was small when compared to the influence of soil organic carbon which was strongly influenced by long-term different tillage application. PCB losses from soil via volatilization would have been lower due to stronger partitioning into soil enriched with organic matter (*Cousins* et al., 1997) as it is the case in the investigated NT soils. Fluxes from soil to atmosphere and vice versa seem to dominate the PCB content at the three different field sites, and this corresponds to other results in the literature (*Alcock* et al., 1996).

Variability in the relationship between PCB_6 load and soil organic carbon content may have been due to the different origins of the soil samples, expressed by the different parameters of the linear regressions listed in Table 3.

Table 3: Parameters of the site-specific linear regressions PCB_6 [g ha^{-1}] = a + b · soil organic carbon [Mg ha^{-1}].

Field site	a	b	R^2	n
sandy loam	0.41	1.15	0.56	24
silty clay loam	1.76	1.62	0.88	24
silt loam	-5.08	2.68	0.83	24

However, besides site-specific climatic conditions, the quality of soil organic matter can markedly influence enrichment behavior of organic contaminants, as could already be proven for naphthalene (*Xing,* 1997). The TOC : N_t ratios calculated from the data in Table 2 indicate that quality of organic matter differed among the soils of the three field sites. After subjecting to ANOVA, a significantly lower mean TOC : N_t ratio of 8.5 was determined for the sandy loam when compared to 11.3 (silt loam) and 11.1 (silty clay loam). The TOC : N_t ratios were on each site consistent for all soil depths and were not influenced by tillage. Nevertheless, the results strongly confirm that statistically significant relationships between soil PCB concentrations and soil organic carbon should be used for site-specific predictions of PCB fate (*Cousins* et al. 1999).

Conclusions

The experimental design with field plots under long-term different tillage systems receiving organic wastes gives reason to further confirm that atmospheric inputs and volatilization losses dominate the PCB content in soils. After one single treatment with maximum allowable load of biosolids and even with threefold application rate of sewage sludge there was no significant increase in soil PCB concentrations. Furthermore, the alteration in the PCB pattern due to fertilization with the organic wastes was not significant. However, non tilled soils, more than conventionally ploughed soils, provide a repository to sequester carbon dioxide. In view of climate protection this is desirable and probably agricultural and environmental policies will support the no-tillage system in the future. However, with increasing organic matter content in soils also the PCB load of soils will increase. In case of changing tillage system from no-tillage to ploughing, increased mineralization rates may promote the release of the organically bound pollutants such as PCBs. Considering the already elevated level of PCBs in non tilled soils, any additional input i. e. through the amendment with organic wastes should be avoided.

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Anhang I

Sorption and bioavailability of heavy metals in long-term differently tilled soils amended with organic wastes

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Abstract

In this study, bioavailability and enrichment studies were focused on Cd, Zn, and Cu in two different soils (sandy loam and silt loam) which were treated with compost and sewage sludge, respectively, both under conventional tillage (CT) and no tillage (NT). Long-term NT resulted in significant increase of Cd and Zn extracted by aquia regia in a soil profile of 0-25 cm depth, especially in the superficial layer. In the sandy loam, slight cadmium increase due to sewage sludge application was observed. Results on EDTA-extractable heavy metals were not consistent but NH_4NO_3-extractable concentrations were clearly reduced in the NT soil. Bioavailability of heavy metals was reduced in long-term NT resulting in lower transfer of Cd and Zn into plants and accumulation in soil. The effect of tillage on enrichment of heavy metal in soils is stronger than the impact of the fertilisation by means of legally allowable application rates of organic wastes. Long-term non tilled soils enriched in heavy metals should not be amended with organic waste.

Introduction

At present, approximately 8 million tons of sewage sludge are produced each year in the member states of the European Union (EU) (*Magoarou,* 2000). Due to increasing efforts with the fractionation of domestic wastes and further improved composting techniques, 6-7 million tons of compost material (*BGK,* 2002) are available for the amendment of agricultural and non agricultural land in Germany. Both materials contain large amounts of organic matter and plant nutrients and therefore European and German policies support their use to substitute mineral fertilizers.

However, not only beneficial ingredients but also undesirable heavy metals end up in organic waste and can cause adverse effects to the environment. The behavior of those heavy metals largely depends on soil properties which may be altered by soil tillage. The content of organic matter which provides a significant sink for heavy metals is changed by the tillage practice (*Blevins* et al., 1983; *Rhoton* et al., 1993; *Singh* et al., 1994). Enhanced cation exchange capacity was reported to improve both soil quality and retardation of nutrients in a superficial enrichment layer of long-term non ploughed soils (*Karlen* et al., 1994). In previous work, we observed enrichment of heavy metals and polychlorinated biphenyls (PCB) in the surface layer of non tilled soils (*Düring* et al., 2002; *Düring* and *Gäth,* 2002).

Accumulation of heavy metals must be considered in the long run, that is: short-term moderate application rates can hardly result in concentration increases which are analytically detectable. Tracing enrichment of heavy metals after treatment with organic waste is further complicated by the mixing effect of ploughing the soil.

Surface application of sludge onto grazing land is banned i. e. in the UK and in Germany, whereas no restrictions exist regarding the soil tillage system. Tillage mechanically mixes the organic waste material into the uppermost 20 – 30 cm of the soil. In case of no-tillage however, the surface-applied organic material is incorporated into the soil merely by biological activity.

The purpose of this paper was to investigate the influence of tillage on total and extractable heavy metal contents and plant uptake of heavy metals which may be introduced into the soil by the amendment with organic wastes.

Material and methods

Soils

The experiments were based on long-term field trials involving two tillage systems on two different soils (sandy loam and silt loam). Properties of the soils and principles of the tillage systems (conventional plough tillage = CT, no-tillage = NT) are given in *Tebrügge* and *Düring* (1999) and *Düring* et al. (2002). In both non tilled soils, enriched organic carbon in a depth of 0-10 cm improved cation exchange capacity when compared to the ploughed soils. Soil pH was not influenced by tillage and ranged in the Eutric Cambisol from 5.2 to 6.1 and in the Luvisol from 6.1 to 6.6. The tillage systems had been applied repeatedly to the same plots for several years (silt loam: 9 yr, sandy loam: 17 yr) until the first organic waste application and sampling.

Organic wastes

The organic waste materials used in this study were digested municipal sewage sludge and finished compost. The mean total organic carbon (TOC) and total nitrogen (N_t) concentrations were 225 and 31 g kg^{-1} d. m. resp., for sewage sludge, and 185 and 15 g kg^{-1} d.m. resp., for compost. The origin and characterization of the applied compost and sewage sludge as well as the application rates which were legally allowable (10 Mg ha^{-1} a^{-1} and 1.67 Mg ha^{-1} a^{-1} for compost and sewage sludge, respectively) were described in *Düring* and *Gäth* (2002).

Soil sampling and pretreatment

Soil sampling, according to the working depths (0-3 cm, 3-10 cm, and 10-25 cm) of the distinctive tillage systems, and further sample pretreatment was reported in detail in *Düring* et al. (2002). In addition to sampling of disturbed soil, volume-based undisturbed soil cores were collected to determine bulk density.

Greenhouse experiments on bioavailability and soil-plant transfer of heavy metals

Soil-cores of 20 cm diameter and 30 cm height were excavated from the NT and CT plots of both field sites. NT soil was collected leaving its structure undisturbed providing the typical stratification pattern of this soil. Disturbed samples from ploughed soil were brought to a bulk density of 1.25 g cm^{-3} and 1.62 g cm^{-3} (according to the determined average density of the respective field samples), for the silt loam and the sandy loam, respectively. Treatments with organic waste were according to 55 and 20 Mg d.m. ha^{-1} of compost and sewage sludge, respectively. Spinach (*Spinacia oleracea*, var. Matador) was planted into the soils, grown under standard environmental conditions (20-25°C), and 60 d after planting, metal concentrations in the shoots were determined. Experiments were carried out in fourfold replicates.

Heavy metal analysis

Total amounts (assessed by *aqua regia* digestion from soil and HNO_3/hydrogen peroxide-extracts from plants), ethylene diamine tetra acetic acid (EDTA)-extractions (5 g soil, 50 mL 0.025 M Na-EDTA, shaken for 90 min) representing the potentially available fraction, and the mobile fraction ammonium nitrate (NH_4NO_3)-extracts (20 g soil, 50 mL 1 M NH_4NO_3, shaken for 120 min) of heavy metals were analysed by atomic absorption spectroscopy (Spectra AA10, Varian, Darmstadt, Germany) according to *VDLUFA* (1991) and *Zeien* (1995).

Sorption experiments

Sorption capacities of the differently tilled soils for Cd were examined in laboratory studies with the batch equilibrium method providing Freundlich-isotherms as described in *Schug* et al. (1999). Sorption isotherms were performed considering soil masses of the different sampling depths:

$$S_m = S \cdot M_s \tag{eq. 1}$$

where:

S_m = [mg ha^{-1}] Cd mass per hectar in a particular soil depth segment (δz).

S [mg kg^{-1}] = concentration of Cd in the solid phase.

M_s = [kg ha^{-1}] soil mass per hectar resulting from volume of a soil depth segment (δz) and bulk density (ρ).

Statistics

Data of heavy metal fractions in soil and concentrations in plants were subjected to ANOVA ($P<0.05$). Tukey's test followed ANOVA to separate means.

Results and discussion

Heavy metals in organic wastes

Aqua regia extractable concentrations of different heavy metals in both organic waste materials and their relation to the existing German limit values in percent, as well as the loads, resulting from the applied doses are given in Table 1.

Table 1: Concentrations of *aqua regia* extractable heavy metals in organic wastes, percent of limit values according to *AbfKlärV* (1992) and *BioAbfV* (1998), respectively, and resulting loads. In brackets: coefficient of variation [%], *n* = 8.

	Mean concentration [mg kg^{-1}]		Percent of limit value		Mean load [g ha^{-1} 3yr^{-1}]	
	Compost	Sewage sludge	Compost	Sewage sludge	Compost	Sewage sludge
Cd	0.68 (3.4)	2.88 (9.9)	45.4	28.8	20.4	14.4
Cu	38 (1.3)	278 (1.1)	54.4	34.9	1142.9	1394.6
Zn	261 (4.4)	1320 (1.4)	87.0	52.8	7833.8	6603.0

Except for Cu, the mean heavy-metal load via compost application was higher when compared to the load resulting from sludge treatment.

Heavy metal distribution in soils

In Table 2 the masses of *aqua regia* extractable Cd, Zn, and Cu per ha in a soil depth of 0-25 cm are shown. Significant differences due to tillage were evident on both field sites for Cd and Zn.

Table 2: Masses of *aqua regia* extractable heavy metals [kg ha^{-1}]in profiles of 0-25 cm depth of differently tilled and fertilized soils, 3 yr after the first treatment with organic wastes, *n* = 4.

Sandy loam		Cd	Zn	Cu
NT	SewSl	0.72 aA	121.69 aA	33.12 aA
	Compost	0.64 aB	122.93 aA	32.29 aA
	Control	0.62 aB	116.67 aA	31.61 aA
CT	SewSl	0.56 bA	120.45 aA	36.54 aA
	Compost	0.43 bB	105.35 bA	33.43 aA
	Control	0.46 bB	106.64 bA	33.41 aA
Silt loam				
NT	SewSl	0.73 aA	155.86 aA	32.27 aA
	Compost	0.82 aA	187.72 aA	43.43 aA
	Control	0.87 aA	204.73 aA	39.97 aA
CT	SewSl	0.63 bA	139.44 bA	31.03 bA
	Compost	0.71 bA	141.66 bA	33.57 bA
	Control	0.67 bA	131.61 bA	32.77 bA

NT = no-tillage, CT = conventional tillage, SewSl = sewage sludge treatment. Different small letters represent significant differences (P<0.05) among tillage systems within a fertilizer treatment. Different capital letters represent significant differences (P<0.05) among fertilizer treatments within a tillage system.

