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THESIS:

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Speciality: Agronomic sciences / Ecology

by **Farida AMUTOVA**

Assessment of bioavailability of organochlorine pesticides in chain
«soil – farm animals – food products»

September 22, 2022

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Résumé

Les polluants organiques persistants (POP) sont des substances hautement toxiques, qui peuvent avoir une stabilité notable dans certaines matrices environnementales, ils sont, de même, facilement bioaccumulables. Largement répandus dans et ubiquitaire, ils peuvent toucher la chaîne alimentaire à différents niveaux. En effet, ces composés peuvent être retenus dans l'environnement pendant plusieurs décennies voir des siècles, passer dans la chaîne alimentaire pour atteindre et finalement s'accumuler dans les tissus des humains et des animaux. Les animaux et les humains accumulent progressivement les POP tout au long de leur vie, tandis que leur bioaccumulation a lieu dans les graisses pouvant se trouver dans différents organes (comme le foie, le tissu adipeux et les muscles). Une fois accumulés, les POP sont difficilement éliminés. Cette élimination demeure possible notamment par leur excrétion dans les fèces, voir la bile lorsque les POP sont absorbés dans l'intestin. En outre, les POP peuvent être excrétés dans le lait maternel pendant la période de lactation, ce qui, contrairement au premier cas, peut entraîner leur transfert aux nourrissons et des conséquences néfastes lors de leur développement.

Cette faible excrétion favorise l'accumulation lors d'expositions chroniques conduisant à une accumulation conséquente dans les tissus cibles de l'organisme. Certains POP peuvent alors causer des dommages divers, notamment le développement de maladies des systèmes immunitaire et reproducteur, de malformations congénitales chez les enfants et de cancers.

La localisation des sols agricoles et des fermes d'élevage à proximité des sources d'émission constitue un grand risque de transfert des POP aux animaux producteurs de denrées alimentaires. Ce risque est lié au fait que les animaux élevés en plein air peuvent ingérer involontairement du sol contaminé ainsi que de la végétation lors de l'exploration de parcelles extérieures et, par conséquent, les POP peuvent être bioaccumulés dans leurs tissus comestibles et excrétés dans le lait et les œufs.

Dans ce contexte, le sol est un important réservoir de stockage pour de nombreux POP, et en même temps il est l'élément-clé dans la chaîne alimentaire. Par conséquent, le sol pourrait être le principal vecteur de transfert des POP aux animaux agricoles et, par conséquent, aux produits alimentaires qu'ils produisent (viande, lait, œufs). Les POP véhiculés via l'alimentation sont le contributeur majeur de l'exposition de l'homme en raison de leur forte persistance dans le sol et de leur capacité de bioaccumulation élevée, ce qui créerait un risque sanitaire important pour les personnes consommant des aliments contaminés.

Par conséquent, une question très pertinente dans ce contexte est de trouver et d'explorer les stratégies qui pourraient d'abord limiter la présence des POP dans l'environnement et ensuite réduire leur transfert du sol aux animaux producteurs de denrées alimentaires. Par conséquent, la question principale de ce travail est de savoir comment réduire efficacement cette exposition et comment limiter la libération des POP à partir de la matrice du sol. La première consiste à étudier le lien entre les différents polluants et les fractions du sol, ce qui devrait permettre de comprendre comment ces composés sont disponibles au cours du processus de digestion du sol contaminé chez les animaux. Ensuite, ces connaissances permettent de réduire la quantité réelle de POP absorbés et par conséquent l'exposition réelle afin de protéger par conséquent le consommateur de ces aliments d'origine animale.

L'amendement des sols contaminés par des POP par des adsorbants riches en carbone (charbon actif (CA) ou biochar (BC)) est une stratégie de remédiation relativement nouvelle pour retenir les molécules toxiques dans le sol. L'assainissement d'un sol ainsi contaminé et amendé avec de l'CA/BC est basé sur des processus de désorption - adsorption et fournit donc un confinement de la substance toxique plutôt que sa dépuration ou son élimination. Ce type de remédiation est appelé stratégie de séquestration et le matériau d'amendement, qui est censé immobiliser les polluants, est défini comme séquestrant ou matériau de séquestration (SM). Le principal effet de la stratégie de séquestration basée sur l'CA/BC est l'immobilisation et la réduction de la biodisponibilité des polluants et donc la diminution du risque de transfert ultérieur. Les principales propriétés qui rendent ces matériaux riches en carbone efficaces et économiquement disponibles pour fixer les POP sont une structure hautement poreuse, une teneur élevée en carbone (jusqu'à 90%) d'une part, et la variété des matières premières, leur disponibilité et leur caractère renouvelable d'autre part.

Cette thèse a été réalisée dans le cadre du programme doctoral bilatéral "Abai-Verne" entre la France et la République du Kazakhstan sous la supervision conjointe de l'unité de recherche UR AFPA de l'Université de Lorraine et de la Faculté de Géographie et de Gestion de l'Environnement de l'Université Nationale Kazakh Al-Farabi (KazNU). Il a été financé par le programme de bourses Abai-Verne, les fonds propres et les programmes de recherche de ces instituts.

En tenant compte des intérêts des relations franco-kazakhes lors de la réalisation de ce travail, la famille des polluants organochlorés (OC) a été choisie comme représentants des POP. Le stockage de ces pesticides obsolètes et interdits représente une question émergente commune à plusieurs pays, dont la France et le Kazakhstan, ce qui a justifié l'étude de leur comportement dans le sol. Parmi les OC sélectionnés figurent le DDT et ses métabolites, les isomères du lindane et le lindane (HCH) ainsi que la chlordécone (CLD). Compte tenu de la collaboration entre le Kazakhstan et la France, dans le cadre de la présente étude, des régions historiquement contaminées ont été

sélectionnées pour échantillonner des sols naturellement contaminés qui ont été intégrés dans la construction d'expériences modèles *in vivo* et *in vitro*. En outre, des adsorbants carbonés de différentes origines, dont des produits localement en France et au Kazakhstan ont également été étudiés. L'utilisation de différents composés peut permettre d'explorer les interactions entre les caractéristiques chimiques des pesticides, les caractéristiques du sol et les propriétés des CA/BC étudiés.

L'objectif de l'étude actuelle était de réduire le transfert des OC dans la chaîne alimentaire "sol - animaux d'élevage - produits alimentaires d'origine animale" par l'application de différents matériaux, qui sont des candidats sérieux pour séquestrer les POP.

La synthèse de la littérature a montré que la contamination du sol par des POP chlorés tels que les dioxines furanes (PCDD/F), les polychlorobiphényles (PCB) et d'autres OC pourrait présenter un risque élevé pour les humains, car le sol représente un vecteur de ces produits chimiques pour les animaux producteurs d'aliments. Les POP se déposent sur la couche supérieure du sol et peuvent être stockés dans cette matrice pendant une très longue période (de plusieurs décennies à plusieurs siècles). Cela s'explique par leurs propriétés physiques et chimiques ainsi que par la matière organique du sol qui peut les lier fortement. Le bétail, en particulier les animaux élevés en plein air, ingère quotidiennement du sol en différentes proportions avec de la végétation, ce qui, en cas de contamination, peut avoir de graves conséquences sur la sécurité des denrées d'origine animale.

Les matériaux carbonés tels que les CA/BC peuvent adsorber les POP en réduisant leur disponibilité dans le sol et, au final, leur biodisponibilité pour les animaux (foie, graisse et muscle). Par conséquent, cet effet a conduit à limiter le transfert des POP du sol vers les animaux d'élevage. Les tests envisagés pour évaluer la disponibilité des polluants dans l'environnement et leur biodisponibilité peuvent être utilisés efficacement pour étudier la stratégie de séquestration basée sur les CA/BC, c'est-à-dire en les utilisant comme source d'amendement du sol.

Avant d'envisager une application *in situ* de la stratégie, une étude préliminaire *in vitro* a été nécessaire portant sur l'étude des principaux paramètres de la stratégie de séquestration : temps de contact (ou vieillissement) et la concentration nécessaire en CA/BC pour obtenir une séquestration efficace, ainsi que l'équilibre et la cinétique de cette adsorption. Ces paramètres sont nécessaires *in fine* pour définir la stratégie *in situ* sur des sols contaminés. Afin de répondre à ces problématiques, la partie expérimentale de la thèse est composée d'une méta-analyse et de 3 études expérimentales.

Une méta-analyse portant sur 41 articles scientifiques a été réalisée pour mieux comprendre le transfert de différentes familles de POP (incluant les PCDD/F, les PCB, les OC et les PBDE) dans

différents aliments d'origine animale. Cette approche statistique a été créée pour synthétiser les connaissances actuelles sur la distribution et l'accumulation de différents POP dans les tissus comestibles des animaux (foie, graisse et les tissus musculaires) et leur excrétion dans le lait et les œufs. En outre, la méta-analyse a montré que les taux de transfert (TR) et les facteurs de bioconcentration (BCF) étaient des outils très utiles pour décrire et évaluer le transfert des contaminants vers les animaux et leurs denrées alimentaires ultérieures. Ils permettent de prédire les niveaux maximaux de POP lorsque le contexte d'exposition (dose ingérée de POP) est connu avec précision et jouent par conséquent un rôle majeur dans les évaluations des risques liés aux contaminations alimentaires. La base de données créée à partir de la littérature publiée a montré que les POP les plus toxiques (dioxines et furanes tétra- à hexachlorés, PCB hautement chlorés, notamment le congénère 126, ainsi que le DDT) sont fortement transférés dans les denrées alimentaires les plus consommés tels que les œufs, le lait et, dans une moindre mesure, la viande. Par conséquent, d'autres expériences se sont concentrées sur l'étude de l'application de différents matériaux carbonés (CA/BC), qui pourraient être des candidats sérieux pour séquestrer les POP.

Une première expérience a été menée pour étudier le comportement d'adsorption et le relier aux propriétés physico-chimiques de plusieurs matériaux de séquestration (SM) qui pourraient être des candidats potentiels pour séquestrer les OC et être appliqués comme séquestrants dans la remédiation des sols ou des eaux contaminés. La présente étude a exploré l'adsorption de POCs de nature hydrophobe différente, sur 4 adsorbants poreux contrastés (CA et BC) et 5 substances de base modélisant la matière organique du sol (SOM) dans des milieux aqueux en utilisant des études cinétiques et isothermiques par lots en mettant l'accent sur la relation entre les capacités d'adsorption et les propriétés physico-chimiques. Les résultats de cette expérience ont permis d'identifier plusieurs MS qui ont été utilisées dans les expériences suivantes pour réduire la disponibilité environnementale des OC dans le sol et leur transfert aux tissus comestibles des animaux.

La deuxième expérience a été réalisée *in vitro* et avait pour but d'étudier 2 CA et 1 BC pour leur capacité à réduire la disponibilité environnementale dans deux sols historiquement contaminés par des OC. Deux paramètres ont été étudiés : le taux d'amendement et la granulométrie des MS. Cette étude a montré que les CA/BC avec un taux d'amendement de 2% pouvaient réduire jusqu'à 90% la disponibilité environnementale du DDT et de ses métabolites dans un sol fortement contaminé. Un effet clair de la granulométrie des MS a également été observé, c'est-à-dire que plus les particules sont fines (<150 µm) et plus le taux d'amendement est élevé (2% de matière sèche), meilleure est la séquestration des polluants cibles.

Enfin, la dernière expérience a porté sur l'étude du potentiel de séquestration de deux CA contrastés par une étude *in vivo* pour retenir efficacement la CLD au cours des processus digestifs des porcelets lorsqu'ils sont apporté soit par incorporation dans l'alimentation, soit par amendement du sol. Les résultats de cette étude ont montré que la manière la plus efficace de réaliser la séquestration pour limiter la contamination des animaux par les POP (et leurs tissus corporels) est de réaliser un amendement du sol en CA/BC plutôt que de l'incorporer dans l'alimentation des animaux. Le coefficient de réduction de la biodisponibilité du CLD a atteint jusqu'à 86% dans le foie et la graisse des porcelets exposés lorsque du CA ont été ajoutés au sol contaminé.

De plus, les résultats ont révélé que 1) les propriétés physiques et chimiques des MS, 2) le taux d'amendement et la granulométrie des MS, 3) le temps de contact entre les contaminants et les MS et 4) les fractions de la matière organique du sol sont des facteurs déterminants l'efficacité de la stratégie de séquestration. La porosité totale, c'est-à-dire la surface spécifique active (SSA) et la distribution de la taille des pores (micro- et mésoporosité), les éléments minéraux (en particulier le carbone) et les groupes fonctionnels des MS semblent être les propriétés clés responsables de la séquestration efficace des OC dans les milieux environnementaux testés (eau et sol). Il a été conclu que 2 % (matière sèche) d'amendement SM avec une taille de particule inférieure à 150 µm sont des paramètres méthodologiques optimaux pour l'application sur le terrain des stratégies de séquestration.

La simulation de scénarios d'impact (Chapitre discussion générale) des OC sur divers systèmes de production animale (viande et produits d'animaux à faible et forte productivité) a montré que l'ingestion de sol est un facteur déterminant, devant être pris en compte lors de l'évaluation des risques d'exposition aux POP dans les exploitations d'élevage. Même une concentration relativement faible de polluants dans le sol peut entraîner des contaminations proches des limites maximales résiduelles (LMR) dans les aliments d'origine animale.

En outre, les résultats ont montré que la stratégie de séquestration peut être particulièrement efficace dans des conditions de contamination modérée du sol, ce qui pourrait réduire considérablement le transfert des polluants dans les produits (jusqu'à 90 %) et, par conséquent, protéger les consommateurs. Avec un taux d'amendement de 2% de CA/BC ajouté au sol contaminé, il est possible de réduire la disponibilité environnementale des POP jusqu'à 90% en les immobilisant dans le sol et ainsi réduire leur transfert ultérieur vers les animaux producteurs de denrées alimentaires sans mettre en danger la sécurité sanitaire.