Treatment with sewage sludge slightly increased Cd amounts in the sandy soil when compared to the control plots which were not treated with organic wastes (Figure 1). However, the impact through fertilisation seems to be of small importance when compared to the tillage effect.

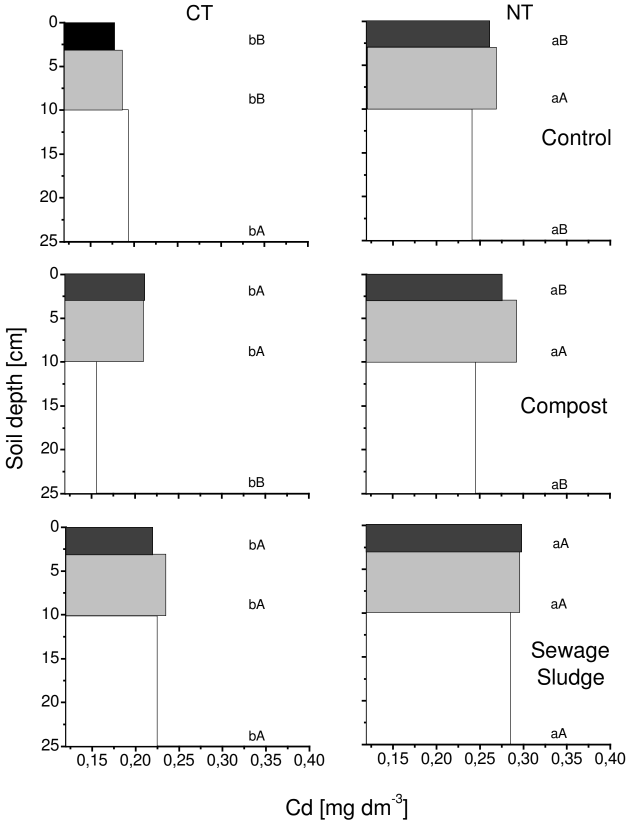

Fig. 1: Masses of aqua regia extractable Cd [g dm^{-1}] in the differently tilled and fertilized sandy loam in soil layers of 0-3; 3-10; and 10-25 cm (CT = conventional tillage, column on the left; NT = no-tillage, column on the right). Different small letters represent significant differences ($P<0.05$) among tillage systems within a fertilizer treatment. Different capital letters represent significant differences ($P<0.05$) among fertilizer treatments within a tillage system, *n* = 4.

Within greenhouse experiments designed to study soil-plant transfer of Cd, Zn, and Cu, their bioavailable and mobile fractions in soil were analysed. As demonstrated in Table 3, EDTA-extracts representing the potentially bioavailable heavy metal fraction (*Fergusson,* 1991) were influenced in some cases by tillage and by organic waste treatment only in the silt loam. Cd concentrations in the EDTA-extracts from the silt loam were rather high and reached approximately 90% of the respective total amounts obtained from the field experiment and indicated an increase in case of the NT soil. However, relationship between potentially bioavailable heavy metals and tillage and fertilizer affected organic matter contents as *Lavado* et al. (1999) could observe, were not clear within our experiments.

Table 3: Potentially bioavailable and mobile fractions of heavy metals in differently fertilized and tilled soils.

		EDTA-fraction			NH_4NO_3-fraction		
		Cd	Zn	Cu	Cd	Zn	Cu
		[mg kg^{-1}]	[mg kg^{-1}]	[mg kg^{-1}]	[µg kg^{-1}]	[mg kg^{-1}]	[mg kg^{-1}]
Sandy loam							
Compost	CT	0.13 aA	5.15 aA	3.04 aA	19.74 aB	1.33 aA	0.08 aA
	NT	0.11 aA	4.91 aA	2.03 bA	13.01 bB	0.88 bA	0.05 aA
SewSl	CT	0.11 aA	4.63 aA	2.60 aA	32.85 aA	2.05 aA	0.09 aA
	NT	0.14 aA	4.66 aA	2.77 aA	13.00 bA	0.50 bA	0.08 aA
Control	CT	0.12 aA	4.52 aA	2.76 aA	31.02 aA	1.81 aA	0.07 aA
	NT	0.11 aA	4.48 aA	2.61 aA	15.78 bA	0.67 bA	0.06 aA
Silt loam							
Compost	CT	0.13 bB	5.19 bA	2.35 bC	7.81 aB	0.06 aA	0.08 aA
	NT	0.16 aB	8.31 aA	3.22 aC	8.15 aB	0.07 aA	0.08 aA
SewSl	CT	0.11 bB	6.29 bA	3.21 bA	8.47 aB	0.10 aA	0.06 aA
	NT	0.20 aB	7.12 aA	3.61 aA	7.59 aB	0.09 aA	0.07 aA
Control	CT	0.19 bA	3.30 aC	2.18 bB	10.48 aA	0.06 aB	0.06 bA
	NT	0.21 aA	2.12 bC	3.71 aB	11.42 aA	0.02 bB	0.08 aA

Concentrations of the NH_4NO_3-extractable Cd and Zn fractions were in the sandy loam always higher in CT.

Sorption capacity of the long-term differently tilled soils was assessed by means of Freundlich isotherms. Considering the tillage-dependent bulk density, sorbed heavy metal masses at a given concentration in solution can be assessed for the different soil depths investigated (Figure 2).

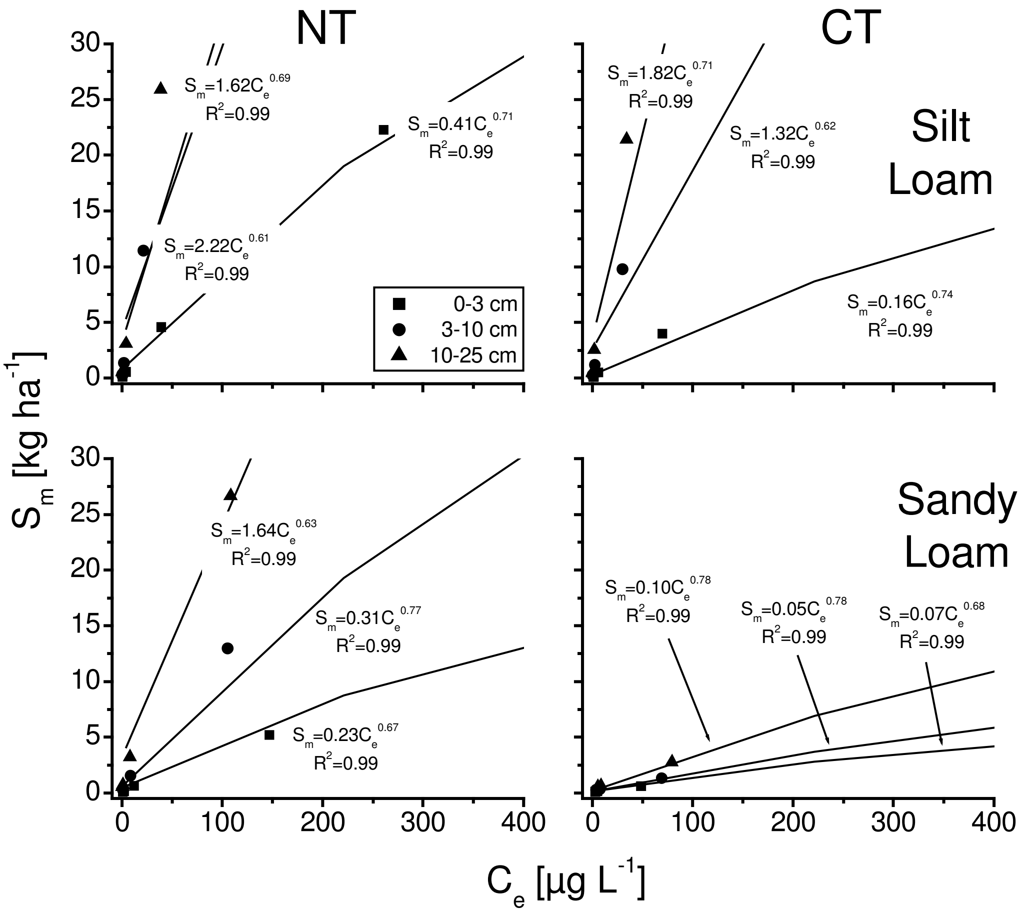

Fig. 2: Cd-sorption isotherms for different sampling depths of differently tilled soils (NT = no-tillage, column on the left; CT = conventional tillage, column on the right). Graphs showing the lower 3 Cd concentration steps of 5 levels, each concentration with 3 replicates, standard deviations were too small to be represented here.

In particular at the soil surface, sorption capacity of the non tilled sandy loam was clearly enhanced when compared to CT soil. In this soil, tillage induced significant alteration of the TOC content (*Düring* and *Gäth,* 2002). Given a WHO guide value of 3 µg L^{-1} in drinking water and applying this value to the soil solution, this would entail different sorbed proportions of Cd in the surface layer (0-3 cm) of 0.21, and 0.09 kg ha^{-1} in the NT and CT soil, respectively. Due to intermixing the soil by tillage, the sorbed heavy metal masses should be integrated over the entire plough layer. The total masses of adsorbed Cd in differently tilled soil profiles of 0 – 25 cm resulting in a Cd concentration in solution of 3 µg L^{-1} are given in Table 4.

Table 4: Cd [kg ha^{-1}] adsorbed in two differently tilled soils at 3 µg Cd L^{-1} soil solution.

	Silt loam	Sandy loam
NT	8.69	4.48
CT	6.94	0.50

Considering a mean Cd load of 6 g ha^{-1} yr^{-1} via frequent application of organic wastes, and negligible losses of particle-bound and dissolved Cd, the capability of the sandy loam to buffer the input of Cd would last for approx. 100 years in the CT soil, whereas in the NT soil this time period would amount to more than 700 years.

However, the effect of tillage on heavy metal accumulation in soils superimposes the impact of the treatment with organic wastes, since after 9 and 17 yr. of continuous application of different tillage systems, Cd and Zn masses were significantly influenced by tillage in the silt loam and the sandy loam, respectively.

Heavy metals in plants

Heavy metal concentrations were significantly elevated in shoots of spinach (*Spinacia oleracea*, var. Matador) grown in ploughed soils, whereas treatment with organic wastes did not affect the plant uptake of heavy metals (Table 5). No significant correlation could be found between EDTA-data and heavy metal concentrations in plants. Our data on Cd and Zn concentrations in plants and NH_4NO_3-extractable showed positive correlation confirming that availability of Zn and Cd for spinach was reduced under no-tillage conditions. However, the results involve various complex processes which determine the uptake by and the transport within plants. It is important that, without soil mixing, heavy metals became concentrated near the soil surface and were not accessible for large proportions of the roots as spinach is characterised by a strong, vertically and deeply penetrating taproot. Nevertheless, roots of plants growing in non tilled soils mostly are more concentrated at shallower depths than plant roots grown in conventionally tilled soils which may be attributable in part to the higher bulk density and water content near the surface in NT soils (*Ball-Coelho* et al., 1998). Literature data on effects of tillage practices on Cd concentrations in plants are rare and generally too inconsistent to allow conclusions to be drawn (*Mench,* 1998).

Table 5: Heavy metal concentrations in shoots of spinach (*Spinacia oleracea*, var. Matador) grown on differently fertilized and tilled soils, 60 d after planting.

		Sandy loam			Silt loam		
		Cd [mg kg-1]	Zn [mg kg-1]	Cu [mg kg-1]	Cd [mg kg-1]	Zn [mg kg-1]	Cu [mg kg-1]
Compost	CT	11.81 aA	565.56 aA	18.19 aA	6.35 aA	229.75 aA	10.05 aA
	NT	7.31 bA	201.80 bA	9.95 bA	1.94 bA	108.16 bA	7.75 aA
SewSl	CT	7.17 aB	490.26 aA	16.29 aA	9.88 aA	371.27 aA	13.68 aA
	NT	2.35 bB	122.54 bA	9.36 bA	2.28 bA	183.23 bA	11.59 aA
Control	CT	12.36 aA	502.42 aA	18.08 aA	7.22 aA	286.41 aA	13.99 aA
	NT	5.86 bA	266.31 bA	10.70 bA	2.57 bA	150.16 bA	11.80 aA

Conclusions

Considering different potential inputs of heavy metals i. e. via organic wastes into soils, their accumulation must be minimized. Possible relevant fluxes from the soil may be the uptake by the cultivated crop, leaching, as well as losses due to erosion and uptake by weeds. Those output fluxes are reduced in case of long-term non-tilled soils resulting in long-term accumulation of elements such as Cd and Zn. Furthermore, diffusive inputs, i. e. via the atmosphere and agrochemicals, seem to be fixed more strongly in non-tilled soils which are enriched in organic carbon. The investigated non-tilled soils did accumulate Cd and Zn and the availability of these elements for spinach was clearly reduced. This means there is not an imminent risk for plant and human health because concentrations in soil water and in growing plants are lower than in the case of conventionally ploughed soils. However, heavy metal accumulating non-tilled soils should be excluded from any management practices utilising organic wastes: Changes in land-use or tillage system may alter crucial soil properties providing a risk for the release of the former enriched heavy metals. If the non-tilled soil will be transferred to fallow land, soil acidity will without liming increase, resulting in increased bioavailability of several heavy metals. If the no-tillage system will be changed to ploughing, increased mineralisation rates may promote the release of the heavy metals.

Acknowledgements

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Anhang J

Regionalization of sorption capacities for arsenic and cadmium

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Plant and Soil, 1999, 213, 181-187

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Abstract

To fulfill the purpose as a sink for trace elements, soils must not be overloaded with As and Cd. Therefore, it is necessary to get knowledge of the sorption capacities of soils on a regional scale. The determination of these sorption capacities for large areas is, however, impeded by the great expenditure of laboratory work involved. With data presented here retention capacities for cadmium and arsenic from routinely determined soil parameters are estimated. In batch experiments the sorption behaviour of 40 soils from the area of Freiberg/Saxony in Germany was examined. The obtained sorption isotherms from the laboratory were fitted to the Freundlich equation ($S = k*C^m$). The two constants (k, m) of this equation were used for multiple linear regression to correlate the sorption capacity and the soil parameters, namely clay content, pH value, total organic carbon, and dithionite extractable Fe contents. Due to long lasting ore mining of Freiberg there exist high background levels in that area for the two surveyed elements As and Cd. Therefore, this study offers two different mathematical procedures to take these contaminations into account. Thus the experimental data were corrected before they were fitted to Freundlich and pedotransfer equations were determined. Using the transfer equation, parameter k and m for cadmium sorption could be estimated with statistical certainties of 91% and 61% (adjusted R^2), respectively, whereas the predictability for the arsenic sorption is not practicable because achieved R^2 values are very low (17% and 7%).

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Introduction

Heavy metals are distributed over all environmental compartments. Soils are preferential immittents both due to natural processes and anthropogenic influences. An important entry path of pollution is the disposal of organic wastes onto soils. Long term application of sewage sludge, for example, may deliver huge loads of heavy metals, resulting in an accumulation of these elements in soils (*Gäth*, 1996). From this awareness the question arises whether all soils can accomplish their assigned function as a sink. Because of their heterogeneous physical and chemical characteristics soils exhibit different retention capacities for trace elements. Hence, most soil properties which influence sorption capacities have to be examined.

With this paper an approach is presented to quantify retention capacities of soils for arsenic and cadmium by examining representative soil profiles of region with intensive ore processing. This data base should make it possible to assess the retention capacities of other soils in this region by a linear function which includes the most important soil parameters for heavy metal sorption. This linear function further will be named as pedotransfer equation (PTE) because ultimately sorption behaviour from the laboratory batch experiments will be transferred to large areas on regional scale.

The aim of the study is a regionalization of retention capacities of soils for the two trace elements As and Cd. reactivity of the components (*Adriano*, 1986; *Alloway*, 1995) and determine the degree of their possible displacement. Given their great extent of inner surfaces, soils offer huge amounts of sorption sites. Thus, trace elements in soils are distributed between solid and mobile phase, respectively. This distribution is controlled by a lot of processes which cannot be enumerated here. However, some soil properties which determine these processes are the clay content, the content of organic matter (*Adriano*, 1986; *Alloway*, 1995), the content of Fe- and Mn-oxides/hydroxides (*Hingston* et al., 1971; *Jarvis* and *Jones*, 1980), and the soil pH-value (*Brümmer*, 1986). This is not a complete compilation, but it includes the most important soil parameters controlling the retardation of trace elements. Those parameters can be preferably determined for this examination due to their decisive influence on the sorption behaviour of trace elements in soils and due to the relative simplicity to obtain these data. The sorption behaviours of As and Cd are examined in laboratory batch experiments. Being aware of the drastic over simplification involved in extrapolating the sorption processes from lab to the field scale, a very simple experimental procedure is assigned to cope with the high number of soil samples. Data obtained from the batch experiments are fitted to Freundlich isotherms. Thus, the specific retention capacity of each soil sample under the adjusted conditions is represented. The shape of the Freundlich isotherm is determined by two constants. These constants are utilized as algebraic units in a multiple regression analysis with the selected soil parameters mentioned above. Following that line of reasoning, so-called pedotransfer equations for estimation of the arsenic and cadmium retention capacities are obtained (see Figure 1). This offers the possibility to transfer these retention capacities to large regional units, always under the premises that the soil parameters for that area are available (*Gäth*, 1996).

Theoretical approach

The behaviour of trace elements in soils is governed by their availability or retardation in the soil. Substancespecific properties and soil characteristics control the reactivity of the components (*Adriano*, 1986; *Alloway*, 1995) and determine the degree of their possible displacement. Given their great extent of inner surfaces, soils offer huge amounts of sorption sites. Thus, trace elements in soils are distributed between solid and mobile phase, respectively. This distribution is controlled by a lot of processes which cannot be enumerated here. However, some soil properties which determine these processes are the clay content, the content of organic matter (*Adriano*, 1986; *Alloway*, 1995), the content of Fe- and Mn-oxides/hydroxides (*Hingston* et al., 1971; *Jarvis* and *Jones*, 1980), and the soil pH-value (*Brümmer*, 1986). This is not a complete compilation, but it includes the most important soil parameters controlling the retardation of trace elements. Those parameters can be preferably determined for this examination due to their decisive influence on the sorption behaviour of trace elements in soils and due to the relative simplicity to obtain these data.

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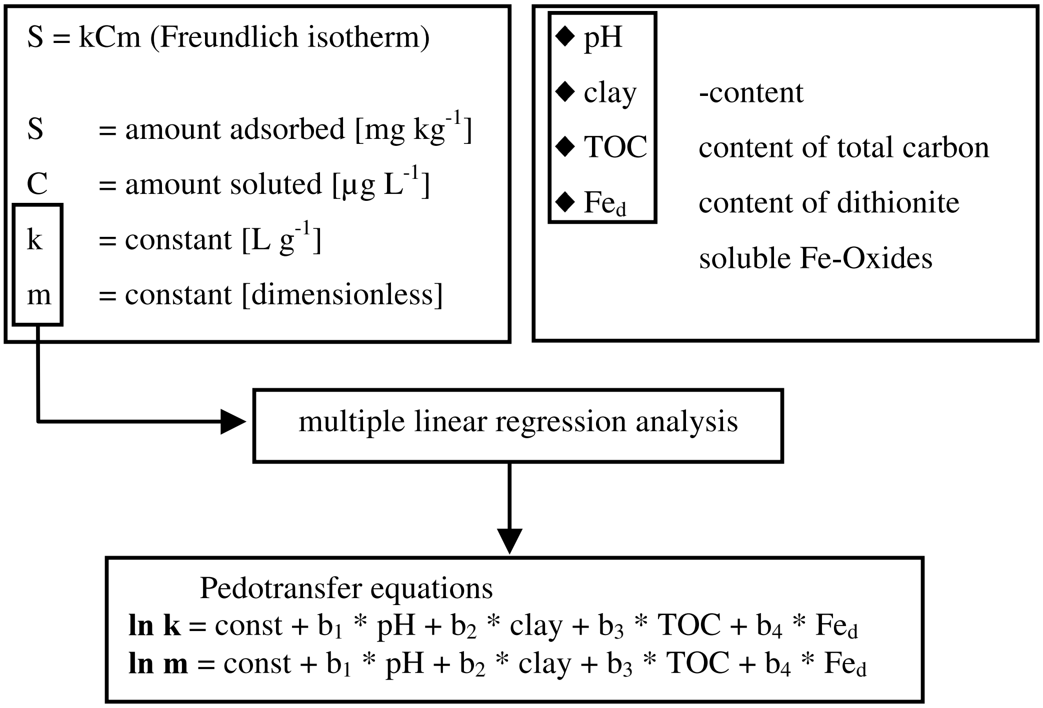

Fig. 1: Scheme for the regionalization of trace element retention capacities of 40 key soil profiles from the area of Freiberg/Saxony.

Material and methods

Soils

Soil samples originate from 40 profiles which are typical for the soils in the region of Freiberg/Saxony in Germany. These soil profiles are considered as representative profiles so that each soil type of that region is entering into the examination (*Sächsisches Landesamt für Umwelt und Geologie,* 1997; pers. comm.). These profiles are depicted on the soil map sheet L5146 Freiberg/Saxony (*Sächsisches Landesamt für Umwelt und Geologie*, 1996a). The sampling sites are located in the north-west of the Erzgebirge, where the prevailing soil type is cambisol consisting of detrital loess or clay above magmatite and metamorphic rocks. In moist areas the mostly sandy cambisols are replaced by eutric gleysols, dystric gleysols and podzols. The actual use of the soils at the sampling sites is manifold. Soils under forests and agricultural land use were examined as well as soils which are disturbed by human activity. Samples were taken from each horizon over the whole depth of each profile resulting in a sample volume of 159 soil samples. The sample collective shows a high heterogeneity in most of the determined parameters. Table 1 gives an impression about the variability of the most interesting parameters for this study.

Table 1: Physical and chemical soil parameters (clay content, pH, content of total organic carbon, dithionite extractable iron oxides) of 159 soil samples originating from 40 key profiles of the area of Freiberg/Saxony (Kartenblatt Freiberg L 5146).

Physical and chemical parameter [unit]	Source	Results		
		Median	Min	Max
Particle size distribution clay content (%)	according to Köhn (DIN 18 123)	11.26	1.86	36.60
pH-value	DIN 19 684 Part 1	4.73	2.87	6.92
Total organic carbon TOC (%)	TGL 25418/04	0.63	< 0.2	5.33
Dithionite extractable iron Fe_d (g/kg)	According to Mehra and Jackson (1960), modified	10.06	0.057	106.86

In general it should be remarked that measurements below detection limit were set to one half of detection limit to include these cases into the statistical analysis. Further experiments were carried out to quantify the contamination of the surveyed soils. According to *Zeien* (1995), the heavy metal contents were determined in extraction solutions of different extraction strength, for estimating the kind of heavy metal binding. The total content was analysed by digestion with aqua regia. The available fraction to plants was extracted with EDTA, and the mobile fraction was determined by means of an extraction with calciumnitrate. For details see Table 2.