Du point de vue économique, il apparaît que l'application de CA est de loin plus coûteux que l'amendement du sol par du BC, ce qui soulève la question de la faisabilité économique. En outre,

la stratégie de séquestration peut être coûteuse lorsqu'elle est appliquée à grande échelle sur plusieurs hectares de terrain en raison de la nécessité d'une grande quantité de MS exigeant une grande capacité de production. Cependant, cette stratégie peut être économiquement viable et bénéfique pour des surfaces plus petites, telles que les jardins privés ou les petites exploitations agricoles, en particulier sur des sols modérément contaminés.

Mots clés: Pesticides organochlorés, Sol, Transfert, Animaux de rente, Séquestration, Charbon actif, Biochar, Biodisponibilité.

Abstract

Soil could be the main vector for the transfer of persistent organic pollutants (POPs) to agricultural animals, and, accordingly, to the food products they produce (meat, milk, eggs). Farm animals especially free-range species could ingest soil in different proportions together with vegetation which in case of contamination context represent a serious consequence to produce insecure food of animal origin. Hereby, this study was mainly focused on sequestration strategies which could ensure the safety of food produced by livestock animals in POP contaminated areas.

The current work was focused on organochlorinated pesticides (OCPs) among the POPs. These forbidden and obsolete chemicals have been stored over long time in facilities, which may have been deteriorated over the decades, which raises issues by their diffusion in the environment in various countries. The aim of the current study was to reduce OCPs transfer in the food chain «soil – farm animals – food products of animal origin» by the application of different carbonaceous materials based on activated carbons (AC) or biochars (BC), which are serious candidates to sequester POPs. The use AC/BC as soil amendment can adsorb POPs reducing its environmental availability but also their bioavailability for free-ranged animals, which may ingest soil and by consequence soil-bound pollutants.

Several scientific concepts such as environmental availability, bioavailability, transfer rate, bioaccumulation factor, adsorption kinetics and adsorption isotherms were integrated into the current study using *in vitro* and *in vivo* approaches in order to investigate application of sequestration strategies based on ACs and BCs as possible solutions for reduction of the OCPs (DDT and metabolites, HCH isomers and CLD) transfer from soil to food products in contaminated areas. Several ACs (DARCO, ORBO, Shubarkol) and BCs (Japanese knotweed, Oak tree, Sargassum) were revealed by the current work as effective sequestrants that could be effectively used in sequestration strategies as soil amendment. In addition, physical and chemical properties of SMs, amendment rate, contact time between contaminants and SMs and fractions of soil organic matter appeared as factors explaining efficiency of sequestration strategies based on AC/BCs.

Finally, sequestration strategy based on AC/BC can be especially effective under conditions of moderate soil contaminations, which could significantly reduce environmental availability of pollutants (up to 90%) and, as a result, transfer to food products.

Keywords: Organochlorine pesticides, Soil, Transfer, Farm animals, Sequestration, Activated carbon, Biochar, Bioavailability

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SCIENTIFIC VALORIZATION OF THESIS WORK AND COLLABORATIONS

PUBLICATIONS

▪ International

Amutova F., Delannoy M., Baubekova A., Konuspayeva G., Jurjanz S. Transfer of persistent organic pollutants in food of animal origin - Meta-analysis of published data. *Chemosphere*. 2021; 262:128351. doi: 10.1016/j.chemosphere.2020.128351.

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▪ **Communications with participation**

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SCIENTIFIC COLLABORATIONS:

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LIST OF ABBREVIATIONS

AC: Activated carbon	PAC: Powder activated carbon
AhR: Aryl hydrocarbon receptor	PAHs: Polycyclic Aromatic Hydrocarbons
AOM: Amorphous organic matter	PBDEs: Polybrominated diphenyl ethers
ATSDR: Agency for Toxic Substances and Disease Registry	PBET: Physiologically based extraction test
BA: Bioavailability	PCDD/Fs: Polychlorinated dibenzodioxins and dibenzofurans
BC: Biochar	PCP: Pentachlorophenol
BC: Black carbon	PDMS: polydimethylsiloxane
BCF: Bioconcentration factor	PEDs: polyethylene devices
BET: Brunauer–Emmet–Teller	PFOA: Perfluorooctanoic acid
BW: Body weight	PFOS: Perfluorooctane sulfonic acid
CLD: Chlordecone	PLE: pressurized fluid extraction
DDD: Dichlorodiphenyldichloroethane	POM: Polyoxymethylene
DDE: Dichlorodiphenyldichloroethylene	POP: Persistent Organic Pollutant
DDT: Dichlorodiphényltrichloroéthane	Pv: Vapor pressure
DL-PCB: dioxin like PCB	PVSDM: Pore volume and surface diffusion model
DM: Dry Matter	RBA: Relative bioavailability
EPA: Environmental Protection Agency	SD: Standard deviation
EVA: ethylene vinyl acetate	SE: Standard error
FAO: Food and Agricultural organization	SM: sequestration material
GAC: Granular activated carbon	SOM: Soil organic matter
GC-MS: Gas chromatography – mass spectrometry	SPMDs: semi-permeable membrane devices
HCH: Hexachlorocyclohexane	SS: Standard soil
HPCD: hydroxypropyl- β -cyclodextrin	SSA: Specific Surface Area
IARC: International Agency for Research on Cancer	TCDD: 2,3,7,8-tétrachlorodibenzo-p-dioxine
I-TEF: International Toxic Equivalent Factors	TEF: Toxic equivalency factor
IUPAC: International Union of Pure and Applied Chemistry	TEQ: Toxic equivalency
KH: Henry's law constant	TR: Transfer rate
Koc: Partition coefficient of the organic carbon	WHO: World Health Organization
Kow: n-Octanol/Water Partition Coefficient	
LD: Lethal dose	
LLE: Liquid-liquid extraction	
LOAL: Lowest Adverse Effect Level	
LOQ: Limit of Quantification	
MAC: Maximum Allowable Concentration	
MRLs: Maximum Residue Level	
MW: Molecular weight	
NDL-PCB: non dioxin like PCB	
NOAEL: Not Observed Adverse Effect Level	
OCDD: Octachlorodibenzodioxin	
OCDF: Octachlorodibenzofuran	
OCPs: Organochlorine pesticides	
OM: Organic matter	

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GENERAL INTRODUCTION

Persistent organic pollutants (POPs) are highly toxic substances, which may have very notable stability in some environmental matrices, and they are easily bioaccumulated (Ritter et al., 2015). Therefore, they are widely spread in the environment all over the world and can touch the food chain at different levels. Indeed, these compounds can be retained in the environment for a several decades and sometimes centuries, pass through the food chain to reach and finally accumulate in the body tissues of humans and animals (MacLachlan and Bhula, 2009; Maervoet et al., 2004; Opinion of the scientific committee on animal nutrition, 2000; Weber et al., 2018). Animals and humans accumulate POPs gradually throughout their lives, while their bioaccumulation take place in fat-containing internal organs (i.e liver, adipose and muscle tissue) (Amutova et al., 2021). The accumulation of POPs in the body occurs due to their poor elimination. However, elimination from the organism is possible during excretion in feces through the bile (Birnbaum L, 1985; Macdonald T., 1983) when POPs are absorbed in the intestine. In addition, POPs can be excreted in breast milk during lactation period, which, unlike the first case, can lead to their transfer to infants and adverse consequences associated with their development (Pratt et al., 2012; Witzak et al., 2021).

This small excretion favors accumulation during chronic exposures leading to consequent accumulation in target tissues of the body. Then some POPs can cause significant harm, leading to the development of diseases of the immune and reproductive systems (Baccarelli et al., 2002; Winneke, 2011), congenital defects in children, and cancer (Alaluusua et al., 2004; Han et al., 2019; Islam et al., 2018; Mouly and Toms, 2016).

There are numerous sources of POPs. Natural or anthropogenic combustion processes produce some POP families such as dioxins or PAHs (Axegård, 2019; Qian et al., 2005a; Xia et al., 2020; Zhang G. et al., 2018). Other compound families (PCBs, PBDEs or pesticides) have been industrially produced (Aoki, 2001; Breivik et al., 2007; de Voogt and Brinkman, 1989; Kocan A, 2004). However, their persistency makes that they will stay present in very different compartments of the environment such as old pesticide landfills, pulp production, hospital and municipal waste incineration and much more (Koistinen et al., 1993; W. Macdonald et al., 2002, 1998; Wang H. et al., 2020). The location of agricultural soil and livestock farms in the vicinity of such sources is a great risk for the transfer of POPs to the food producing animals (Behnisch and Šír, 2015; Guo et al., 2019; Pan et al., 2014; Summary, 2018; Tao et al., 2011, 2009). This risk is associated with the fact that free ranged food producing animals could consume contaminated soil together with a

vegetation during exploration of outside plots (Rychen et al., 2008) and as consequence POPs could be bioaccumulated in their edible tissues and excreted to milk and eggs (Amutova et al., 2021; Weber et al., 2019a, 2018).

In this context, soil is a huge storage reservoir for many POPs, and at the same time it's the key element in many food chains as well as its play an important role for water management systems. Therefore, soil could be the main vector for the transfer of POPs to agricultural animals, and, accordingly, to the food products they produce (meat, milk, eggs). This pathway is the most highly exposure way of human to POPs because of their high persistence in soil and highest bioaccumulation ability, which would create a great health risk for people consuming contaminated food.

Therefore, a very relevant issue in this context is to find and explore the strategies which could firstly limit POPs presence in the environment and secondly to reduce their transfer from soil to the food producing animals. Therefore, **the main question of this work** is how effectively reduce this exposure and how to limit the POPs release from the soil matrix? The first mean investigation of the link between the different pollutants and soil fractions, which should allow to understand how these compounds are available during the digestive process of the contaminated soil in the animals. The second, such knowledge permit then to reduce the real amount of absorbed POPs and by consequence the real exposure in order to protect by consequence the consumer of these food of animal origin.

Amendment of soil contaminated with POPs by carbon-rich adsorbents (activated carbon (AC) or biochar (BC)) is a relatively new remediation strategy to retain toxic molecules in the soil (Beesley et al., 2011; Rakowska et al., 2012; Y. Wang et al., 2013 (Delannoy et al., 2015, 2018, 2020; Feidt et al., 2021; Ranguin et al., 2021)). The remediation of so contaminated soil amended with AC/BC is based on desorption - adsorption processes and therefore provides containment of the toxic substance rather than its depuration or removal. (Cho et al., 2009). This type of remediation is called sequestration strategy and the amendment material, which is supposed to immobilize pollutants, defined as sequestrant or sequestration material (SM). The main effect of AC/BC based sequestration strategy is immobilization and reducing pollutant bioavailability and therefore lowered risk of a further transfer (Brändli et al., 2008; Cho et al., 2009). The main properties making these carbon-rich materials efficient and economically available for binding POPs are a highly porous structure, elevated carbon contents (up to 90%) on the one hand, and variety of raw materials, its availability and renewability on the other hand.

This dissertation was completed within the framework of the doctoral program of the Government of France and the Republic of Kazakhstan "Abai-Verne" under the joint supervision of the UR-AFPA University of Lorraine and the Department of Geography and Environmental Management of Al-Farabi Kazakh National University. It was funded by the Abay-Vern scholarship program and by the own funds of two partner institutes.

The current study will focus especially on organochlorinated pesticides (OCPs) among the POPs as the storage of obsolete and forbidden OCPs is a common emerging question in several countries including France and Kazakhstan justifying to investigate their behavior in soil. The use of different compounds can allow to explore the interactions between the chemical characteristics of the pesticides, soil characteristics and the properties of the studies AC/BCs. Taking into account the Kazakh-French collaboration, within the framework of this PhD study, historically contaminated regions were selected for sampling naturally contaminated soils which will be integrated in building *in vivo* and *in vitro* model experiments. In addition, locally produced carbonaceous adsorbents from France and Kazakhstan were also investigated.

The aim of the current study was to reduce OCPs transfer in the food chain «soil – farm animals – food products of animal origin» by the application of different materials, which are serious candidates to sequester POPs.

The bibliographic synthesis of the dissertation consists of three parts. The first part is a characterization of different families of POPs in terms of their main physicochemical properties that affect on their behavior and interactions in the chain soil - farm animals - food products. The second part consisted of a review of the existing methodology for determining the availability of soil bound contaminants, including *in vivo* and *in vitro* assays. The third part reviewed the sequestration strategy including different types of sequestering materials, their production, physical and chemical properties on the one hand, as well as interactions with POPs in the soil.

The experimental section of the dissertation is presented in the form of 4 parts that respond to the hypothesis. The first part was a meta-analysis assessing the degree of transfer of various families of POPs from contaminated ingested matrices (including feed, soil) to food of animal origin (meat, milk, eggs). The second part characterizes the adsorption between OCPs and different SMs which included porous and non-porous organic adsorbents. The third part evaluates reduction of environmental availability of OCPs in naturally contaminated soils using tree contrasted SMs. The fourth part evaluates the reduction of the bioavailability of the organochlorine pesticide

chlordecone on piglets after oral exposure provided either via feed incorporation or via soil amendment and, as a result, reduce the transfer of the contaminant to animal organs.

Finally, the general discussion analyses in detail the influence of different characteristics of sequestration matrices on OCPs bioavailability. Practical recommendations for comprehensive estimation POPs transfer will be proposed which could optimize and improve environmental monitoring system for livestock farms located near sources of POPs.

CHAPTER 1: BIBLIOGRAPHIC SYNTHESIS

PART I: Chlorinated POPs and their place in the food chain

Persistent organic pollutants (POPs) are a class of organochlorine compounds, which contain halogens (chlorine, bromine or fluorine atoms).

There are several families of POPs that are classified according to their origin. POPs include organochlorine pesticides, industrial chemicals and some unintentionally generated by-products that are formed during certain combustion and chemical processes. Examples of POPs are DDT, PCBs and dioxins (Ritter et al., 2015). All POPs share several common properties. As a result, the term "persistent organic pollutant" or "POPs" began to be used as a general term for the whole a class of chemicals that have these properties. POPs are organic chemicals, which means they have a chemical structure that contains carbon and hydrogen. They have the following four specific properties:

1) Persistence: POPs are chemical pollutants that are hardly physically, chemically and biodegradable. Therefore, once a POP is in the environment, it remains there for a long time.

2) Ability to accumulate in biological matrices: POPs are chemicals that are lipophilic (readily soluble in fats). Therefore, they accumulate in tissues of living organisms up to concentrations that significantly exceed those in the environment.

3) Ability to travel for a long distance: POPs can travel long distances in the environment and can cause harm in locations remote from the original source of the POPs release into the environment. POPs are mainly carried by air currents, but they can also be carried by water masses or migratory animal species.

4) Toxicity: POPs are chemicals that have a negative impact on human health due to their carcinogenicity, mutagenicity, teratogenicity, ability to disorder of the immune and reproductive systems and etc.

Thus, POPs possessing the above properties pose a growing threat to human health and the environment. To control and reduce POPs pollution in the environment, the so-called Stockholm Convention entered into force on 17 May 2004 was established a list of substances defined as POPs, their classification and methods for their control and reduction in environment (Stockholm Convention, 2019). According to Stockholm Convention, POP are grouped as following:

1) POPs that should be eliminated: Aldrin, α -Hexachlorocyclohexane, β -Hexachlorocyclohexane, Chlordane, Chlordecone, Decabromodiphenyl ether, Dicofol, Dieldrin,

Endosulfan, Endrin, Heptachlor, Hexabromobiphenyl, Hexabromocyclododecane, Hexabromodiphenylether und Heptabromodiphenylether, Hexachlorobenzene, Hexachlorobutadiene, Lindane, Mirex, Pentachlorobenzene, Pentachlorophenol and its salts and esters, Perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds, Polychlorinated biphenyls (PCBs), Polychlorinated naphthalenes, Tetrabromodiphenyl ether and pentabromodiphenyl ether, Short-chain chlorinated paraffins (C10–13; chlorine content > 48%) and Toxaphene.

2) POPs that should be restricted: DDT, Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride.

3) POPs that unintentionally produced: Hexachlorobenzene, Hexachlorobutadiene, Pentachlorobenzene, Polychlorinated biphenyls (PCBs), Polychlorinated dibenzodioxins und dibenzofurans (PCDD/PCDF), Polychlorinated naphthalenes.

The countries of all over the world regularly conduct environmental monitoring of territories including soils used for agricultural needs, water, vegetation sources, but also feed and food. The presence of POPs in soil is fraught with their transfer to the human body through food of plant and animal origin. One of the pathways across the food chain carrying POPs to the human body is "soil - farm animals - food" (Amutova et al., 2021; Weber et al., 2019, 2018). This transport is the most highly exposure way of human to POPs, because of their lipophilicity and the richness of fat in animal tissues. This, in turn, poses a great health risk for people consuming contaminated food. Therefore, the understanding of this main transmission pathway "soil – animal – food" is a crucial step to protect the consumers.

This chapter will define toxicological properties and health effects, the main physical and chemical properties, emission sources, environmental fate of chlorinated POP in soil and transfer of POPs from soil to farm animals and food of animal origin. In addition, worldwide regulations, and restriction of chlorinated POPs in the context of different countries will be described.

1. Toxicity and health effects

Toxicity is the degree to which a chemical or a certain mixture of substances can harm the body. It can refer to exposure to the entire body, such as a human or animal, bacteria or plant, or to a substructure of the body such as a cell (cytotoxicity) or an organ such as the liver (hepatotoxicity) ("Understanding Toxic Substances," 1986).

The main concept of toxicity is that the effects of the toxicant are dose dependent. Therefore, even water can lead to water intoxication if too large dose is ingested, whereas even for a very toxic substance such as snake poison there is a dose below which no toxic effect is found. The sensitivity to toxicity varies between species, making cross-species analysis difficult. Therefore, toxic doses are generally expressed per kg BW⁻¹ (body weight). Moreover, metabolic differences between individuals of the same population may enhance variations of sensitiveness to toxic compounds.

The toxicity of a substance usually depends on the exposure pathway (dermal contact, ingestion, inhalation, or injection), on the time of exposure (single dose, i.e. acute or several doses over time, i.e. chronic exposure) the exposure dose (per kg BW) and other parameters of the substance and the physiology of the species on which the exposure occurs. Acute toxicity is a single exposure to a substance that results in serious harm in organism or death. Acute exposure can last no more than one day. Chronic toxicity is exposure to a toxic substance over an extended period of time, often measured in months or years; this can cause irreversible side effects (Neumeister L. and Aktions-Netzwerk P., 2001).

One of the main parameters to express acute toxicity is LD₅₀ which defined as a lethal dose of toxicant which killed 50% of exposed animals. Values of LD₅₀ usually conducted in controlled laboratory conditions on rodents or fish. Table 1 compares the acute toxicity of different POPs families based on LD₅₀. It shows that the most toxic compounds are TCDD, followed by PCBs, by pesticides DDT and lindane. In absence of available LD₅₀ data, assessments are made by comparison with known similar toxic substances or with similar effects on similar organisms. “Safety factors” are then added to account for uncertainties in the data and estimation processes. For example, if a dose of a toxic substance is safe for a laboratory rat, one-tenth of that dose can be assumed to be safe for humans, with a safety factor of 10 to account for interspecies differences between the two mammals; if the data are from fish, a factor of 100 can be used to account for the larger difference between the two classes of chordates (fish and mammals) (Dorne and Renwick, 2005). In the same way, an additional protection factor can be used by little-studied toxic compounds, having data on the properties of another substance. In such a case, an additional protection factor of 10 can be assigned to account for possible differences in effects, which are probably much smaller.

Table 1– Some POPs LD₅₀ in rats

Compound	LD50 for rats, (mg kg BW ⁻¹)	Reference
TCDD	0.296	Chapman & Schiller, 1985
Arochlor 1254 (PCB mix)	1.0-1.3	Garthoff et al., 1981; Linder et al., 1974

DDT	113-800	ATSDR, 2019
Lindane	88-91	ATSDR, 2005
Chlordecone	91-132	ATSDR, 2020

Even if situations of acute poisoning by POPs may happen, the most frequent health concerns due to POPs are on chronic oral exposure over generally long or very long durations. The toxicity in conditions of chronic exposure has to be evaluated differently. As for previously described acute toxicity, dose and specie effect has to be précised for each compound. Moreover, the duration of exposure and the target tissue make differ the toxicity evaluation of different compounds.

Indeed, one single compound may enhance simultaneously adverse effects in different tissues what make the toxicologic evaluation of the compound more complex. Indeed, in study of Beard, 2006 reviewed several adverse health effects of DDT such as reproductive and neurological abnormalities, endocrine disruption, and cancer.

Generally, the lowest dose with a proven adverse effect is retained to indicate the toxic level at chronic exposure. Such level can be expressed as the Lowest Adverse Effect Level (LOAL), i.e. lowest dose on which any effect was stated, or – contrarily as the lowest dose on which Not Observed Adverse Effect Level (NOAEL) has been detected (Parasuraman, 2011).

Moreover, toxicity can be due to simultaneous presence of different compounds, which may have cumulative effects on health. Therefore, the NATO created in 1989 the International Toxic Equivalent Factors (I-TEF) to compare the toxicity between different compounds (EPA, 2010). This concept has been enlarged and developed by the World Health Organization in 1998 to the Toxic Equivalent Factors (TEF), which are nowadays largely used to compare and evaluate the toxicity the most dangerous of POPs (Kutz et al., 1990; van den Berg et al., 1994). Indeed, the most dangerous compound (2,3,7,8, TCDD) has been arbitrarily defined as TEF =1 and the toxicity of all other compounds is expressed in comparison to this reference value. TEF values for PCDD/Fs and PCBs are presented in table 2. The attributed TEFs are regularly actualized depending on new knowledge.

Table 2 – Toxic equivalency factor (TEFs) for PCDDs and PCDFs recommended by the World Health Organization (WHO)

POPs	congeners	WHO ₂₀₀₅ TEF
	2,3,7,8-TCDF	0.1
	1,2,3,7,8-PeCDF	0.03

Furans (PCDFs)	2,3,4,7,8-PeCDF	0.3
	1,2,3,4,7,8-HxCDF	0.1
	1,2,3,6,7,8-HxCDF	0.1
	2,3,4,6,7,8-HxCDF	0.1
	1,2,3, 7,8,9-HxCDF	0.1
	1,2,3,4,6,7,8-HpCDF	0.01
	1,2,3,4,7,8,9-HpCDF	0.01
	OCDF	0.0003
Dioxins (PCDDs)	2,3,7,8-TCDD	1
	1,2,3,7,8-PeCDD	1
	1,2,3,4,7,8-HxCDD	0.1
	1,2,3,6,7,8-HxCDD	0.1
	1,2,3,7,8,9-HxCDD	0.1
	1,2,3,4,6,7,8-HpCDD	0.01
	OCDD	0.0003
non-ortho PCBs	PCB 77	0.0001
	PCB 81	0.0003
	PCB 126	0.1
	PCB 169	0.03
mono-ortho PCBs	PCB 105	0.00003
	PCB 114	0.00003
	PCB 118	0.00003
	PCB 123	0.00003
	PCB 156	0.00003
	PCB 157	0.00003
	PCB 167	0.00003
	PCB 189	0.00003

Moreover, this concept allows also to express the global toxic doses by cumulating all TEFs of a cocktail exposure with the amount of the compound in the considered intake matrix to formulate a Toxic Equivalent Quantity (TEQ). Indeed, it is a simple sum of the concentration of each POP and its TEF. Finally, the total amount of TEQ globalize the toxicity of all POPs contained in a given intake matter, expressed in relation to the body weight (BW) of the considered organism.

PCDD/Fs are the most toxic family among POPs (LD₅₀ values in Table 1). The estimated average lethal dose of dioxin for humans in a single dose is 70 µg/kg body weight. TCDD, the most toxic of the dibenzodioxins and classified by the International Agency for Research on Cancer (IARC) as a Group 1 carcinogen.

PCDD and PCDF have been shown to cause carcinogenicity, disruption of the endocrine and immune systems, and neurotoxicity. One of the main adverse health effects of PCDD/Fs are mediated by their action on the cellular receptor, the aryl hydrocarbon receptor (AhR) (Bock and Köhle, 2006). PCDD/Fs reduce immunity (Baccarelli et al., 2002) and intensely affect the processes of cell division and specialization (Eskenazi et al., 2002), provoking the development of a number of cancers (Domingo et al., 2017; Fabbrocini et al., 2015). Also, these substances destabilize the complex work of the endocrine glands (Pavuk et al., 2003), interfere with reproductive function, dramatically slowing down puberty and causing infertility (IARC, 1997). Some studies have confirmed that dioxins cause malformations and developmental problems in children (Alaluusua et al., 2004; Peterson et al., 2008).

PCBs. The toxicology of PCBs mainly depends on the specific congener. According to their structure and toxicity, PCBs are commonly divided into two groups called *non-ortho*-substituted [arene substitution patterns](#) and *ortho*-substituted congeners.

Non-ortho PCBs have a structure with two phenyl rings in the same plane which make the whole structure to be rigid and therefore to be more stable. This group of PCBs are very similar to PCDDs and therefore they tend to act like PCDDs as an agonist of the aryl hydrocarbon receptor (AhR) in organisms. Non-ortho PCBs are also called dioxin-like congeners therefore considered as the most toxic PCB congeners.

The second group, *ortho*-substituted PCBs with chlorine atoms in *ortho*-positions can cause neurotoxic and immunotoxin effects (Winneke, 2011), but only at very high concentrations, much higher than the concentrations usually associated with dioxins. However, because they are usually found in much higher concentrations in biological and environmental samples, they also pose a health hazard, especially to developing organisms (Jacobson et al., 1990; Stewart et al., 2003). Since they do not activate AhR, they are not considered part of the dioxin group (Council, 2001; Winneke et al., 1998).

In 2013, the IARC classified dioxin-like PCBs as human carcinogens (Lauby-Secretan et al., 2013). According to the US Environmental Protection Agency (EPA), PCBs cause cancer in animals, and evidence supports their cancer-causing effects in humans. According to the EPA,

studies have found an increase in the incidence of malignant melanoma and rare cases of liver cancer in workers handling PCBs (US EPA, 2016).

There are several global scandals associated with mass PCDD/Fs and PCBs contamination of feed and food product which showed the huge negative impact on the human and animal health. One of them are contamination of nearly 2000 people and called Yusho's disease (Masuda, 2009; Onozuka et al., 2021, 2009). Another major incident Belgian Dioxin Crisis was caused by animal fat highly contaminated with PCBs in chicken feed (Bernard et al., 2002; Covaci et al., 2008; van Larebeke et al., 2001).

OCPs. Agency for Toxic Substances and Disease Registry (ATSDR) (Atlanta, Georgia) within the U.S. Department of Health and Human Services reported top list of toxic substances including OCPs. OCPs are frequently in the top 60 chemicals on the list, with DDT at №13, dieldrin at №18, DDE at №21, chlordane at №22, aldrin at №25, toxaphene at №32, endosulfan at №44 and methoxychlor at №55.

The liver is the main organ for bioaccumulation of most POPs. The liver metabolizes pesticides, and often they can contribute to liver carcinogenesis by changing the mechanisms of cell adhesion, oxidative stress, genotoxicity, tumor stimulation, immunotoxicity and hormonal action (Gomaa et al., 2008; X. Jin et al., 2014).