Table 2: Methods to obtain aqua regia digestible, EDTA- and $Ca(NO_3)_2$-extractable cadmium and arsenic contaminations from 159 soil samples taken in Saxony.

Extraction solution	Method	Source
Aqua regia	HCl (37%) 18 mL and HNO_3 (65%) 6 mL 5 g ground soil, <0.1 mm heated for 2 h to 160 °C filled up to 100 mL with HNO_3	*VDLUFA* (1991)
EDTA	50 mL 0.025 *M* Na-EDTA, pH 4.5 5 g sieved soil, <2 mm extracted 90 min on a horizontal shaker with 175 rpm	According to *Zeien* (1995), modified
Calciumnitrate	50 mL 0.01 *M* $Ca(NO_3)2$ 5 g sieved soil, <2 mm extracted 90 min on a horizontal shaker with 175 rpm	According to *Zeien* (1995), modified

Sorption experiments

The sorption isotherms were established by means of batch experiments. A 0.1 *M* calciumnitrate solution, spiked with different heavy metal concentration levels (see Figure 2), was supplied to the soil, with a soil: solution weight ratio of 1: 2.5. While shaking the soil: solution suspension the trace elements were allowed to equilibrate. After the equilibrium was established the aqueous phase was separated from the soil by centrifugation. Supernatant was filtered off and the clear solution was then analysed for metal concentration.

<table>
<tr><td colspan="2">sample preparation:
air drying of the soils
sieving to 2 mm</td></tr>
<tr><td colspan="2">preparation for the experiment:
polypropylene and polyethylene vessels were soaked
for 24 h in diluted HNO_3
and rinsed twice with ultrapure water (MILLIPORE®)</td></tr>
<tr><td>arsenic batch-experiment:
soil mass: 50 g
added solution: 125 mL, 0.01 M $Ca(NO_3)_2$
As addition: 25; 62.5; 125; 250 mg/kg
added as NaH_2AsO_4</td><td>cadmium batch-experiment:
soil mass: 20 g
added solution: 50 mL, 0.01 M $Ca(NO_3)_2$
Cd addition: 6*10-4; 00.6; 1.1; 11; 55; 110 mg/kg
added as $CdCl_2$; ^{109}Cd addition: 935 Bq</td></tr>
<tr><td colspan="2">sorption:
establishing equilibrium 15 h
horizontal shaker 175 rpm room temperature</td></tr>
<tr><td colspan="2">separating the two phases:
centrifugation (15 min, 8360*g)
filtration (0.45 µm) with polypropylene syringe-filter (WHATMAN®)</td></tr>
<tr><td>analysis of arsenic:
hydride-generation – (Varian VGA 76)
atomic absorption spectrometry (Varian AA 10)
measurement: 197.2 nm; slid width: 0.5 nm
atomisation: in a quartz glass flow-cell by
air/acetylene-flame
AsH2-generation (on-line): 0.6% NaBH4
0.5% NaOH; 7 M HCl</td><td>analysis of cadmium:
Liquid scintillation counter:
(Beckman LS 6500)
scintillator: INSTA GEL II (Packard)
preset time: 15 min
counting precision: 2%
window set: 0-50 keV
quench correction</td></tr>
</table>

Fig. 2: Scheme of the experimental procedure to obtain Freundlich isotherms by sorption batch experiments using two different techniques as conventional and radioanalytical methods for the two elements arsenic and cadmium, respectively.

One important difference in the experimental set up of the two elements is that cadmium was used as the radioisotope ^{109}Cd whereas arsenic was analysed as the stable isotope ^{75}As.

Radioanalysis is preferable in heavy metal research at the laboratory scale because sorption onto laboratory vessels can be easily observed, and the detection limit is far lower than that which can be achieved by means of conventional analytical methods. Moreover, the sample storage is not a problem because after separating the two phases it does not matter whether ^{109}Cd is sorbed on vessel-walls since the activity of the solution is counted *with* these vessels.

The approach to carry out radioactive batch experiments follows a method according to *Schlüter* (1997). Those radioactive experiments differ in only one point from classic nonradioactive ones. The solutions with different heavy metal concentration levels were spiked with radioactive ^{109}Cd. These tracer-solutions were added to the soil. After equilibration and separation the remaining radioactivity in the filtrate was counted in a liquid scintillation counter. Figure 2 shows schematically the experimental approach.

Results and discussion

The examination of the sorption capacities was preceded by an inventory control of cadmium and arsenic contents in the soils. It showed wide ranges depending on the element surveyed and the kind of solute chosen for the extraction (see Table 3).

Table 3: Values of arsenic and cadmium contaminations in 159 soil samples from the area of Freiberg/Saxony obtained by $Ca(NO_3)_2$-(0.01 *M*) and EDTA-extraction (0.025 *M*) and aqua regia digestion (HCl/HNO_3; 3:1), respectively

Element		Extraction / digestion method		
		$Ca(NO_3)_2$	EDTA	aqua regia
		(mg/kg)	(mg/kg)	(mg/kg)
As	min	<0.15	<0.15	0.74
	max	4..39	346	6690
	median	<0.15	0.25	23.6
Cd	min	<0.03	<0.03	<0.03
	max	4..33	15.3	18.5
	median	<0.03	0.05	0.2

The levels of cadmium and arsenic total contents observedwere in some cases extremely elevated above the background contents present in Saxon soils. The median value of the background contents for cadmium amounts to 0.2 mg/kg (*Sächsisches Landesamt für Umwelt und Geologie*, 1996b) whereas the measured contents for the surveyed soils resulted in 1.12 mg/kg. Arsenic shows median values of 9.2 mg/kg (*Sächsisches Landesamt für Umwelt und Geologie*, 1996b) and 61.05 mg/kg, respectively. The increased metal contents are due to ore processing in this region (*Sächsisches Landesamt für Umwelt und Geologie*, 1993). With respect to the influence these contents, herein after referred to as ‘initial contents’, are having onto the exchange processes in soils, they have to be incorporated into the sorption isotherms. To avoid an underestimation of sorption capacities, the initial contents have to be considered at each measured point so that the whole sorption isotherm is adjusted.

In spite of heterogeneity of bond types and forces, the question arises which fraction of the initial content has to be considered.

This problem is already discussed by other authors. *Springob* et al. (1997) followed an absolute empirical mathematical strategy. They postulated to incooperate an initial content at a level which confirms the linearity of the double log-transformed Freundlich isotherm. Numerical variation resulted in values of 50% of EDTA-extractable content and 40% of aqua regia digestible content of Cd, respectively. Theses portions have to be considered as hypothetical initial content. This method presupposes the validity of the Freundlich equation especially at the lowest concentration level. However, *Alloway* et al. (1985) found that at the lower end of any sorption isotherm for cadmium a linear equation describes the adsorption most suitable. Therefore, this method does *not* provide a definitive solution.

Filius et al. (1991) elected the whole EDTAextractable fraction to include the potentially exchangeable amount. Therefore, the EDTA fraction is added to the sorbed amount in the soil after equilibration. Following this path, the sorption isotherms for arsenic in this paper were adjusted.

This procedure requires that the initial contents completely remain sorbed while the different amounts of arsenic were added. Indeed it is a matter of fact that beside the added amounts the initial contents are distributed between the solid and the aqueous phase as well. Using conventional analysis without radioisotopes the portion remaining on the solid phase cannot be assessed.

Since cadmium was analysed by radioanalysis there is another possibility to include the initial contents into each point of the sorption isotherms. Due to the two classes of Cd-isotopes used in the batches it is possible to estimate the sorption behaviour only of the added heavy metals alone. Considering that the EDTA fraction competes with the added fraction for sorption sites, these two fractions are combined for the calculations (see Equation 1).

$$Ct_{(stable)} = \frac{C_{t(^{109}Cd)}}{C_{0(^{109}Cd)}} \cdot (C_{0(stableCd)} + EDTA_{Cd}) \tag{1}$$

where

$C_{t(^{109}Cd)}$ = radioactive cadmium after equilibration [cpm], measured
$C_{0(^{109}Cd)}$ = radioactive cadmium added to the batch [cpm]
$C_{0(stableCd)}$ = stable cadmium added to the batch [μg/l]
$EDTA_{Cd}$ = EDTA extractable amount of cadmium [μg/l]
$C_{t(stableCd)}$ = stable cadmium in solution after equilibration [μg/l], calculated.

By means of this equation the initial contents are prorated to the solid and to the aqueous phase.

Figure 3 shows the results of the batch experiments of at least two soils (one for each element). These soils are representative for most of the examined soils. The x-axes represent the measured element concentration in the solution phase after 16 h of equilibration, y-axes represent the element concentration in the soil at the same time. The measured data were fitted to the Freundlich isotherm. The quality of the fit (R^2) of 159 soil samples was within a range of 0.89–0.99 for cadmium and 0.81–0.99 for arsenic.

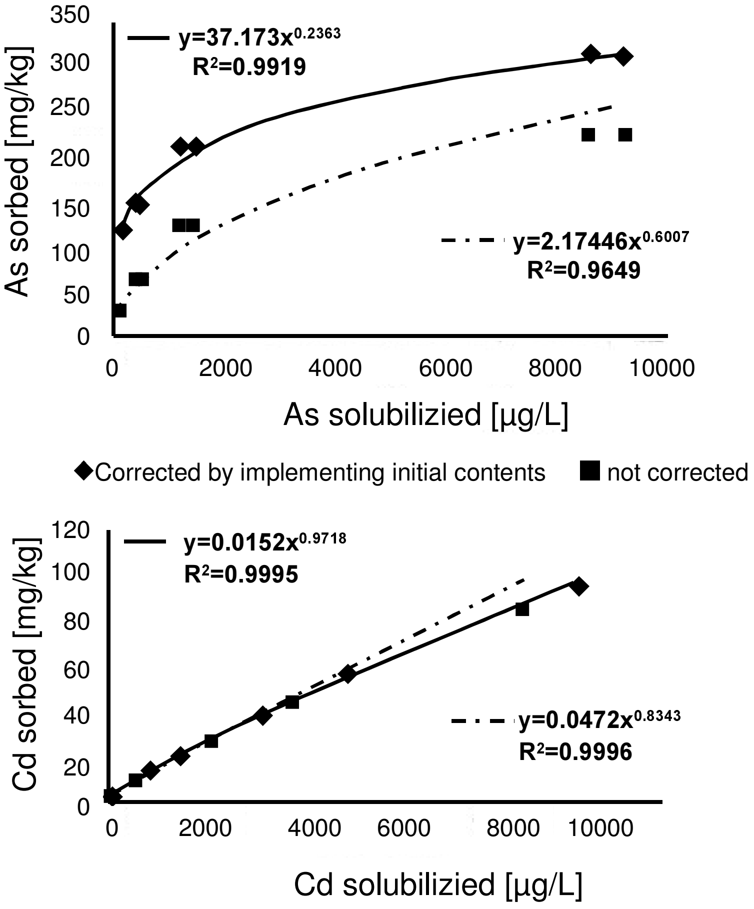

Fig. 3: Alteration of the curve of Freundlich isotherms determined by batch experiments with and without correction of the data by implementing EDTA-extractable As and Cd amounts (initial contents).

The continuous lines give an impression about how the curvature is influenced by the different correcting procedures. As it can be seen, the level of adsorption increases drastically in case of arsenic whereas the shape of the curve is not changed. Suspicion arises that this way of data revision might be biased too strongly. The correction by using radioanalysis does not result in increased adsorption levels but in weak changes of the curves. Adjusted isotherms show a smaller gradient which illustrates lesser sorption capacities.