Several studies reported that DDT and methoxychlor are weak estrogens and weak anti-androgens (Lemaire et al., 2006; Maness et al., 1998; Sonneveld et al., 2005), and cause a variety of diseases including cancer (Cohn et al., 2019). In addition, some OCPs including DDT, lindane and cyclodienic pesticides endosulfan, heptachlor, aldrin, dieldrin and chlordane can depress the central nervous system (Costa, 2015; Keifer and Firestone, 2008).

Sometimes OCPs can transfer to the embryos of living organisms (Qu et al., 2010), thereby affecting the early stages of their ontogenesis and disrupting the structure of the genetic apparatus. DDT, lindane and other pesticides can be detected in breast milk from many places in the world (Souza et al., 2020; Witczak et al., 2021b) which is likely to be transmitted to infants.

2. Physical and chemical properties of chlorinated POPs

The main physical and chemical properties of PCDD/Fs, PCBs and OCPs such as molecular structure and stereochemistry, partition coefficients, Henry's law constants, vapor pressures, and persistence will be reviewed.

2.1. Molecular structure and stereochemistry of the main families

Physical and chemical properties determine the nature and behavior of POPs in the environment. They are determined by the atoms of the molecule and their structure. Depending on the structure of the molecule, the physicochemical properties cover a huge range of values. Most of the substances in the POPs group are persistent, mobile, and toxic (Jones, 2021).

The carbon-chlorine bonds in the molecule of these compounds are resistant to hydrolysis. Most chlorinated POPs are typically ring structures with a chain or branched chain framework. The greater the number of chlorine substitutions or functional groups (Cl_n) in the benzene ring, the more stable the compound is to degradation. Consequently, organic pollutants decompose very slowly and do not lose their activity for many decades which is responsible for their persistency (Ritter et al., 2015).

Polychlorodibenzo-p-dioxins (PCDDs) and Polychlorinated dibenzofurans (**PCDFs**) commonly called dioxins, are compounds with similar chemical properties and therefore generally grouped as PCDD/Fs. There are 75 PCDDs and 135 PCDFs, each differing in the number and position of the chlorine atoms but only the 17 congeners with at least 4 chlorine atoms and at least in the 2, 3, 7 and 8 positions are considered to be relevant for human health (fig. 1). These 17 congeners of dioxins and furans are relatively resistant to metabolic degradation and accumulate in the body (ATSDR, 1998, 1994).

Each compound of PCDD/Fs comprises two benzene rings interconnected by oxygen atoms. In the case of PCDDs, the benzene rings are joined by two oxygen bridges, and in the case of the PCDFs, the benzene rings are connected by a carbon bond and an oxygen bridge. Each individual PCDD or PCDF is termed a congener (giving 210 in total), while groups of congeners with the same number of chlorine atoms are called homologues (Sadegh et al., 2014). The homologue groups are commonly named as, tetrachloro-CDDs and CDFs (PCDD/Fs with four substituted chlorine atoms) are abbreviated to TCDDs and TCDFs, respectively, while the fully chlorinated octachloro congeners (eight substituted chlorine atoms) are abbreviated to OCDD and OCDF, respectively (ATSDR, 1998, 1994).

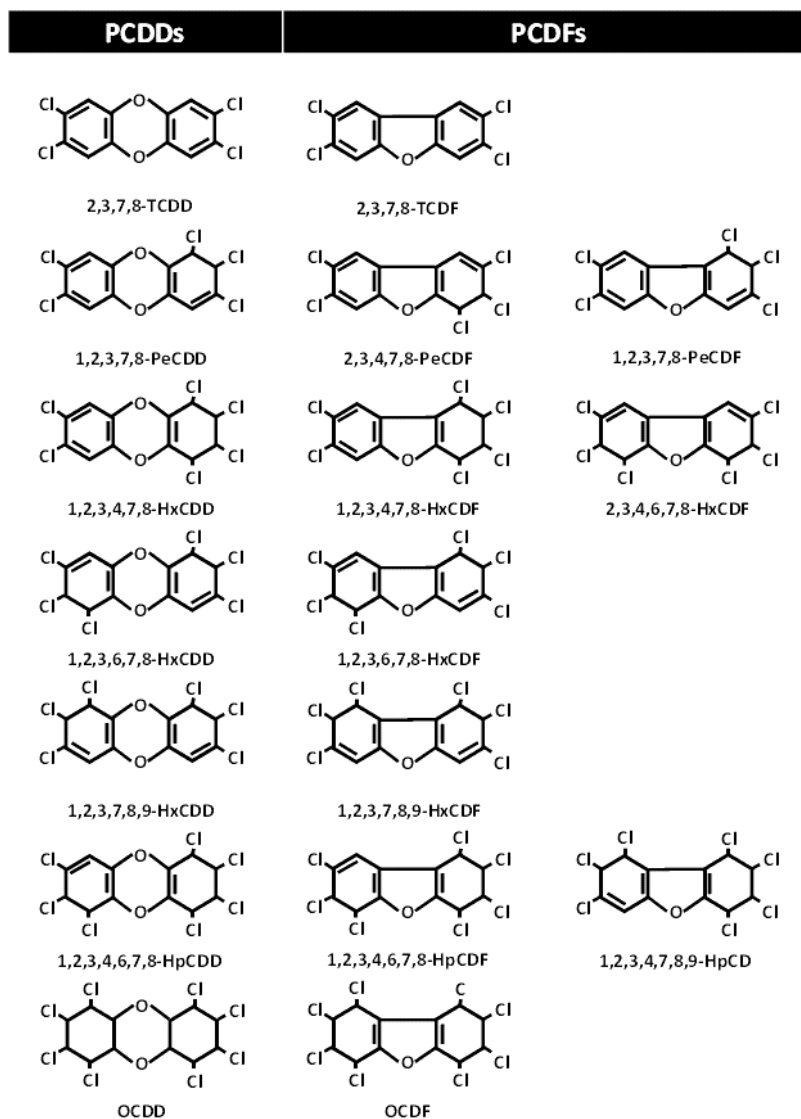


Figure 1 - Structures of 17 PCDD/Fs congeners which are considered to be the most toxic for organisms

Polychlorobiphenyls (PCBs) belong to the class of aromatic compounds consisting also of two benzene rings and connected through an internuclear C-C bond and substituted by one to ten chlorine atoms in the *ortho*- (1,2), *meta*- (1,3), or *para*- (1,4) positions as shown on Figure 2. There are 209 individual PCB congeners, differing in the number and position of chlorine atoms in the molecule, having the general formula: $C_{12}H_{10-n}Cl_n$, where $n = 1-10$ (ATSDR, 2000).

In the literature, PCBs are often studied by grouping different isomers under different logics:

Logic 1: seven *ortho*-substituted PCBs (congeners 28, 52, 101, 118, 138, 153 and 180) are used, which are also known as indicator biomarker PCBs. These 7 indicator PCBs are used to estimate a human body burden by PCBs (Figure 2).

Logic 2: Dioxin like PCBs group (congeners 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) which have at least 4 chlorines and the ability to obtain a planar molecular structure showing similar adverse effects and persistence properties as the PCDD/Fs.

Additionally, different commercial PCB mixtures were marketed in different countries under the following names Arochlor (USA and United Kingdom), Sovtol (Russia), Phenoclor (France), Kanechlor and Pyroclor (Japan) and other (IARC Monographs, 2018). Each of these commercial mixtures differs by its isomer composition, which could moreover vary depending on the period of production. For example, Aroclor 1254 and Aroclor 1260 contains 54% and 60% chlorine by weight respectively. Therefore, a special attention has to be paid in the analysis of published studies which mixtures or groups has been investigated.

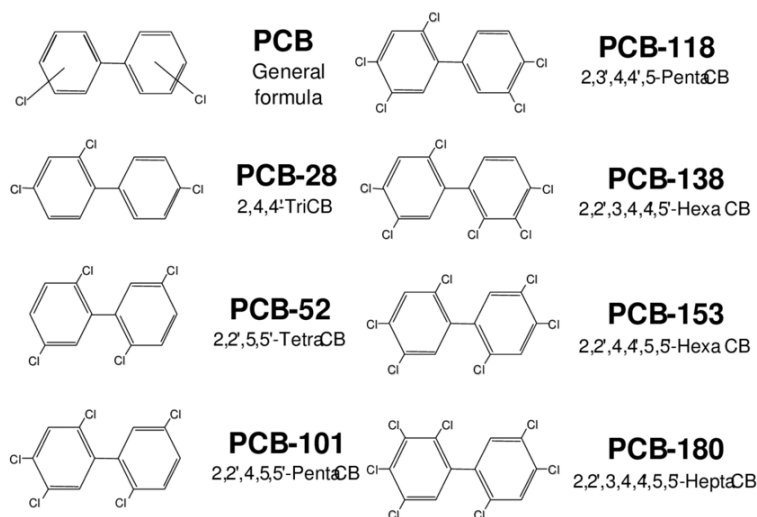


Figure 2 - General structures for PCBs and 7 indicator PCB congeners

Organochlorinated pesticides (OCPs) consisted of the chemical point of view in chlorinated hydrocarbons attached to five or more than five chlorine atoms (Figure 3). The first and most widely used insecticide in OCPs family is Dichlorodiphenyltrichloroethane (DDT). DDT and its metabolites DDE and DDD (Figure 3) have 2 isomer configurations: chlorine atoms in *para* and *ortho*- positions and abbreviated as *p,p'*(4,4') and *o,p'*(2,4'), respectively. Para isomer is the most prevalent compound in the nature (ATSDR, 2019). Technical-grade DDT contains 65–80% *p,p'*-DDT, 15–21% *o,p'*-DDT, and up to 4% of *p,p'*-DDD.

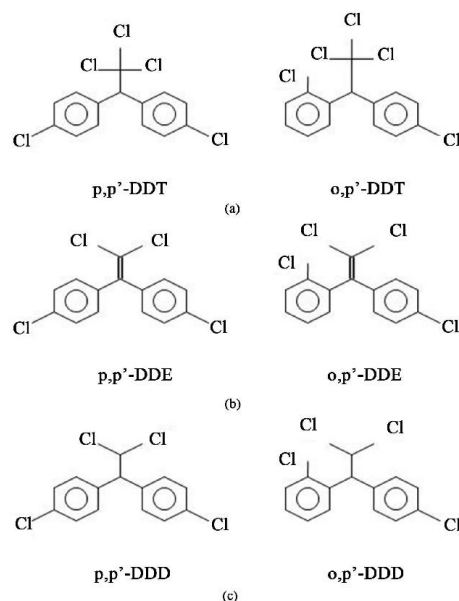


Figure 3 – Structures of DDT and its metabolites

Eight isomers are known for hexachlorocyclohexane (**HCH**): alpha, beta, gamma, delta, epsilon, zeta, eta, and theta. Technical HCH is often a mixture of several stereoisomers, which usually contain four isomers, namely α -HCH, β -HCH, γ -HCH and δ -HCH, constituting 67-70%, 5-6%, 13% -15% and 6% technical HCH, respectively (Fig 4). γ -HCH, also called lindane, is the most effective component of technical HCH for pest control (ATSDR, 2005).

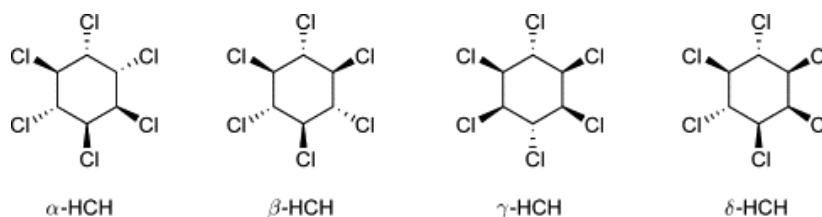


Figure 4 – Structures of HCH isomers

Aldrin and dieldrin, are chlorinated cyclodienes (Figure 5). Aldrin is rapidly converted to dieldrin through epoxidation of the double bond (ATSDR, 2021).

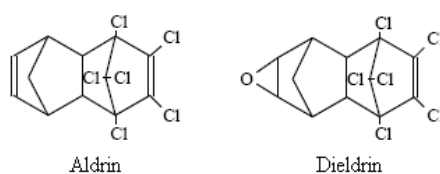


Figure 5 – Structures of aldrin and dieldrin isomers

Chlordecone is a cyclic ketone and represents a degradation product of mirex (Figure 6).

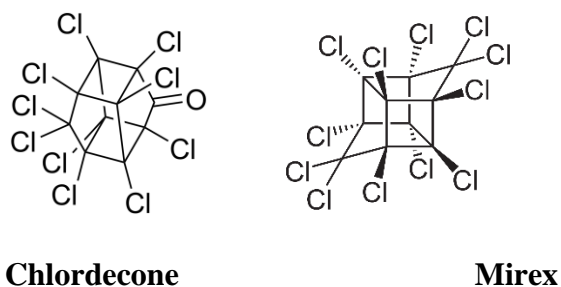


Figure 6. Structures of chlordecone and mirex

The physical and chemical properties of POPs such as molecular weight, partition coefficient n-octanol-water (K_{ow}), partition coefficient of the organic carbon (K_{oc}), Henry's law constant (KH) and vapor pressure (Pv) play an important role in explanation of their environmental distribution and transfer, exposure and bioaccumulation(ATSDR, 2021, 2019, 2005, 2000, 1998, 1994) (Table 3).

Table 3 – Some selected physical and chemical properties of chlorinated POPs: molecular weight (M.W), number of chlorine atoms (Cl_n), partition coefficient n-octanol-water (K_{ow}), partition coefficient of the organic carbon (K_{oc}), Henry's law constant (KH) and vapor pressure (Pv).