By correlation tests with the selected soil parameters the relevancy of the constants (k; m) determining the Freundlich equation were affirmed. Indeed, different parameters are decisive for the retardation of the different elements. The sorption of Cd is highly affected by the pH of the soil (*Soon*, 1981; *Kabata Pendias* and *Pendias*, 1992) (Figure 4).

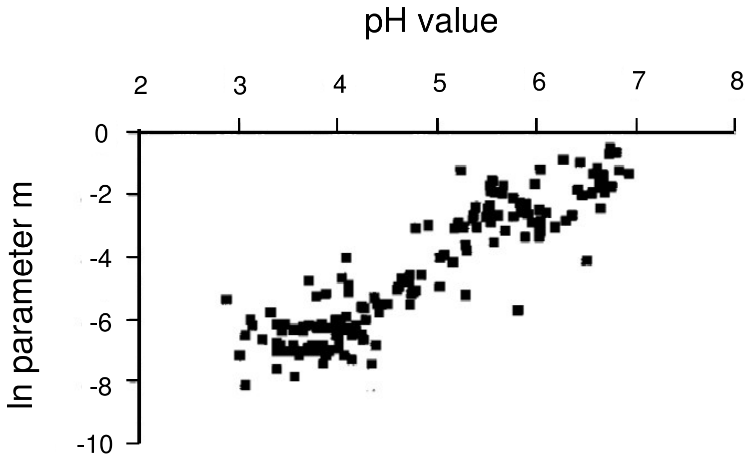

Fig. 4: The correlation between the measured pH-values of the surveyed soils and the natural logarithm of parameter *k* for cadmium of the Freundlich equation determined by batch experiments illustrates the strong dependency of cadmium sorption from soil pH.

The results of the linear multiple regression analysis confirm the strong correlation between pH and Cd sorption (Table 4) as long as the beta coefficient of pH is the highest for all explanatory variable. The partial regression coefficient of pH significantly (α = 0.05) influences the determination of the Freundlich parameters ln *k* and ln *m*. In addition to pH the total organic carbon, dithionite soluble iron, and the silt content significantly influence ln of parameter *k*. The natural logarithm of parameter *m* is significantly (α = 0.05) influenced by pH and total organic carbon content. In general the obtained linear functions, the so-called pedotransfer functions (PTEs), reach adjusted regression coefficients which are significantly (α = 0.05) different from 0.

Table 4: Results for Cd from a linear multiple regression analysis from 159 soil samples. The natural logarithm of Freundlich parameter *k* and *m* were estimated on the basis of pH-value, clay content, content of total organic carbon and the content of dithionite extractable iron oxides.

Parameter ln *k*			Adjusted R^2 0.907 Signif. 0.000		Parameter ln *m*		Adjusted R^2 0.607 Signif. 0.000	
	b	Beta	*T*	Signif.	*b*	Beta	*T*	Signif.
Const.	-13.65		-56.69	0.00	0.124		7.84	0.00
pH	1.71	0.91	34	0.00	$-4.97*10^{-2}$	-0.83	-15.02	0.00
Fe_d	$9.26*10^{-3}$	0.06	2.5	0.01	$9.13*10^{-5}$	0.02	0.37	0.71
TOC	0.54	0.26	10.01	0.00	$-7.84*10^{-3}$	-1.12	-2.213	0.03
Silt	$6.35*10^{-3}$	0.06	2.3	0.023	$3.38*10^{-4}$	0.11	1.86	0.065

Sorption of arsenic is controlled by different parameters (*Jacobs* et al., 1970) like the content of dithionite soluble iron, the total organic carbon, but also the pH (*Livesy* and *Huang*, 1981; *Masscheleyn* et al., 1991). However, the coherence between the soil parameters listed above and the sorption of arsenic could only be *partially* observed in the presented batch experiments. As the factor for total organic carbon, clay and dithionite soluble iron is significant ($\alpha = 0.05$) for the natural logarithm of parameter *k*, the influence of pH could not be verified. The ln of parameter *m* only is significantly influenced by the total organic content (Table 5).

Table 5: Results for As from a linear multiple regression analysis from 159 soil samples. The natural logarithm of Freundlich parameter k and m were estimated on the basis of pH-value, clay content, content of total organic carbon and the content of dithionite extractable iron oxides.

Parameter ln *k*			Adjusted R^2 0.174 Signif. 0.000		Parameter ln *m*		Adjusted R^2 0.072 Signif. 0.005	
	b	Beta	*T*	Signif.	*b*	Beta	T	Signif.
Const.	1.22		2.84	0.01	-0.71		-5.52	0.00
pH	$1.26*10^{-2}$	0.01	0.16	087	$1.4*10^{-2}$	0.05	0.61	0.54
Fe_d	$4*10^{-2}$	0.26	3.47	0.01	$6.42*10^{-3}$	-0.15	-1.85	0.07
TOC	-0.24	-0.22	-2.83	0.01	$6.94*10^{-2}$	0.23	2.77	0.01
Silt	$1.59*10^{-2}$	0.2	2.63	0.01	$2.07*10^{-3}$	-0.09	-1.14	0.26

In fact the regression coefficients are significantly different from zero, but with 17 and 7% the fit is so poor that a prediction of the sorption behaviour of arsenic is not possible by means of the obtained PTEs.

Compared to former examinations by *Fahrenhorst* (1993) the R^2-values are clearly lower for both elements. elements. One reason for this may be the great difference between the sample collectives. As *Fahrenhorst* (1993) examined only *one* single soil type, in our survey 40 different soils are considered. The resulting 159 soil samples vary in wide ranges in different parameters like pH-value, clay content or content of total organic carbon. Subdividing the soil samples in groups of similar properties does not result in an increase of R^2-values but changes the factor combination of explaining variables in the regression analysis (statistical data not presented here). Assorting the samples in case of cadmium in groups of TOC above and below detection limit (<0.2%) shows that in the presence of organic material sorption is significantly ($\alpha = 0.05$) influenced by pH and the amount of TOC. If TOC is very low, other sorption sites like silt and iron oxides/ hydroxides become more important (significant $\alpha = 0.05$). In case of arsenic the parameters TOC, clay and dithionite soluble iron are significant in presence of organic material, while only pH is significant when there is predominantly mineralic material in soil. In general the fit for arsenic is unsatisfactory. Probably one or more important parameters influencing the sorption (e.g. redox potential) are still missing in the statistical analysis.

Another problem are the high initial contents of Cd and As which influence the shape of the sorption isotherms. Consequently, the regression analyses to calculate the PTEs are influenced, too (Figure 2). Also for this reason the validity range of the obtained PTEs is limited to the examined region.

In conclusion further research is needed to address the question how to incorporate 'initial contents' into the process of trace element adsorption. Furthermore, the handling of the heterogeneity of a sample collective remains uncertain. To fill these gaps, further examinations in other regions of Germany are planned. With this enlarged data base the authors will be able to subdivide the soil samples into groups of similar properties which will contain enough data to perform statistical analysis.

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Anhang K

Comparison of decision support systems for an optimised application of compost and sewage sludge on agricultural land based on heavy metal accumulation in soil

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Abstract

Two different decision support systems (DSS) for the application of organic wastes on agricultural land were developed. Both DSS calculate the maximum application period of organic waste considering the exhaustion of the uptake potential of soils for heavy metals. The definition of the uptake potential differs between the DSS alternatives. In the first DSS (DSS-AR), the uptake potential is derived from the difference of actual total heavy metal concentration in soil (according to *aqua regia* digestion) and the respective statutory limit value. The other DSS (DSS-SI) calculates the remaining sorption capacity of the soil for a heavy metal, i.e. the difference of a predefined maximum and the actual heavy metal concentration at the sorbent. The concentration of sorbed heavy metal is derived from pedotransfer functions (general purpose Freundlich isotherms) using predefined limit concentrations in soil solution (WHO drinking water quality standards) or the actual concentration of soluble heavy metal (according to neutral salt extraction), respectively. For evaluation of their individual characteristics, both DSS were tested in model scenarios using soil data (basic physicochemical properties; Cd, Pb, and Zn concentrations) from various agricultural regions and German guidelines for organic waste application. The DSS-SI showed a better performance than the DSS-AR in this context. The capacity of the soil for heavy metal uptake was used with higher efficiency, i.e. the potential was scooped while environmental limit values were still regarded. Further, the DSS-SI offered a better approximation to the natural variability of soil conditions by combination of an extended set of soil properties in comparison to the DSS-AR. Despite of these indications of good DSS-SI performance, the approach requires improvement with regard to the implemented pedotransfer functions in order to consolidate and extend the range of predictions. Further, one has to regard that the assessment of the DSS-SI is influenced by the availability of data and is only valid under the current environmental and statutory framework at the observed regional scale. For this reason, the transfer of the results of this study into regions with other administrative structure and/or environmental conditions is critical. An individual testing of the DSS-SI and the DSS-AR is required prior to the intended transfer, i.e. the implementation of the approaches in the decision support process.

Sci. Tot. Environ., angenommen

Introduction

The recycling of organic wastes (e.g. compost and sewage sludge) as an approach to simulate ecological cycles of elements has become a major task in environmental policy of the European Union (EU) during the last decades (*European Council*, 1986; *European Communities*, 1999). Since organic wastes are regarded as a potential source of various plant nutrients (European *Commission*, 2000a; *German Council* of *Environmental Advisors*, 2000), their application as fertilisers on agricultural land has evolved as the preferred option for recycling (*European Commission*, 2000b).

The EC directive 86/278/EEC (*European Council*, 1986) regulates the application of sewage sludge. It is reported that 11 members of the EU have transferred the directive into national acts, and the recycling rates vary from 11% to more than 50% (*European Commission*, 2000a). The EU intends to force the recycling of sewage sludge on agricultural land as an increase of the actual sewage sludge production of about 40% until 2005 is expected (*European Commission*, 2000a). Further, it is discussed to extend the actual regulation on compost and other organic wastes (*European Commission*, 2000c).

As organic wastes carry a variable load of toxic elements (e.g. heavy metals – *Deportes* et al., 1995; *Tichý* et al., 1997; *Han* et al., 2000) and organic compounds (e.g. polychlorinated biphenyls and estrogenic alkylphenols – *Johnson* and *Sumpter*, 2001; *Düring* and *Gäth*, 2002), it is necessary to confine their application. Limit values for the concentration of heavy metals in soil and sludge as well as maximum application rates of sludge are defined in the EC directive 86/278/EEC (*European Council*, 1986), the framework for the application of sewage sludge on agricultural land. The proposals for a revision of the current EU legislation suggest more restrictive limit values in order to assure a sustainable organic waste management up to 2025 (*European Commission*, 2000a; 2000c).

However, the concept of sustainability is based on the idea of protection and regeneration of natural resources, i.e. the perpetuation of a constant ‘stock’ of natural capital (*Pearce* and *Atkinson*, 1995). In the context of organic waste application in agriculture this criterion is not fulfilled as the soil’s buffer capacity for toxic ions, representing a resource for prevention of plant and groundwater contamination, is reduced. This reduction in buffer capacity is due to heavy metal accumulation, which results from an imbalance of input by waste application and other sources (e.g. traffic) and output by vertical transport into groundwater or plant uptake (*McGrath* et al., 2000).

The decision to apply organic wastes on agricultural land should be governed rather by the knowledge of the resource characteristics of the soils on a regional scale, i.e. their specific local potential to buffer heavy metal input, than by the idea of sustainability. The actual regulations for organic waste application, using limit values for heavy metals in soils and wastes, represent an implicit realisation of the resource concept. The definition of limit values exhibits understanding of soil as limited resource, while an explicit definition of a resource measure, i.e. an individual uptake capacity of the soil for heavy metals, is not considered.