Chlorinated POPs	M.W	Formula	Cl_n	Partition coefficients		Pv at 25°C, mm Hg	K_H at 25°C, Atm - m3 mol ⁻¹
				K_{ow}	K_{oc}		
Organochlorine pesticides¹							
Aldrin	364,9	C ₁₂ H ₈ Cl ₆	6	6,5	7,7	1,2 x10 ⁻⁴	4,9 x10 ⁻⁵
Dieldrin	380,9	C ₁₂ H ₈ Cl ₆ O	6	6,2	6,7	5,9 x10 ⁻⁶	5,2 x10 ⁻⁶
Endrin	380,9	C ₁₂ H ₈ Cl ₆ O	6	5,6	5,2	2,0 x10 ⁻⁷	4,0 x10 ⁻⁷
Chlordane	409,8	C ₁₀ H ₆ Cl ₈	8	5,5	3,5	2,2 x10 ⁻⁵	4,8 x10 ⁻⁵
DDT	354,4	C ₁₄ H ₉ Cl ₅	5	6,9	5,2	1,6 x10 ⁻⁷	8,3 x10 ⁻⁶
DDE	318	C ₁₄ H ₈ Cl ₄	4	6,5	4,7	6,0 x10 ⁻⁶	2,1 x10 ⁻⁵
DDD	320	C ₁₄ H ₁₀ Cl ₄	4	6	5,2	1,3 x10 ⁻⁶	4,0 x10 ⁻⁶
Heptachlor	373,3	C ₁₀ H ₅ Cl ₇	7	6,1	4,3	3,0 x10 ⁻⁴	2,9 x10 ⁻⁴
Mirex	545,5	C ₁₀ Cl ₁₂	12	5,3	3,8	3,0 x10 ⁻⁷	5,2 x10 ⁻⁴
Toxaphene	414	C ₁₀ H ₁₀ Cl ₈	18	3,3	3	6,7 x10 ⁻⁶	6,0 x10 ⁻⁶
α-HCH	290,8	C ₆ H ₆ Cl ₆	6	3,8	3,6	4,5 x10 ⁻⁵	6,9 x10 ⁻⁶
β-HCH	290,8	C ₆ H ₆ Cl ₆	6	3,8	3,6	3,6 x10 ⁻⁷	4,5 x10 ⁻⁷
γ-HCH (Lindane)	290,8	C ₆ H ₆ Cl ₆	6	3,7	3,6	4,2 x10 ⁻⁵	3,5 x10 ⁻⁶

δ -HCH	290,8	C ₆ H ₆ Cl ₆	6	4,1	3,8	3,5 x10 ⁻⁵	2,1 x10 ⁻⁷
Chlordecone	490,6	C ₁₀ Cl ₁₀ O	10	4,5	3,4	3,0 x10 ⁻⁷	2,5 x10 ⁻⁸
Pentachlorobenzene	247,8	C ₆ HCl ₅	5	5,2	ND	2,0 x 10 ⁻³	7,0 x10 ⁻⁴
Hexachlorbenzene	284,8	C ₆ Cl ₆	6	5,7	6,1	1,1 x10 ⁻⁵	5,8 x10 ⁻⁴
Endosulfan	406,9	C ₉ H ₆ Cl ₆ O ₃ S	6	3,8	4	1,0 x10 ⁻⁵	6,5 x10 ⁻⁵
Pentachlorophenol	266,3	C ₆ HCl ₅ O	5	5	4,5	11,0 x10 ⁻⁴	3,4 x10 ⁻⁶
Dicofol	367,9	C ₁₄ H ₉ Cl ₅ O	5	5	>5000	3,9 x10 ⁻⁷	2,4 x10 ⁻⁷
indicator PCB^{s2}:							
28	257,5	C ₁₂ H ₇ C ₁₃	3	5,6	4,6	1,95 x10 ⁻⁴	2,0 x10 ⁻⁴
52	292	C ₁₂ H ₆ C ₁₄	4	5,8	3,4	1,8 x10 ⁻⁷	2,0 x10 ⁻⁴
101	326,4	C ₁₂ H ₅ C ₁₅	5	6,3	-	2,52 x10 ⁻⁵	0,9 x10 ⁻⁴
118	326,4	C ₁₂ H ₅ C ₁₅	5	6,7	-	8,9 x10 ⁻⁶	4,0 x10 ⁻²
138	360,9	C ₁₂ H ₄ C ₁₆	6	6,5	5,2	4,0 x10 ⁻⁶	0,21 x10 ⁻⁴
153	360,9	C ₁₂ H ₄ C ₁₆	6	6,8	4,8	9,0 x10 ⁻⁷	0,23 x10 ⁻⁴
180	395,3	C ₁₂ H ₃ C ₁₇	7	7,2	5,8	1,3 x10 ⁻⁹	0,1 x10 ⁻⁴
PCDDs¹							
2,3,7,8-TCDD	322	C ₁₂ H ₄ Cl ₄ O ₂	4	6,8	-	1,5 x10 ⁻⁹	2,5 x10 ⁻⁵
1,2,3,7,8 -PeCDD	356,4	C ₁₂ H ₃ Cl ₅ O ₂	5	8,6	-	6,6 x10 ⁻¹⁰	2,6 x10 ⁻⁶
1,2,3,4,7,8-HxCDD	390,9	C ₁₂ H ₂ Cl ₆ O ₂	6	7,6	-	3,8 x10 ⁻¹¹	44,6 x10 ⁻⁶
1,2,3,6,7,8-HxCDD	390,9	C ₁₂ H ₂ Cl ₆ O ₂	6	7,6	-	-	-
1,2,3,7,8,9-HxCDD	390,9	C ₁₂ H ₂ Cl ₆ O ₂	6	7,6	-	-	-
1,2,3,4,6,7,8-HpCDD	425,3	C ₁₂ HCl ₇ O ₂	7	8	-	5,6 x10 ⁻¹²	1,3 x10 ⁻⁶
OCDD	460	C ₁₂ Cl ₈ O ₂	8	8,4	-	8,2 x10 ⁻¹³	6,7 x10 ⁻⁶
PCDFs¹							
2,3,7,8-TCDF	305,9	C ₁₂ H ₄ Cl ₄ O	4	6,5	5,6	9,2 x10 ⁻⁷	1,5 x10 ⁻⁵
1,2,3,7,8-PeCDF	340,4	C ₁₂ H ₃ Cl ₅ O	5	7	-	2,7 x10 ⁻⁷	2,6 x10 ⁻⁵
2,3,4,7,8-PeCDF	340,4	C ₁₂ H ₃ Cl ₅ O	5	7,1	-	1,6 x10 ⁻⁷	2,6 x10 ⁻⁵
1,2,3,4,7,8-HxCDF	374,9	C ₁₂ H ₂ Cl ₆ O	6	7,5	-	6,1 x10 ⁻⁸	2,8 x10 ⁻⁵
1,2,3,6,7,8-HxCDF	374,9	C ₁₂ H ₂ Cl ₆ O	6	7,6	-	6,1 x10 ⁻⁸	2,8 x10 ⁻⁵
1,2,3,7,8,9-HxCDF	374,9	C ₁₂ H ₂ Cl ₆ O	6	7,7	-	3,7 x10 ⁻⁸	2,8 x10 ⁻⁵
2,3,4,6,7,8-HxCDF	374,9	C ₁₂ H ₂ Cl ₆ O	6	7,6	-	3,7 x10 ⁻⁸	2,3 x10 ⁻⁵
1,2,3,4,6,7,8-HpCDF	409,3	C ₁₂ HCl ₇ O	7	8	-	1,7 x10 ⁻⁸	4,1 x10 ⁻⁵
1,2,3,4,7,8,9-HpCDF	409,3	C ₁₂ HCl ₇ O	7	8,2	-	9,8 x10 ⁻⁹	4,1 x10 ⁻⁶
OCDF	443,8	C ₁₂ Cl ₈ O	8	8,6	8,6	-	1,7 x10 ⁻⁶

¹Partition coefficients, vapor pressure and Henry's law constant were derived from toxicological profiles of the correspondent compound.

² Partition coefficients, vapor pressure and Henry's law constant were derived from Brunner et al. 1990.

Generally, POPs have a medium *molecular weight* (*M.W*) ranged between 247 to 545 (OCPs), 257 to 395 (PCBs), 322 to 460 (PCDD/Fs) which allow these toxic molecules easily pass through the pores of cellular biological membranes and therefore accumulate in tissues. Besides, medium molecular weight also responsible for semi-volatile nature of the compounds and therefore their migration and distribution in food chains.

2.2. Lipophilicity

Chlorinated POPs are known by their ability to accumulate in lipid-rich tissues. Lipophilicity is the ability of a chemical compound to dissolve in lipids (for example in animal and human tissues) and in oils (for example in a feed of plant origin). Lipophilicity of the compounds is classically expressed as the logarithm of the partition coefficient k between octanol and water (K_{ow}) i.e. the more K_{ow} value of the compound the more hydrophobic the pollutant. Chlorinated POPs could be divided on 2 groups depending on the Kow value: highly hydrophobic compounds with the $Kow \geq 4.0$ and water-soluble compounds with the $Kow < 4.0$ and which presented on the Figure 7.

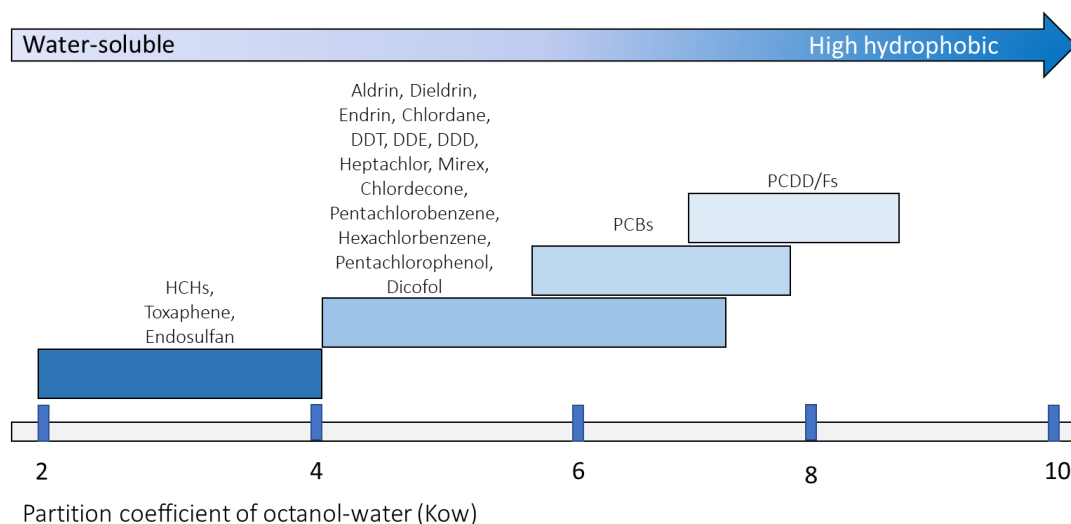


Figure 7 – Chlorinated POPs distribution depending on K_{ow}

Reported K_{ow} for PCDD/Fs ranged from 7.2 to 8.6 (except only TCDD and TCDF 6.6 and 6.5 respectively). (Chen et al., 2001; Covers and Krop, 1998) They are characterized by extremely low water solubility and have a tendency for being strongly adsorbed on surfaces of particulate matter.

The water solubility of PCDD/Fs decreases and the solubility in organic solvents and fats increase with increasing chlorine content.

PCB compounds with K_{ow} ranged from 5.6 to 7.6 (Zhou et al., 2005). They are less hydrophobic than PCDD/Fs, however PCBs also have high solubilities in most organic solvents, oils, and fats. The non-polar nature of PCBs means that they are strongly hydrophobic and thus strongly lipophilic. They exhibit a high predilection for smooth surfaces, and combined with their lipophilic and hydrophobic properties, this explains their presence absorbed into soil and sediment particles. The high surface concentration of lipids and organic compounds tend to concentrate and stabilize PCBs on the surface of water bodies.

OCPs generally are less hydrophobic than PCDD/Fs and PCBs. In addition, OCPs could be conditionally divided into 2 groups: with more hydrophobic compounds such as DDTs, aldrin, dieldrin and etc. and on water soluble compounds such as HCHs, toxaphene and endosulfan (Figure 7).

The log k_{ow} of POPs is well correlated to this partition coefficient of the organic matter or organic carbon (K_{oc}), especially comparing both coefficients for the given compound (Table 3). Indeed, partition coefficient is an adsorption coefficient normalized to the organic carbon (K_{oc}) content of the soil. It shows the binding capacity of the pollutant on organic matter of soil and sewage sludge. This parameter can be estimated through correlations with the water solubility and the n-octanol/water partition coefficient.

Comparing K_{ow} of different families of POPs (Figure 7) it could be concluded that the most lipophilic POPs (mainly not soluble in the water OCPs) tend to accumulate in the organic matter of soils. Therefore, partition coefficients could be a good prediction tool for estimation of the migration and accumulation of POPs in environment. Usually, partition coefficients are expressed as logarithm.

2.3. Volatility

Some POPs (particularly PCBs, DDT, HCHs) acquire the potential for long-range environmental transport due to their semi-volatile nature, which allows them to spread around the world through long-range transboundary atmospheric transport. These compounds evaporate from soils and water matrixes and can therefore be transported long distances from sources and uses. For example, trace amounts of DDT have been found in the Antarctic and in the Southern Ocean, despite their remoteness and geographic isolation (Bidleman et al., 1993; Bigot et al., 2016; Geisz et al., 2008;

Kallenborn et al., 2013). However, volatility of POPs depends on the temperature and climatic conditions of the environment, and as consequences POPs go through various volatilization-deposition cycles before being deposited in cold areas (Wania, 2003).

Volatility can be characterized by two parameters: the Henry's law constant (K_H) and the vapor pressure. The K_H (also called the *air-water* partition coefficient) is the ratio of a compound's partial pressure in air to the concentration of the compound in water at a given temperature. Values for Henry's law constants are expressed in units of atmospheres for air to moles per cubic meter for water ($\text{atm}\cdot\text{m}^3/\text{mol}$) (Table 3). A compound with a Henry's law constant $<5 \times 10^{-5} \text{ atm}\cdot\text{m}^3 \text{ mol}^{-1}$ is considered soluble and tends to remain in water (Olsen R. L. and Davis A., 1990).

Vapor pressure (P_v) is a tendency of compounds to «evaporate», i.e. to change the form from a solid or liquid into a vapor. In general, compounds with low vapor pressures are less likely to turn into a vapor and therefore will stay in the matrix. Molecules with high vapor pressures are more likely to get into the air. Typically, vapor pressure is expressed at 25 °C in torr or mm Hg (Table 3). This parameter together with molecular weight is responsible for the semi-volatile nature of POPs. Therefore, they can migrate over long distances, and by consequence reach regions that are far away from their emission source and deposited. These substances are found on all continents, including remote regions such as the oceans, deserts, the Arctic and Antarctica, where few emission sources exist. Indeed, many organochlorine compounds including PCBs, DDT, toxaphene and chlorobenzene have been found in Arctic cod (*Boreogadus saida*) (Prevet and Kolenosky, 1988), in polar bears (Dietz et al., 2013; McKinney et al., 2011; Sonne et al., 2004) and seals from the southeastern Canadian Arctic (Houde et al., 2019).

2.4. Persistence

The common property of all POPs is their persistence, which is expressed as their half-life ($t_{1/2}$). POPs have long half-lives in soils, sediments, air and biota. However, there are no defined values of half-life for a given family of POPs in a given media. For example, persistence of OCPs in soil could vary from moderate persistence with $t_{1/2}$ of approximately 60 days to high persistence with $t_{1/2}$ up to 10–15 years (Jayaraj et al., 2016). Study of Toan et al., 2009 experimentally investigated 14 years trend of DDT and metabolites and HCH isomers in soil which showed that half-life times of $\sum\text{DDT}$ and $\sum\text{HCH}$ are 6.7 and 4.9 years, respectively. This data is well correlated with established half-life values for OCPs in soil-sediment matrixes provided by Mackay et al., 2006). In addition, half-life of PCBs in sediments varies depending on congeners but generally could achieve 10 years (Beurskens et al., 1993; Lake et al., 1992). Half-life of PCDD/Fs have extremely

high values in sediments which could achieve 100 years (Kjeller & Rappe, 1995; Paustenbach et al., 2009).

The half-life of the target compound could allow to predict the duration of their presence in environmental media, but also in plant and animals. This parameter depends on the nature and behavior of the substance and the environmental conditions; therefore, it is impossible to unambiguously establish a fixed value for it. However, a reliable half-life range can be established for each compound in a studied environmental matrix. Thus, it is used for estimation of POPs elimination in living organisms, especially considering edible tissues of animal and plants.

The half-life can be effectively used to assess the risk of accumulation in different foods when the animals are exposed to such compounds. Indeed, when farm animals are raised near to POP sources, it becomes necessary to assess the transfer of these pollutants to meat, milk and eggs. Several investigations reported half-lives of POPs even if the reported half-lives can vary significantly between different compounds of the same family depending on the studied animals and experimental conditions. Indeed, half-lives have been estimated for PCDD/Fs at 7 weeks in laying hens (Traag et al., 2004) but only 50 days in lactating dairy cows (Firestone et al., 1979a; Olling et al., 1991). PCBs presented also different half-lives according to their chlorination: half-life of PCB 101 in lactating goats were reported at <4 days whereas PCB 180 showed $t_{1/2} > 8$ days (Fournier et al., 2013). Half-life of DDT in egg yolk was estimated at 7.6 days (Furusawa and Morita, 2001). Finally, the use of half-lives in risk assessment approaches should integrate the life expectancy of the studied animal. Generally short life expectancy as for ex. in broilers would not allow to hope significant reduction of tissue concentrations contrarily to animals with longer life cycles as hens (around 1 year) and cattle (approximately 2 years). Moreover, when long life cycle animals excrete eggs or milk, then the half lives in body tissues would be even shorter due to the excretion of POPs in these fatty products.

3. Emission sources

PCDD/Fs do not have a technical application and therefore it's unintentionally formed compounds. In most cases PCDD/Fs could be formed during production of pentachlorophenol (PCP) (Qian et al., 2005; Sein et al., 1994), during combustion processes and steel production (Rappe, 1994; R. zhi Zhang et al., 2018). In addition, solid residues from any combustion process such as bottom ash, slag and fly ash could be also one of the main emission sources of PCDD/Fs. The pulp and paper industry are also associated with dioxin releases (Axegård, 2019; R. zhi Zhang et al., 2018). Studies reported that possible sources of PCDD/Fs may be sewage sludge (Öberg

and Rappe, 1992; San-Román et al., 2020; Xia et al., 2020) and animal waste composts (Ng et al., 2008) in which they are naturally formed.

PCBs were first discovered more than 100 years ago, and their production and commercial use dates to 1929. PCBs have excellent electrical insulation properties and fire resistance. Therefore, these compounds are widely used as insulators and coolants in transformers and electrical equipment. Flammable insulating fluids have been successfully replaced with PCBs, thereby reducing the risk of fires in buildings (Rossberg et al., 2006)

The leader in the production of PCBs was the United States, which is estimated to have produced more than 640 thousand tons from 1930 to 1977 (de Voogt and Brinkman, 1989). After the Second World War, Europe also began to manufacture PCBs. In the world as a whole, over 1.3 million tons of PCB-based oils were produced between 1920 and 1989 (Breivik et al., 2007). However, as a result of several serious and dangerous incidents involving PCBs, production has ceased since 1983 in most countries (Aoki, 2001; Kocan A et al., 2004) with the exception of a few countries in Eastern Europe

Most countries have never produced PCBs. Nevertheless, PCBs were imported and used as technical mixtures, and were also used in components of various products, including electrical equipment.

OCPs are synthetic chemicals used in agriculture against insects and pests, called insecticides. The widespread application of OCPs in agriculture, due to their effectiveness was from the 1940s to the 1960s in the United States and Europe (US Geological Survey, 2016). Indeed, the first and the most infamous pesticide is DDT which has been used extensively against vectors of malaria, as well as against mosquitoes. Most of the OCPs are found their application in the past century as effective treat against pest of a variety of crops, fruits, plant, seeds, and animal husbandry. However, studies reported that only a small percentage (0.3%) of the used pesticides enter to the target pest, while about 99% is transferred to environmental matrices (Pimentel, 1995). Unfortunately, due to the high bioaccumulation, stability to degradation and adverse health effects, these chemicals led to an increase an environmental pollution - soil, water and air.

4. Environmental fate and interactions of studied POPs in the food chain soil - farm animals - food products

The negative effects of POPs on the environment are observed in almost all countries of the world. The sources of emissions of persistent toxic compounds (section 3) and their pathways are varied.

Figure 8 represent the main links between sources of POPs emissions and pathways through the food chain, including human exposure. The transfer of POPs along the food chain soil - farm animals - food products is an object of the current study (Figure 8). Therefore, environmental fate and interactions of POP in these food chain will be discussed detailly in subsequent sections.

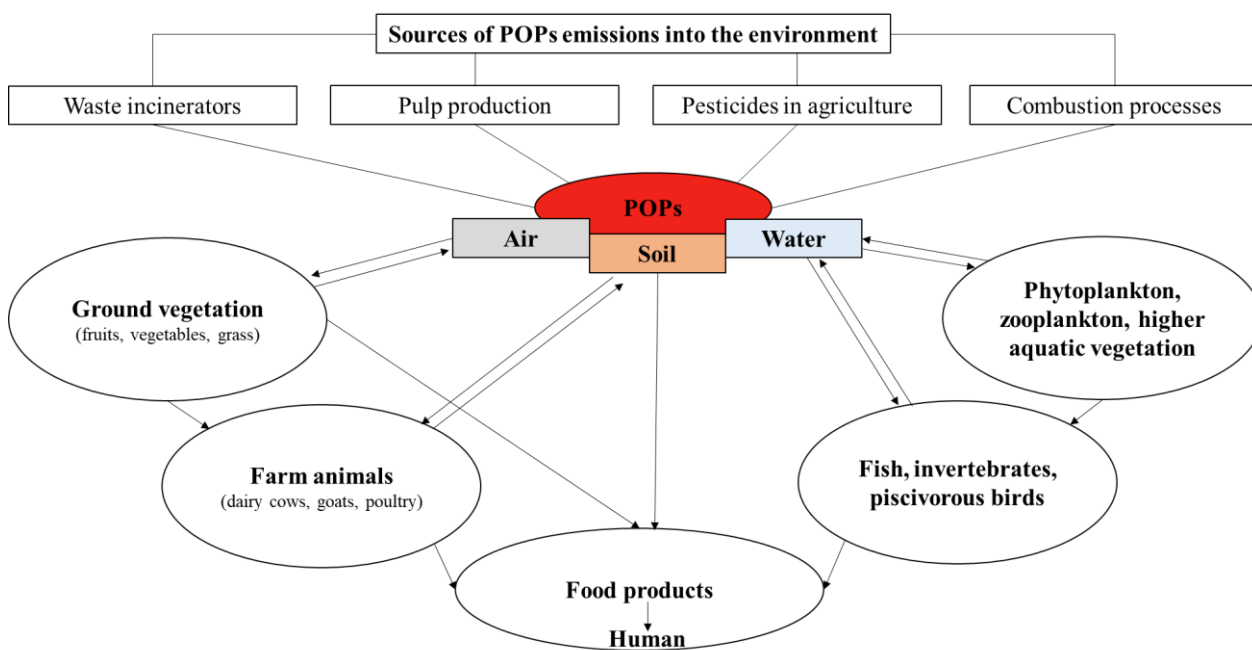


Figure 8 - Sources of emissions of POPs into the environment and ways of their distribution in food chain

4.1. Environmental fate of POPs in soil

Soil is powerful reservoir of different toxic substances including POPs. Indeed, POPs with their high persistence and long half-life can deposit in soil for many years (Bakoglu et al., 2005; Cheng et al., 2003; Danielovič I. et al., 2014; Deng et al., 2011; Domingo et al., 2000). The main route of POPs entering the soil is atmospheric transport depositions and anthropogenic activities (spraying of pesticides, combustion processes) (Wang et al., 2016).

Soil contamination with POPs is influenced by soil composition, water content and soil organic matter (SOM) (Nam et al., 2008). Soils with favorable conditions for the accumulation of POP are usually characterized by moderate to high humidity, which makes it easier for substances to settle and penetrate into it, and even migrate into deeper layers. For example, such soils include forest and mountain soils with a rich humus composition (Brorstroè M-Lundeâ & Loè, 1998; Nizzetto et al., 2006).

Soil organic matter (SOM) is composed of amorphous organic matter (AOM) and carbonaceous materials such as black carbon (BC), coal and kerogen. The SOM content varies widely, being particularly abundant in temperate forests, grasslands, and peat. SOM is a very important soil property since organic matter such as humic and fulvic acids in soils have a high affinity for POPs (Li et al. 2018; Persson et al. 2007). Organic matter has been accepted as the principal factor in controlling sorption of organic chemicals in soils and sediments (Burgess and Lohmann, 2004; Cornelissen et al., 2005; Sweetman et al., 2005). Depending on the amount of organic matter and its high retention capacity, soil (as well as sediments) is considered to be sink and source of re-release of POPs through volatilization, decomposition and leaching (Ukalska-Jaruga et al., 2020). The organic fraction of soils can vary from 2% in spodosol to over 60% in vertisols (Andreux F., 1996). These differences, and in general the SOM composition, are expected to greatly affect the accumulation of POPs in soils (Backe et al., 2004; Danielovič I. et al., 2014). Due to the high sorption capacity of the soil, the dispersion and migration of any pollutants occurs much slower than it is observed in the water and air. Light sandy soils (sand, sandy loam) are less resistant to organochlorine compounds, which can therefore easily move down through soil profile, polluting groundwater. POPs such as PCDD/Fs, PCBs and OCPs remain in humus-rich soils for a long time in the upper horizons, mainly in the layer up to 20 cm (Fries, 1982; Jones et al., 1989; Stevens & Gerbec, 1988). Therefore, soil usually contain higher in order of magnitudes POP concentrations than in other environmental media.

4.2 Transfer of POPs from soil to farm animals and food of animal origin

POPs can transfer to animals and birds (and humans) through several routes: oral consumption, inhalation, and through dermal adsorption.

There are no literature data reported about animal exposure through inhalation of contaminated air, exposure through the skin and consumption of contaminated water, probably due to their negligible effect. Therefore, the main route of POPs exposure to ruminants and poultry is the oral consumption of contaminated feed and soil (Rychen et al., 2008).

Feed of plant origin (corn and maize silage, wheat, soybeans, ground nuts, sugar beet and many others) used for feeding farm animals are subject to constant monitoring in many countries. Historically, there have been many cases of massive contamination of animal feed, leading to severe spread of POPs contamination through the food chain. Examples are the Belgian dioxin crisis in 1999 (Bernard et al., 2002), dioxin accident in Ireland in 2008 (Pratt et al., 2012),

unintentional contaminated feed supply examples such as ball clays in poultry (Hayward, 1999), kaolinic clay in Netherlands (Ábalos et al., 2016). POPs from feed could be transferred to animals and bioaccumulate in their organs (Aulakh et al., 2006; Feil et al., 2000; Lorenzi et al., 2020; MacLachlan and Bhula, 2009). However, feed is not the only one route through direct consumption for farm animals.