In this paper we present two approaches to define the uptake capacity of soils for heavy metals. The approaches are regarded as alternative proposals to supplement the current regulations in order to intensify the idea of resource management on individual agricultural sites. As a representative for current regulation in the European Community, German legislation on organic waste application (*German Parliament*, 1992; 1998) is used if calculations require a reference to actual standards. The approaches are referred to as DSS-AR and DSS-SI, meaning ‘decision support system based on *aqua regia* extraction’ and ‘decision support system based on sorption isotherms’, respectively. The abbreviations are considered as a combination of the main function of the approaches and the key factors for decision support. The following chapters include an introduction to the proposals and an evaluation of their adaptability in resource management practice resulting from model scenarios with data from various agricultural sites in Germany.

Outline of the decision support systems

Decision support system based on aqua regia extraction (DSS-AR)

Within current legislation (*German Parliament*, 1992; 1998) the concentration of heavy metals in soil as extracted by *aqua regia* is one major criterion of organic waste application. In dependence of soil texture and soil pH, limit values for *aqua regia* extractable Cd, Zn, Pb, Cr, Cu, Ni and Hg have been defined (Table 1).

Table 1: Overview of *aqua regia* limit concentrations of heavy metals in organic wastes and soils (mg kg^{-1} dry matter) for permission of organic waste application according to German law (German Parliament, 1992; 1998).

		Cd	Zn	Pb	Cr	Cu	Ni	Hg
Organic waste								
Compost^a		1.0	300	100	70	70	35	0.7
Sewage sludge^b		10 (5)^c	2500 (2000)^c	900	900	800	200	8.0
Top soil								
Compost	Clay^d	1.5 (1.0)^e	200 (150)^e	100	100	60	70	1.0
	Loam^d	1.0 (0.4)^e	150 (60)^e	70	60	40	50	0.5
	Sand^d	0.4	60	40	30	20	15	0.1
Sewage sludge	pH > 5	1.5 (1.0)^c	200 (150)^c	100	100	60	50	1.0

[a] Application rate: 6.7 t ha^{-1} yr^{-1}.
[b] Application rate: 1.7 t ha^{-1} yr^{-1}.
[c] Soils with 5 < pH < 6 and clay < 50 g kg^{-1}.
[d] Classification according to German particle size distribution scheme (AG Boden, 1994).
[e] Soils with pH < 6.

Considering the actual heavy metal status of the soil as indicated by *aqua regia* extractable heavy metals, the uptake potential of the soil for a specific heavy metal can be defined as the difference of limit and actual concentration of the element in soil:

$$UP_{HM} = AR_{HM,Limit} - AR_{HM,Actual} \tag{1}$$

where UP (mg kg^{-1}) is the uptake potential of the top soil for the respective heavy metal indicated by HM (e.g. Cd, Pb, Zn), $AR_{\underline{\mathrm{HM,\ Limit}}}$ (mg kg^{-1}) and $AR_{\underline{\mathrm{HM,\ Actual}}}$ (mg kg^{-1}) are the limit value and the actual concentration of *aqua regia* extractable heavy metal in soil, respectively.

For ease of calculation, the uptake capacity is referred to the top soil (up to 30 cm depth) of an agricultural site of 1 ha:

$$\overline{UP}_{HM} = \int_A \int_z UP_{HM} \cdot \rho \cdot dz \cdot dA \tag{2}$$

where $\overline{UP}_{HM}$ (mg) is the uptake capacity of the top soil of 1 ha; $\underline{\rho}$ (kg dm^{-3}) is soil bulk density (assumed 1,500 kg m^{-3}), $\underline{z}$ (m) is depth of top soil (defined as 0.3 m) and $\underline{A}$ (m^2) is reference area (defined as 10,000 m^2).

In the context of resource management, the prediction of application periods is of major importance for the development of long-term application strategies. The application period of organic wastes according to a specific heavy metal can be calculated as the ratio of the heavy metal uptake potential and the annual balance of the heavy metal at the considered scale (1 ha, top 30 cm):

$$D_{HM} = \frac{\overline{UP}_{HM}}{I_{HM} - O_{HM}} \tag{3a}$$

where $D_{\underline{\mathrm{HM}}}$ (yr) is the application period of organic wastes according to the specific heavy metal, $I_{\underline{\mathrm{HM}}}$ (mg yr^{-1}) and $O_{\underline{\mathrm{HM}}}$ (mg yr^{-1}) are the annual input and output of this heavy metal on the agricultural site, respectively.

Equation (3a) is based on the assumption that heavy metal input to soil exceeds the output, i.e. that heavy metals accumulate in soil. Various studies on agricultural sites treated with compost or sewage sludge prove that this assumption is valid (*Alloway*, 1995).

Assuming the organic waste application dominates the input of heavy metals and output can be neglected, equation (3a) can be simplified:

$$D_{HM} = \frac{\overline{UP}_{HM}}{q_{HM}} \tag{3b}$$

where q_{HM} (mg yr^{-1}) is input of heavy metals by organic waste application.

After calculation of D_{HM} for all different heavy metals included in the data set, the maximum application period of organic wastes according to DSS-AR is determined by the smallest value in the set of D_{HM}:

$$D_{DSS-AR} = \min(D_{HM}) \tag{4}$$

where $D_{DSS\text{-}AR}$ (mg kg^{-1}) is the maximum application period of organic wastes according to DSS-AR.

Decision support system based on sorption isotherms (DSS-SI)

The uptake of heavy metals in soil is governed mainly by the process of heavy metal sorption to soil surfaces offered by various soil components, mainly soil organic matter, clay minerals, and oxides (*Shirwal* and *Deshpande*, 1984; *Christensen*, 1989; *Sauvé* et al, 2000b; *Weng* et al., 2001). The second approach (DSS-SI) is based on this relationship between the ability of the soil to serve as a sorbent and its resource function by definition of the uptake potential in dependence of the soil sorption characteristics.

A common mathematical approach for the description of sorption in soil is the definition of sorption isotherms (*Travis* and *Ethnier*, 1981; *Hinz*, 2001). In the context of heavy metals, the Freundlich sorption isotherm proved as a reliable relationship:

$$S = k \cdot (C)^m \tag{5}$$

where $\underline{S}$ (mg kg^{-1}) is sorbed phase concentration of the heavy metal, $\underline{C}$ (mg L^{-1}) is solution phase concentration of the heavy metal, and $\underline{k}$ (mg^{1-m} L^m kg^{-1}) and $\underline{m}$ (dimensionless) are empirical parameters.

In resource management the sorption characteristics of the soil are required at least on a regional scale. As the analytical effort to determine the sorption isotherms for the demanded sampling grid exceeds the level of applicability, the sorption characteristics have to be estimated from other soil properties by pedotransfer functions (PTF). *Chardon* (1984) and *van der Zee* and *van Riemsdijk* (1987) introduced a PTF for sorption of heavy metals in soil using an extension of the coefficient $\underline{k}$ in equation (5):

$$k = \beta_0 \cdot \prod_{i=1}^{n} (X_i)^{\beta_i} \tag{6}$$

where X_i are the soil properties considered relevant for sorption, $\beta_{\underline{i}}$ are empirical parameters.

In the context of this study, we refer to the PTF of *Schug* et al. (2000), which is based on the most extensive homogeneous data collective presented in the literature. The PTF can be written in general:

$$S = \beta_0 \cdot (H^+)^{\beta_1} \cdot (SOC)^{\beta_2} \cdot (CLAY)^{\beta_3} \cdot C^m \tag{7}$$

where H^+ (mol L^{-1}), *SOC* (% by mass) and *CLAY* (% by mass) consider the influence of pH, SOC, and clay content in soil, respectively. Schug (2000) and *Horn* and *Gäth* (2001) parameterised equation (7) for Cd, Pb, and Zn by linear regression analysis of the logarithm of the equation. A summary of the estimation results is given in Tab. 2.

In order to calculate the uptake potential for a specific heavy metal *HM* from the parameterised PTF the user has to consider two conditions of heavy metal pollution in soil at first:

The actual status of heavy metal pollution, i.e. the current concentration of the heavy metal in soil solution ($C_{HM,\ Actual}$) and at the sorbent ($S_{HM,\ Actual}$) according to equation (7). In this study, the concentration in soil solution is approximated by the amount of heavy metal extractable with solutions of neutral salts. This approximation is in accordance with the experimental set-up of Schug et al. (2000) who used 0.01 *M* calcium nitrate as background electrolyte for derivation of the PTF.

Table 2: Estimated parameters, variable ranges and statistical measures of the general purpose Freundlich isotherms for Cd, Pb, Zn (data compiled from Schug, 2000 and Horn and Gäth, 2001).

	Cd	Pb	Zn
Parameters			
ß$_0$	0.00515	7.889	0.179
m	0.887	0.327	0.546
ß$_1$	-0.661	-0.289	-0.437
ß$_2$	0.662	0.281	0.488
ß$_3$	-	0.155	-
Variable ranges			
pH (-)	2.9 – 7.8	2.9 – 7.8	3.5 – 6.4
SOC (g kg^{-1})	1.0 – 568.0	1.0 – 568.0	3.0 – 83.0
CLAY (g kg^{-1})	2.0 – 708.0	2.0 – 708.0	125.0 – 428.0
Statistics			
$R^2_{adj.}$	0.957	0.654	0.848
Number of data sets	2671	2085	583

The maximum tolerable heavy metal pollution, i.e. the limit concentration of the heavy metal in soil solution ($C_{\underline{\mathrm{HM,\ Limit}}}$) and at the sorbent ($S_{\underline{\mathrm{HM,\ Limit}}}$) according to equation (7). In this study, the former WHO drinking water quality standards (Cd: 5 µg L^{-1}; Pb: 50 µg L^{-1}; Zn: 5000 µg L^{-1} – WHO, 1996) are used by default to define the limit concentration in soil solution. The former standards are preferred in comparison to the actual WHO quality criteria, because they represent the only consistent legislative framework, which includes all elements observed in this study. Considering the standards are applied to soil solution, which is not identical to drinking water, the difference of the former standards to the actual WHO values is of minor importance.

The difference of the limit and the actual concentration of the heavy metal at the sorbent results in the sorption capacity of the soil, which is a similar resource indicator as the uptake potential of the DSS-AR. If the sorption capacity is referenced to the top soil of 1 ha as in the DSS-AR, it can be calculated as follows:

$$\overline{\overline{\delta S}}_{HM} = \int_A \int_z \left(S_{HM,Limit} - S_{HM,Actual}\right) \cdot \rho \cdot dz \cdot dA \qquad (8)$$

where $\overline{\overline{\delta S}}_{HM}$ (mg) is the sorption capacity of the top soil referring to an area of 1 ha.

The application period according to the specific heavy metal and the maximum application period according to the DSS-SI, $\underline{D}_{\underline{\mathrm{DSS\text{-}SI}}}$, can be calculated from the sorption capacity using equations (3) and (4), respectively.

Model scenarios

In order to test the performance of the two DSS, we calculated application periods after simulation of continuous organic waste application on top soils in various agricultural regions in Germany. The data of the top soils were selected from the literature, and detailed information on the soil characteristics and the experimental procedures for soil analysis is given in the respective studies.

Düring et al. (2002) provided pH values, SOC contents and particle size distributions as well as concentrations of total (i.e. *aqua regia* extractable according to the international standard ISO 11466) and soluble (i.e. 1 *M* ammonium nitrate extractable according to the German standard DIN 19730) Cd, Pb and Zn of 18 soil samples from two locations within the German federal state of Hesse. At the first location, the soil was characterised as an Eutric Cambisol in Pleistocene aeolian sand. The soil at the second field site was characterised as a Luvisol in silt loam (Pleistocene loess).