Indeed, recent meta-analysis of published data about transfer of POPs to farm animals (Amutova et al., 2021) highlighted that soil is a very strong sink for POPs and transfer vector to food producing animals.

Several studies have reported that ruminants would consume in normal grazing conditions up to 10% of soil in daily dry matter intake (Collas et al., 2019; Healy, 1968; Jurjanz et al., 2012) and even up to 30% in the rigorous conditions as winter grazing (Abrahams and Steigmajer, 2003). Poultry also ingest soil along pecking contaminated feed from the ground. In unbalanced feeding conditions, the soil intake in laying hens may reach up to 23% (Jondreville et al., 2010; van der Meulen et al., 2008). During such soil intake, persistent organic pollutants (POPs) deposited on the upper soil can be ingested by livestock (Fries, 1982; Jones et al., 1989; Stevens and Gerbec, 1988) and transferred into their subsequent food products. Previous studies have demonstrated that contaminated soil is the main source of exposure to pollutants for livestock, especially when soil is contaminated by chlorinated POPs (Diletti et al., 2014; Tao et al., 2009). Some studies have reported transfers of OCPs and PCBs to livestock after atmospheric deposition leading to contamination of water, soil and vegetation (Pan et al., 2014b) by regular floods (Abrahams and Steigmajer, 2003; Rose et al., 2012) and others.

Field and laboratory investigations concerning POPs transfer from contaminated feed and soil showed that different animals accumulate pollutants in their tissues, especially in the liver and adipose fat and to excreted products such as milk and eggs (Aulakh et al., 2006; Costera et al., 2006; Diletti G et al., 2009; Feil et al., 2000; Fernandes et al., 2011; Fournier et al., 2015, 2013, 2012; Fries et al., 2002; Hoogenboom et al., 2004). As a result, consumption of such contaminated food would be a possible route of POP exposure for humans (Mclachlan et al., 1990), and the correct quantification of the POP transfer from contaminated environmental matter to food products is essential for a reliable risk assessment.

5. Worldwide regulations to limit POPs wide spreading in the environment and food products

The increasing number of scientific Congresses in the late nineties focusing on the global problems due to POPs showed that the world community began to structure a global approach to limit their

income in the environment. Consequently, various conferences and meetings aimed to create international agreements to limit POPs production, use and release or if possible, to eliminate these toxic substances.

The first international convention to control, to reduce or to eliminate POPs in the environment was the Aarhus Convention (or Aarhus Protocol), adapted in 1998 and entered into force in 2004 (UNECE, 1998). This convention includes 46 states and the European Union. The Aarhus Convention was a prerequisite for the development of a larger document called the Stockholm Convention.

The Stockholm Convention represents a final version of all this work of structuring how to ban POPs. It is an international agreement defining for each family of POPs, rules for their prohibition, restriction their use or at least limiting their unintentional production. This document was adapted in May 2001 at a conference in Stockholm, Sweden, and was adopted in May 2004. The original POPs list only included 12 groups of substances known as the "dirty dozen". Most of them were pesticides; industrial chemicals or unintentional by-products of industrial and combustion processes (WHO, 2003). The entire list of substances with all annexes is presented in the Stockholm Convention website (Stockholm Convention, 2019). Since then, more and more countries signed and applied these restrictions and in September 2019, 184 states (183 states and the European Union) are parties to the Convention. European union countries, Australia and China were the first states entered in force the Convention (2004-2006). Russia and Kazakhstan accepted the Convention measures in 2011 and 2008, respectively. All countries-members incorporated Stockholm Convention into their law and regulation on the governmental level. Notable states that have not ratified the Convention include the United States, Turkey, Israel, Malaysia, and Italy.

To establish hazardous limits for the concentration of POPs in various matrices, and to assess the exposure degree, standard sanitary and hygienic thresholds were adopted, generally on the level of the country. Such thresholds are the maximum allowable concentration (MAC) and maximum residual levels (MRL) targeting to reduce the human exposure to levels which should not harm human health.

The MAC characterizes the maximum concentration of a substance that can be present in the given matrix at given time without harming to living organisms. Depending on the matrix, which contains a particular POP, its MAC is expressed in units expressed to the matrix, i.e. per m³ in air or per L in water.

Pesticides are the only POPs for which the maximum concentration of their residues in Feed and Food are expressed as Maximum Residue Level (MRL). Indeed, this regulatory value defines the

maximum tolerated residue of a pesticide (expressed in mg/kg) in a given in food and animal feed on the base of Good Agricultural Practice (GAP) (FAO, 2016). The MRL may vary for a given matrix, depending on the country. There are many MRL databases for food of animal and plant origin and animal feed.

For example, here below listed several MRL databases accepted in some countries:

- 1) Codex Alimentarius database (Codex Alimentarius, 2019)
- 2) EU MRL database (EU Pesticides Database (v2.2), 2022)
- 3) USA MRL database (Code of Federal Regulations, 2022). MRLs are in part 40, section 180
- 4) Australian MRL database (Food Standards Australia & New Zealand, 2021), MRLs are in Schedule 20
- 5) Russian Federation MRLs (Hygienic standards for the content of pesticides in environmental media, 2013) Search for document series '1.2.3111-13'.

MRLs databases generally are taking into consideration the Codex Alimentarius (Codex Alimentarius, 2019) designed by FAO and WHO. The Codex Alimentarius is a set of internationally accepted food-related standards and related texts presented in a uniform format. The Codex aim to protect consumer health and ensure fair trade in food internationally. This means that Codex Alimentarius publications usually used as a guidance and assistance in the development of definitions and requirements for food products that would increase the level of harmonization of requirements and thereby contribute to the development of international trade. Codex standards and related texts are not replacements or alternatives for national legislation but are solid basis that various countries may use to develop and approve their own MRLs and pesticide legislation. In 2021, the Codex Alimentarius Commission accounted 189 Codex members - 188 countries and 1 organization (EU), which means representatives of 99% of the world population.

There is no single international direct regulation of POPs contents in different soils, drinking water and food. However, USA and some countries of EU, Commonwealth of Independent States (CIS) have a normative regulations established for limitation of PCDD/Fs, PCBs and OCPs in soil and drinking water as well as in food. For example, in USA (EPA, 2022), Czech Republic (Commission Regulation (EC) No 169/2002, 2002; Commission Regulation (EC) No 343/200, 2001), Poland (Commission Directive 2002/69/EC, 2002; Commission Regulation (EC) No 2375/2001, 2001) and CIS countries (GN 1.2.3539-18, 2018; GN 2.1.5.1315-03, 2007; SanPin 4630-88, 1989). The limit values derived from European

Commission Report (Commission Regulation (EC) No 1881/2006, 2006; ENV.C.2/SER/2002/0085, 2004), Russian and CIS countries normative documents, toxicological profiles for PCDD/Fs (ATSDR, 1998, 1994), PCBs(ATSDR, 2000) and OCPs(ATSDR, 2019, 2005) presented in Table 4.

6. Intermediate conclusions

Summing up the review, several intermediate states could be concluded:

1) Chlorinated POPs such as PCDD/Fs, PCBs and OCPs have different toxicity, persistency and adverse effects which is based on their physical and chemical properties.

2) Soil together with vegetation is the main pathway of POPs for farm animals as oral consumption represent the biggest contribution to exposure than inhalation or dermal contact. Soil is rich with organic matter which has a high affinity to accumulate POPs, and therefore soil usually contained more concentrations than plants.

3) POPs deposited in soil could be transferred to livestock animals during free grazing and finally reach food products such as milk, meat and eggs. In this context, further chapter will focus on different methodologies for POP transfer assessment in food chain soil – livestock – food products.

Table 4 – Regulations applicable to PCDD/Fs, PCBs, DDTs and HCHs in soil, water, air, milk, meat and eggs in different countries.

Object	POPs	EEC countries ¹	USA	European countries
Drinking water	PCBs, µg/L	1	0.5	0.01
	PCDD/Fs, mg/L		3×10^{-8}	
	DDTs, mg/L	0.1	3×10^{-8}	0.001
	HCHs, mg/L	0.002	2×10^{-3}	2
Soil	PCBs, mg/kg	0.1	0,027	0.02 (background) 0.1 (MAC)
	PCDD/Fs, ng/kg TEQ	0,33	-	0.5 (background), 5 (MAC)
	DDTs, mg/kg	0.1		
	HCHs, mg/kg	0.1		
Milk	PCBs, mg/kg fat	1.5	1.5	0.1
	PCDD/Fs	5.2 ng/kg fat		3 WHO TEQ pg/g fat
	DDTs, mg/kg	0,05		0.04
	HCHs, mg/kg	0,05		0.01
Meat	PCBs, mg/kg fat	-	3	0.2
	PCDD/Fs	3.3 ng/kg fat		Ruminants -3 Poultry -2 Liver – 6 WHO TEQ pg/g fat
	DDTs, mg/kg, fat	0.1		1
	HCHs, mg/kg fat	0.1		0.01
Eggs	PCBs, mg/kg fat	-	0.3	0.2
	PCDD/Fs	3.3 ng/kg fat		3, WHO TEQ pg/g fat
	DDTs, mg/kg fat	0.1		0.05
	HCHs, mg/kg fat	0.1		0.01

¹EEC countries means Eurasian Economic Community countries

PART II: Methodology to determine the availability of soil bound contaminants

As it shown in previous chapter, farm animals' exposure via ingestion of POPs contaminated soil and feed represented the highest contribution to bioaccumulation in their tissues and excreted products (milk and eggs) compared to exposure via inhalation or dermal contact. Soil may contain high content of organic matter known to possess a high affinity to POPs. Therefore, soil a well-known reservoir to lipophilic contaminants and usually present higher lipophilic pollutant concentration than other environmental matrices.

The standard tool widely used to assess the risk of exposure to POPs from natural matrices is the determination of the total extractable concentration. For example, to determine the total extractable concentration of POPs in soil, 2 main steps are used: exhaustive extraction stage (Dean J.R. and Scott W.C, 2004) and gas chromatographic analysis. Methods for extracting POPs from soil include Soxhlet extraction, ultrasonic extraction, shake flask extraction, and modern instrumental approaches using supercritical fluid extraction, microwave extraction, and pressurized fluid extraction (PLE) (Dean J., 2003). After, the extract is examined by gas chromatography with different detection such as mass spectrometric detector and an electron capture detector. However, the total extractable concentration of a pollutant cannot provide information on the amount of a chemical available for uptake and bioaccumulation. By consequence, the risk assessment would overestimate the exposure leading to an excessive destruction of contaminated material (feedstuffs, produced vegetables and foodstuffs and living animals) with large economic and social consequences in a situation of crisis, i.e., for example when there is a contamination of agricultural and livestock farms. Therefore, in recent years, in addition to the total concentration of substances, it is customary to conduct a study on the bioavailability of POPs, which significantly complements the approach and refine the risk assessment (Rostami & Juhasz, 2011; Wittsiepe et al., 2007) in order to limit all destruction of contaminated matters to the absolutely necessary level (Alexander M., 2000; Collins et al., 2015).

Bioavailability is a degree to which chemicals present in the soil, can be absorbed or metabolized by a human, animals, or other ecological receptor, or be available for interaction with biological systems (Fries et al., 1989; ISO 17402:2008). The bioavailability of soil borne POPs is the result of its transfer to the exposed organism. Three stages appear to be decisive in pollutant-organism interactions (Figure 9 and Figure 10):

1) Solubilization of the POPs, including its desorption from its original matrix and the acquisition of a potentially assimilable form.

2) Absorption of the POPs by the organism by passage through the biological membranes and separating from the external to the internal environment (skin, digestive mucosa, alveolar epithelium, etc.).

3) The achievement of the biological target by the contaminant and possible realization of the biological effect (accumulation, metabolism, toxicological effect, etc.).

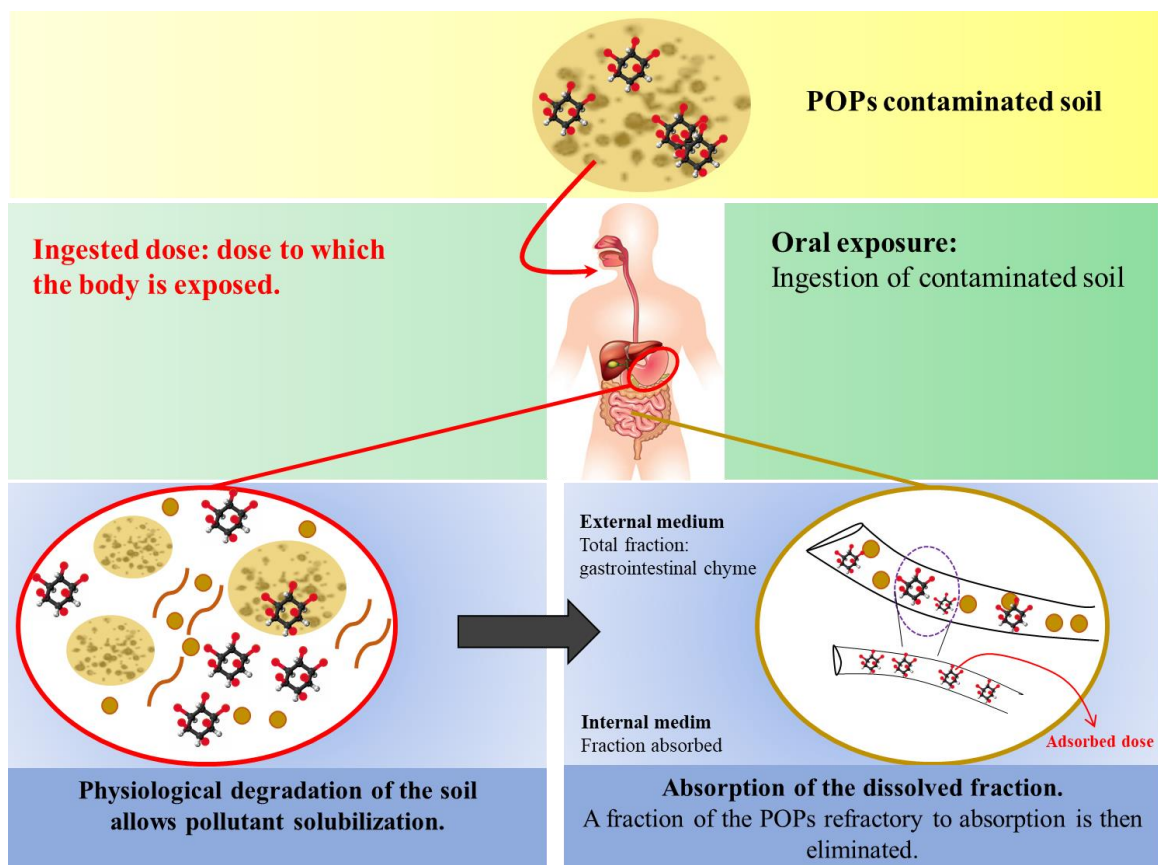


Figure 9 - The place of bioavailability in the assessment of exposure to persistent organic pollutants (scheme adopted from Delannoy M., 2014).