Schug (2000) worked in the same region and investigated 49 samples of Cambisols and Luvisols (in Pleistocene periglacial slope deposits from mixtures of weathered Carboniferous rocks and loess) using the same analytical methods as *Düring* et al. (2002) with the exception of extracting soluble heavy metals by 0.01 *M* calcium nitrate instead of ammonium nitrate. Due to the similarities of the investigations of *Schug* (2000) and *Düring* et al. (2002), their data are treated as one data collective of 67 samples in this study. In the following, the data collective is indicated as CH.

A second data collective was taken from *Springob* and *Böttcher* (1998) who investigated 24 samples of the catchment 'Fuhrberger Feld' 30 km north east of Hannover (German federal state of Lower Saxony; data collective indication: FF). The soils were mainly podzolic and gleyic types as well as intermediates, which developed in Pleistocene sands. Analytical procedures for soil analysis were similar to *Schug* (2000), but the soils had only been investigated for Cd.

Ingwersen (2001) provided a third data collective of 154 samples collected at the waste water irrigation area 10 km north west of Braunschweig (German federal state of Lower Saxony; data collective indication: BR). The investigation area is situated on a river terrace, which was formed during the last Pleistocene ice age. Soil investigations included pH values and SOC as well as Cd concentrations in *aqua regia* and soluble Cd according to extraction with 0.0025 *M* calcium chloride. The soils of the river terrace had been classified as sands (< 50 g kg^{-1} clay) and loamy sands (< 80 g kg^{-1} clay), but no specific particle size distributions for the samples were available. As the clay content is crucial for the decision of organic waste application, it was assumed in this study that all soils described by *Ingwersen* (2001) contained less than 5 g kg^{-1} clay, i.e. further calculations considered a worst case situation.

In order to define organic waste application rates in the model runs, two basic application strategies were considered. In a first scenario, all soils were fertilised exclusively with sewage sludge at the maximum rate and with maximum heavy metal concentrations as defined by the respective German regulation (*German Parliament*, 1992; Tab. 1). The second application scenario worked similar using compost instead of sewage sludge and the respective application rates and heavy metal concentrations as shown in Tab. 1 (*German Parliament*, 1998). Calculation of application periods was performed using the simplified approach according to equation (3b) in both scenarios.

Results and discussion

Data collectives as representatives of natural variability

Prior to the evaluation of the DSS, the data collectives used for the comparison of the two different DSS approaches should be tested for their representativeness of natural variability.

Regarding pH and SOC (Fig. 1) the data collectives showed considerable variation. Nevertheless, the sector of pH 5.0-6.5 and SOC 5-20 g kg^{-1} is emphasised as indicated by the higher spot density in the plot. This sector covers the typical range of pH and SOC for agricultural soils resulting from human activity. Regarding clay content (Fig. 1), the data collectives also show considerable natural variability. In this case, the samples reflect their different geogenic origin.

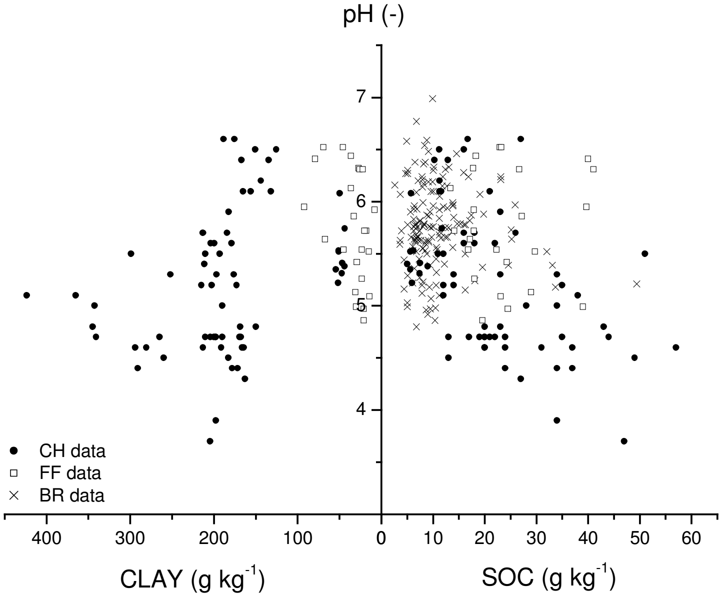

Fig. 1: Soil properties of samples from three data collectives taken from literature (CH: data from *Schug*, 2000 and *Düring* et al., 2002; FF: data from *Springob* and *Böttcher*, 1998; BR: data from *Ingwersen*, 2001).

Fig. 2 gives an overview of total and soluble heavy metal concentrations of the three data sets. The plot of soluble Cd from the three data collectives (Fig. 2a) implies that these data represent natural variability. However, this interpretation should be regarded with care as different extractants had been used to derive the fraction of soluble Cd. These extractants do not yield stringently similar results as the comparative evaluations of *Beckett* (1989), *Boekhold* et al. (1993) and *Aten* and *Gupta* (1996) show.

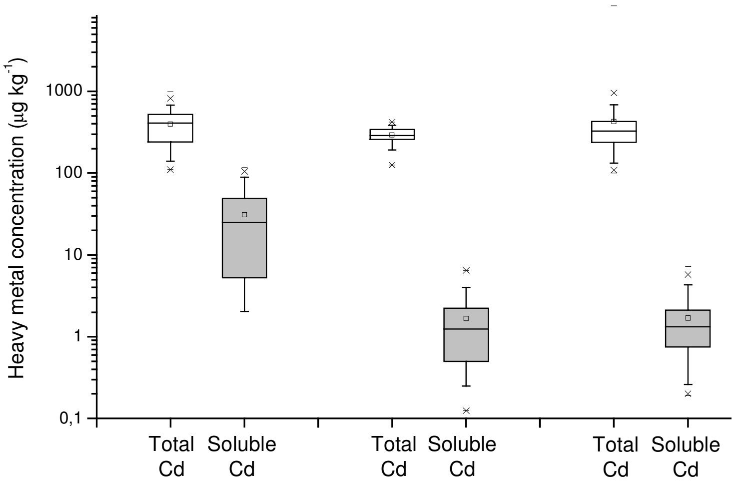

Fig. 2: Concentrations of total and soluble heavy metals in the soil samples, (a) Cd concentrations for all samples of the three data collectives, (b) Cd, Pb and Zn concentrations for the CH samples (samples labelled 'below detection limit' not shown).

Explanation of box-whisker-plots: horizontal lines in the box: 25th, 50th, and 75th percentile values; error bars: 5th and 95th percentile values; symbols below the 5th percentile error bar: 0th and 1st percentiles; symbols above the 95th percentile error bar: 99th and 100th percentiles; square symbol in the box: mean value.

The combination of data from varying analytical procedures, though entailing uncertainties, was performed because of the limited availability of data from the literature. In the DSS comparisons presented in the following sections, the results proved independent of the experimental individualities. The differences observed between both DSS occurred similarly in all data collectives.

Comparison of Cd application periods for all data collectives

Fig. 3 shows Cd application periods for all data collectives with respect to sewage sludge as well as compost application. Regarding the projections of the DSS-AR, the similarity of the predictions for the three data sets within an application scenario becomes apparent. The maximum difference of the three medians in each of the two DSS-AR application scenarios is 17 yr (sewage sludge) and 75 yr (compost). The result for the compost scenario is strongly influenced by a great share of CH samples (40%), which are characterised by an *ab initio* exhaustion of the uptake potential. These samples lead to a distribution of CH sewage sludge application periods with two peaks not applicable for the interpretation. Excluding the CH data from the calculation, the remaining data sets show a distinctly smaller median difference of 25 yr.

Regarding the difference of the three interquartile ranges in each of the two DSS-AR scenarios the maximum values are also small (sewage sludge 30 yr, compost 51 yr). The main reason for the similarity of the DSS-AR results is the minor variation of the basic data for calculation of application periods, i.e. the concentration of *aqua regia* extractable Cd in the samples (Fig. 2).

In contrast, much stronger differences can be observed for application periods calculated according to the DSS-SI. The maximum difference of the three medians in each application scenario amounts to 143 yr (sewage sludge) and 211 yr (compost), the maximum difference of the three interquartile ranges is 235 yr (sewage sludge) and 306 yr (compost). However, the major fraction of the observed difference is contributed by the data of FF. As the FF data collective is distinctly smaller than the other data sets and the calculated application periods scatter considerably, the statistical analysis may be biased and lead to a misinterpretation of the results. If the DSS-SI results for FF data are excluded from interpretation, the observation of strong differences between the medians still holds true (sewage sludge 77 yr, compost 127 yr). The differences between interquartile ranges decrease distinctly (sewage sludge 2 yr, compost 14 yr), but a direct comparison of the DSS-AR and DSS-SI interquartile ranges for each scenario still shows that all interquartile ranges of the DSS-SI are larger than those of the respective DSS-AR. This variation is assumed to offer a better approximation of the observed natural variability of the soils. The ability of the DSS-SI for this improved representation originates from the fact that it depends on more soil variables than the DSS-AR thus offering considerably more degrees of freedom to express the individuality of a soil. The concentration of *aqua regia* used as the single environmental indicator in the DSS-AR proved insufficient sensitivity. These results are in agreement with the findings of *Gupta* et al. (1996) and *Houba* et al. (1996) who criticised the use of *aqua regia* concentrations in the decision support process because of the discrepancy between these concentrations and the respective fraction of mobile and bioavailable heavy metals.

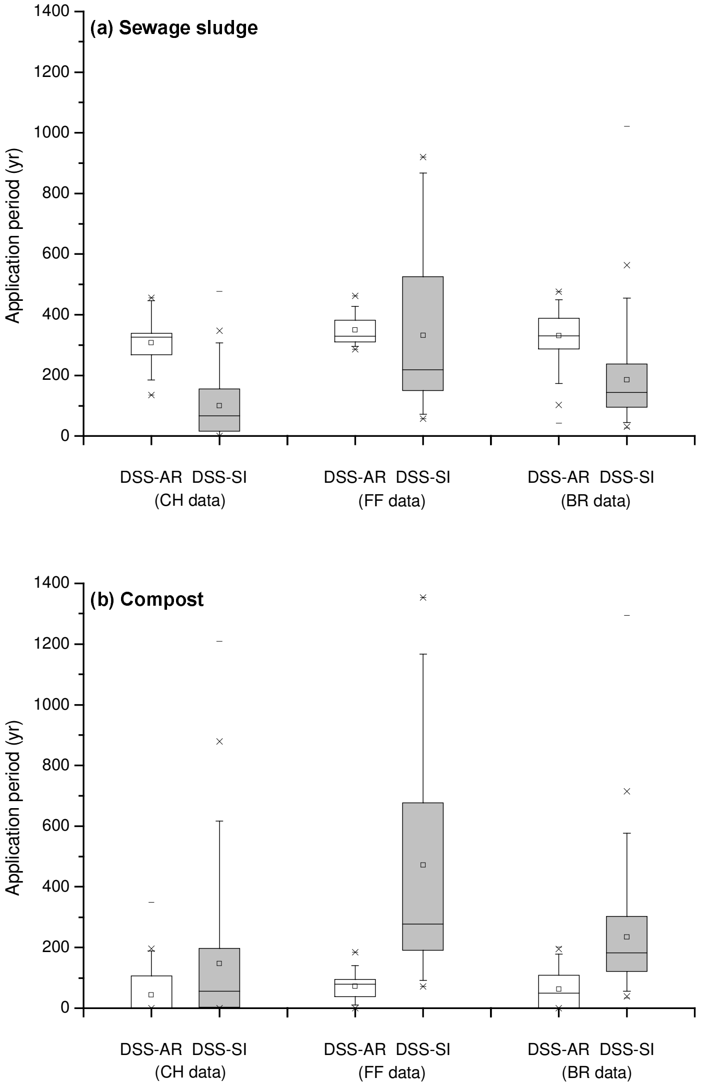

Fig. 3: Application periods of (a) sewage sludge and (b) compost for the three data collectives as predicted by DSS-AR and DSS-SI using Cd concentrations in soil. Samples prohibited from sewage sludge application by law (i.e. D_{HM} = 0 yr) are not shown as the calculation of application periods is not based on uptake potential considerations. Definition of symbols as in Fig. 2.

Regarding the median recommended application periods for the three data sets in each application scenario, the predictions of the DSS-SI differ distinctly from those of the DSS-AR. In case of sewage sludge application, the DSS-SI recommends shorter application periods than the DSS-AR, i.e. following the DSS-AR recommendation might lead to higher concentrations of heavy metals in the soil solution than described by the WHO drinking water quality standards. However, one may not finally conclude ground water hazard from this finding. The chemical composition of the soil solution can change considerably during transfer to ground water by interaction with deeper soil horizons.

In case of the median compost application periods, the DSS-SI predicts longer application periods than the DSS-AR, i.e. the concentration of heavy metals in soil solution after application according to DSS-AR recommendations will remain lower than the WHO drinking water quality criterion. For environmental protection purposes, this result is advantageous whereas from an economical perspective the DSS-AR does not exploit the entire uptake potential and compost application is interdicted too early.

Comparison of maximum application periods for CH data

For the CH data collective the maximum application periods were derived according to equation (4). Fig. 4 shows box-whisker-plots of maximum application periods for both DSS in each application scenario. The plots express the same DSS characteristics as interpreted from Fig. 3.

On the right side of Fig. 4 the relative importance of limiting factors of organic waste application for each DSS in the respective application scenario is illustrated. In both scenarios, the DSS-AR shows a larger share of samples excluded *ab initio* from application than the DSS-SI. In case of sewage sludge, the interdiction is statutory, i.e. application is prohibited because the soil pH value is below the limit value (pH = 5) of the German regulation (*German Parliament*, 1992). However, soil pH is only one major factor for heavy metal mobility in soil (*Barrow* and *Whelan*, 1998; *Sauvé* et al., 2000a). In comparison to the multivariate DSS-SI, the DSS-AR exhibits a limited representation of relevant system parameters. Nevertheless, the stronger restriction of sewage sludge application may compensate partially for the potential hazard caused by the comparatively prolonged application periods described above.

In case of compost application, the German regulation (*German Parliament*, 1992) does not define any minimum pH value, but lower limit values for *aqua regia* extractable Cd and Zn in soil are prescribed in case of pH < 6 (Tab. 1). This regulation leads to the direct exclusion of 72% of CH samples from compost application in the DSS-AR (Fig. 4). In contrast, the DSS-SI interdicts application for only 19% of the samples, and application periods are distinctly longer than in the DSS-AR. This result gives further evidence that the potential for compost application in the framework of the selected data from literature is underestimated by the DSS-AR.

Comparing the two DSS, the DSS-AR is more sensitive to the limit concentration of Zn whereas in the DSS-SI the limit concentration of Cd is more critical. Regarding the DSS-AR, two crucial aspects determine the majority of the Zn criterion: First, when relating initial total heavy metal concentration in soil to the respective *aqua regia* limit value, Zn shows higher limit exploitation than Cd and Pb in many samples. For example, the median concentrations of total Cd, Pb and Zn in the CH data collective yield 40% (Cd), 50% (Pb) and 68% (Zn) of the limit value in compost and 27% (Cd), 35% (Pb) and 51% (Zn) in sewage sludge. Second, the annual load by organic waste application in the scenarios is highest for Zn.

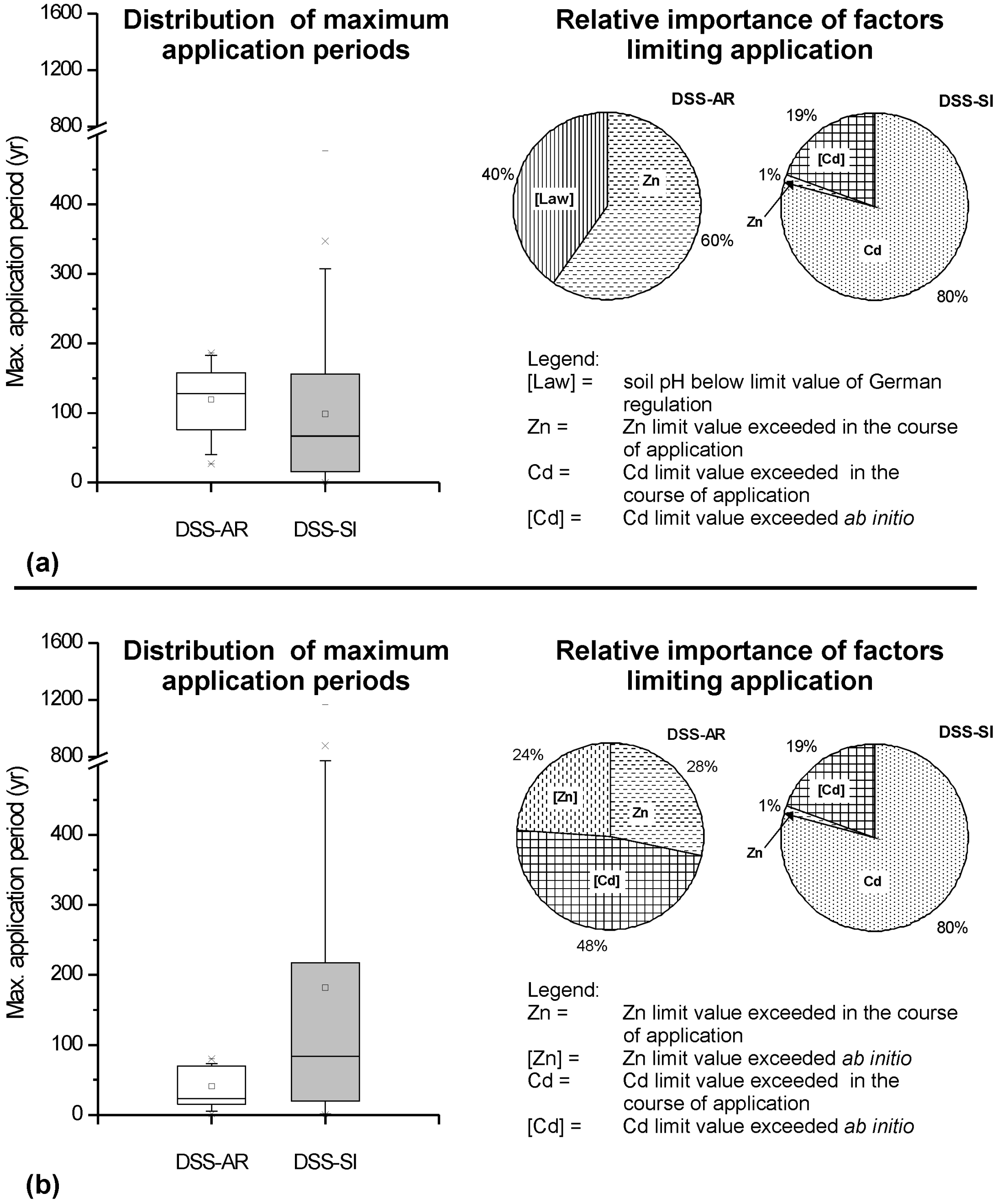

Fig. 4: Left: Maximum application periods of (a) sewage sludge and (b) compost for the CH data collective as predicted by DSS-AR and DSS-SI using Cd, Pb and Zn concentrations in soil. Samples prohibited from sewage sludge application by law are not shown as the calculation of application periods is not based on uptake potential considerations. Definition of symbols as in Fig. 2. Right: Relative importance of limiting factors for organic waste application in the respective scenarios. Values denote the share of samples for which the limiting factor takes effect. Labels in brackets indicate that the uptake potential was exhausted *ab initio*.

In case of the DSS-SI, other parameters and mechanisms must be considered to explain the predominating Cd criterion: First, when relating initial concentration of soluble heavy metal in soil to the respective WHO limit value, the burden with Cd is higher than that of Pb and Zn in many samples. Further, Cd shows distinctly lower affinity to the solid phase in comparison to Pb and Zn. Considering a typical soil of the CH data collective (pH = 5.5; SOC = 10 g kg^{-1}; CLAY = 200 g kg^{-1}), the Freundlich coefficient as an indicator of sorption affinity is 22.2 for Cd, but 45.3 for Zn and 487.7 for Pb, and they agree with findings of other authors (*Welp* and *Brümmer*, 1999; *Thiele* and *Leinweber*, 2000). The combination of low sorption affinity and high initial concentration of Cd is responsible for the high impact of the Cd limit criterion in the DSS-SI scenarios.

Conclusions

The two different DSS approaches presented in this study are advanced concepts for the evaluation of organic waste application considering the spatio-temporal variability of soil properties in a heterogeneous landscape. Both approaches offer the opportunity to calculate the individual uptake potential of a soil for heavy metals.

The DSS were tested with model scenarios based on various data collectives, which can be regarded as representatives of natural field conditions with large variability of soil characteristics. The DSS-SI seems to be feasible to balance ecological and economical demands for organic waste application. The individual uptake potential of a soil is used efficiently, i.e. the potential is scooped and environmental limit values are still taken into account. Further, the DSS-SI is more sensitive to the natural variability of soil conditions by combination of an extended set of soil properties in comparison to the DSS-AR.

Nevertheless, some aspects of the DSS-SI require improvement for optimisation of DSS performance. At first, the goodness of fit of the PTF for Pb and Zn and the validity of all functional relationships need to be improved. Further, PTF for other heavy metals (Cr, Cu, Ni, Hg) should be established for a more enclosing evaluation of the sorption capacity.

The two DSS were designed with the intention of applicability in daily practice and they were kept as simple as possible in order to reduce data requirements to a minimum. This approach implies several assumptions (e.g. equilibrium sorption, no competitive effects of ion species) and restrictions (e.g. no regard of heavy metal loss in the system by leaching, plant uptake and erosion), and for this reason, it distinguishes from a fully parameterised water and solute transport model. Most of the assumptions and restrictions result in a reduction of application periods, and as the DSS aim at pointing out realistic worst case scenarios, the simplifications are not considered to hamper modelling objectives.

Though it was attempted to minimise the data requirements of the DSS, the availability of consistent data collectives is still critical for daily work. In this context, the user might prefer the DSS-AR as it requires even less data than the DSS-SI. On the other hand, in this study the

DSS-SI proved considerable flexibility with respect to deficits in input data. The use of different extractants for derivation of concentration of soluble heavy metals in soil had no impact on the DSS-SI results.

The calculations of the DSS rely on a framework of current legislation, which is not definite. In case of changes to this framework, the DSS results require a re-evaluation. For example, if the EU defines more restrictive limit values as intended in organic waste application (*European Commission*, 2000a; 2000c), the actually observed inefficiency of the DSS-AR in compost application might diminish or even turn to a situation bearing potential hazard according to legislation.

The lack of a well-founded legal framework is a major disadvantage for the development of sophisticated DSS. Therefore, further scientific and political efforts should aim at the improvement and final definition of conclusive, objective limit criteria. The results of the DSS in this study give evidence that this task is realistic.

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