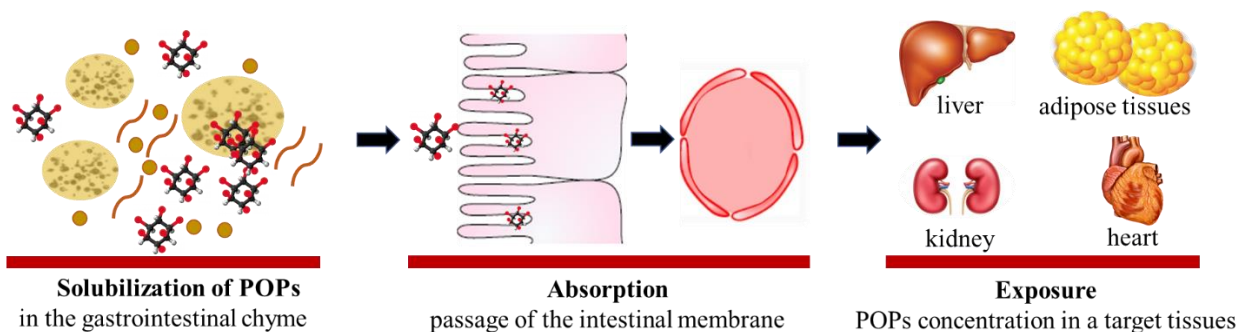


Figure 10 – Stages of bioavailability. Schematic representation of main steps which should be considered at exposure risks associated with POPs contaminated soil (scheme adopted from Delannoy M., 2014).

Thus, the bioavailability of POPs is an important risk assessment tool that requires a correct quantitative calculation and can be used in estimation the transfer and exposure of POPs on organism as well as it could be utilized in development of remediation strategies (Rostami & Juhasz, 2011).

This chapter will review existing *in vivo* and *in vitro* methodologies for estimating the exposure and transfer of soil-borne POPs to animal organism. Generally, the methods will include bioavailability assays utilizing animal models (*in vivo*), surrogate assays (*in vitro*) for estimating *in vivo* POPs bioavailability, the validation of surrogate assays and further research are needed steps in order to estimate accurately POP bioavailability.

1. Concepts of evaluate a pollutant transfer

There are several scientific concepts that can be used to evaluate transfer and quantify the exposure level of POPs. These concepts include 2 groups depending on performing conditions:

- 1) *In vitro* methods: environmental availability (i) and bioassessibility (ii);
- 2) *In vivo* methods: relative or absolute bioavailability (iii), bioconcentration factor (BCF) (iv) and transfer rate (TR) (v).

Figure 11 shows how the concepts are connected and pass from one to another, which accordingly characterizes:

- i) **Environmental availability:** fraction of contaminant physico-chemically driven by desorption processes potentially available to organisms (ISO 17402:2008).
- ii) **Bioassessibility:** pollutant solubilization and mobilization during digestion processes.

iii) **Bioavailability** (absolute or relative): pollutant passage through the intestinal membrane and its distribution to target tissues. Absolute bioavailability is defined as “the fraction of a dose of pollutant from an ingested matter, and from the gastrointestinal tract, skin, or lungs to the systemic circulation” (Ruby et al., 1999). Relative bioavailability is defined as “comparison of the bioavailability of contaminants present in the studied ingested matter compared to a reference matrix having the same concentrations of organic contaminants and more stable than the study matrix” (Ruby et al., 1999).

iv) **Bioconcentration factor** expresses a bioaccumulation rate of pollutants into the organs which is based on a ratio of pollutant concentration in the target tissue to concentration of pollutant in the intake matter.

v) **Transfer rate** expresses an elimination of pollutants from the organism to excreted products such as milk or eggs. Transfer rate could be estimated as a ratio of between ingested and excreted amounts of the pollutant to milk or eggs.

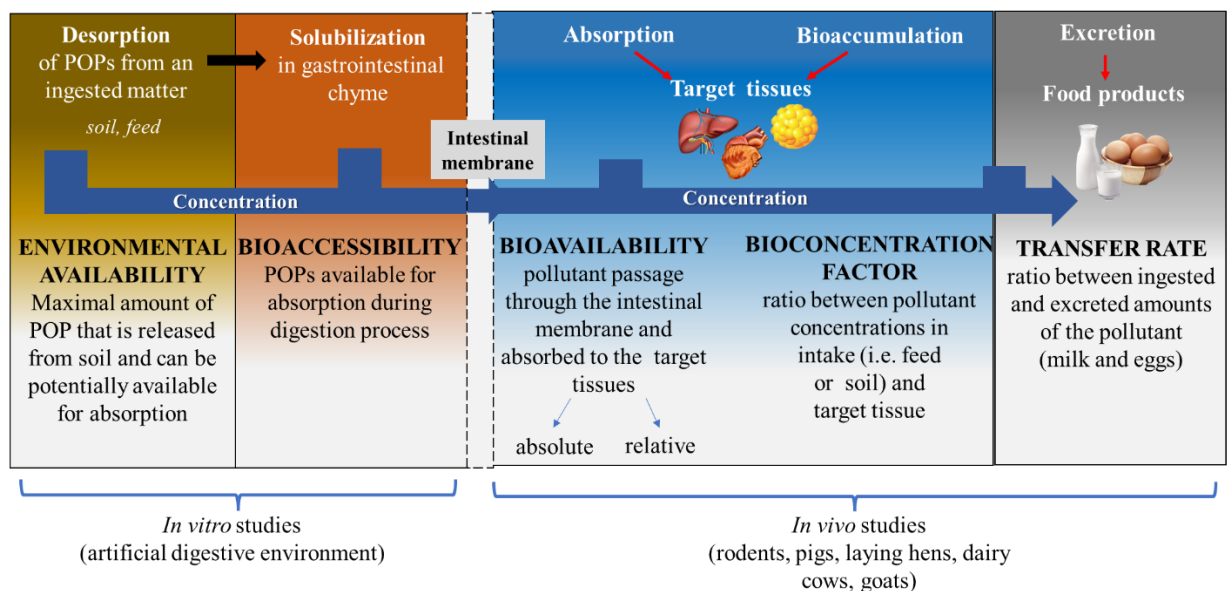


Figure 11 – Relationship between different concepts which allow to evaluate POPs transfer: environmental bioavailability, bioaccessibility, bioavailability, bioconcentration factor and transfer rate (adapted from Collins et al., 2015).

2. *In vitro* tools

2.1 Environmental availability assays

The concept of environmental availability characterizes the global availability of soil borne contaminants for absorption by a biological system. To assess environmental availability, there are

methods that include the step of “mimicking” uptake by various organisms and are called “mimicking methods”, while other methods are used to determine certain chemical parameters of POPs exposure (Cuypers et al., 2002; Doick et al., 2005; Kelsey and Alexander, 1997). All these methods are conditionally divided into two types:

Type 1: Partial extraction methods for assessment of environmental availability of POPs using an adsorbent such as Tenax, XAD resin or cyclodextrin. Detailed analytical procedures are found for mild solvent extraction (Kelsey and Alexander, 1997; Liste and Alexander, 2002), cyclodextrin extraction (Cuypers et al., 2002; Reid et al., 2000), Tenax extraction (Cornelissen et al., 1997, 2001).

Type 2: application of passive samplers based on the principle of equilibrium sampling. For example, some procedures are based on the use of polyethylene devices (PEDs) (Cho et al., 2009), semi-permeable membrane devices (SPMDs) (Huckins et al., 1990; Zimmerman et al., 2004), polyoxymethylene (POM) sampler, thin ethylene vinyl acetate (EVA) or polydimethylsiloxane (PDMS) coatings (Arthur and Pawliszyn, 2002; Hunter et al., 2008; Mayer et al., 1999). These methods are well reviewed in elsewhere (Cui et al., 2013; Dean, 2007; Dean & Scott, 2004; Scott & Dean, 2005) including main working principle, advantages and disadvantages. In this review only non-exhaustive extraction (first type) based on Tenax and cyclodextrin will be discussed as they found as the most promising and effective approaches of the last years (Bernhardt et al., 2013).

Non-exhaustive extraction methods for determining the environmental availability of POPs are a simple shaking extraction procedure and are based on the release of POPs from the soil matrix through the aquatic media onto a strong adsorbent such as Tenax and cyclodextrin (Cui et al., 2013; ISO 16751:2020). Chemicals dissolved in an aqueous solution are adsorbed on the surface of the Tenax beads or are retained by the hydrophobic surface of the cyclodextrin, and thus removed from the aqueous medium. In this case, the aqueous environment plays the role of a “receiver phase”. Thus, this approach mimics the absorbing and accumulative activity of biological systems (e.g. microorganisms, worms, farm animals), and hence the total potentially environmentally available fraction of POPs is achieved (Bernhardt et al., 2013; Collins et al., 2015).

Cyclodextrin extraction procedure. Cyclodextrin is a cyclic oligosaccharide with a hydrophilic surface and a non-polar toroidal cavity, and as a result is able to strongly adsorb POPs from a solid matrix (Dean, 2007). The studies most frequently use hydroxypropyl- β -cyclodextrin (HPCD) to assess availability. The main steps of the HPCD methodology are shown in Figure 12.

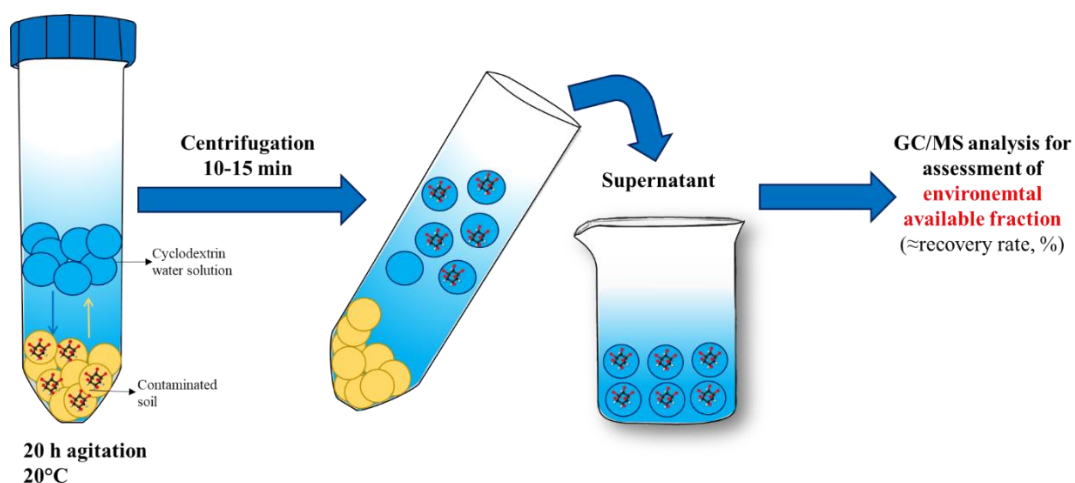


Figure 12 – Standard methodology of extraction based on the hydroxypropyl- β -cyclodextrin (HPCD) (modified from (Cui et al., 2013; Reid et al., 2000).

The HPCD-based extraction procedure involves adding an HPCD solution to a soil sample, mixing for a predetermined time interval (for example 20 hours), and then centrifuging to obtain a supernatant to be used for analysis. For example, this method has been used to predict the environmental availability of OCPs and PCBs in soils or sediments (Puglisi et al., 2007; Wong and Bidleman, 2010).

The main advantages of HPCD are the relative ease of sample preparation, while the main disadvantages are animal species dependent characteristics and limited extractive power of HPCD, which can lead to underestimation of availability (Hartnik et al., 2008).

Tenax extraction. Tenax is a beadlike, porous polymer based on 2,6-diphenyl-p-phenyleneoxide which has a high sorption capacity to substances such as POPs (Bernhardt et al., 2013; Cornelissen et al., 2001; la Cal et al., 2008). The general steps for Tenax-based extraction are shown in Figure 13.

Extraction based on Tenax begins with mixing the Tenax beads directly with the soil suspension in centrifuge tubes. After that, to separate the adsorbed fraction of POPs on Tenax, centrifugation is carried out. The density of Tenax is lower than the density of water, due to which the granules float to the surface after centrifugation and are easily removed from the supernatant by filtration. This property, combined with the hydrophobic nature, makes it easier to measure the desorption of POPs. After filtration, the collected Tenax pellets are extracted with an organic solvent such as hexane (Bernhardt et al., 2013; Cornelissen et al., 2001). After removing Tenax from the centrifuge tube, a fresh portion of Tenax is added to the soil and the above steps are repeated.

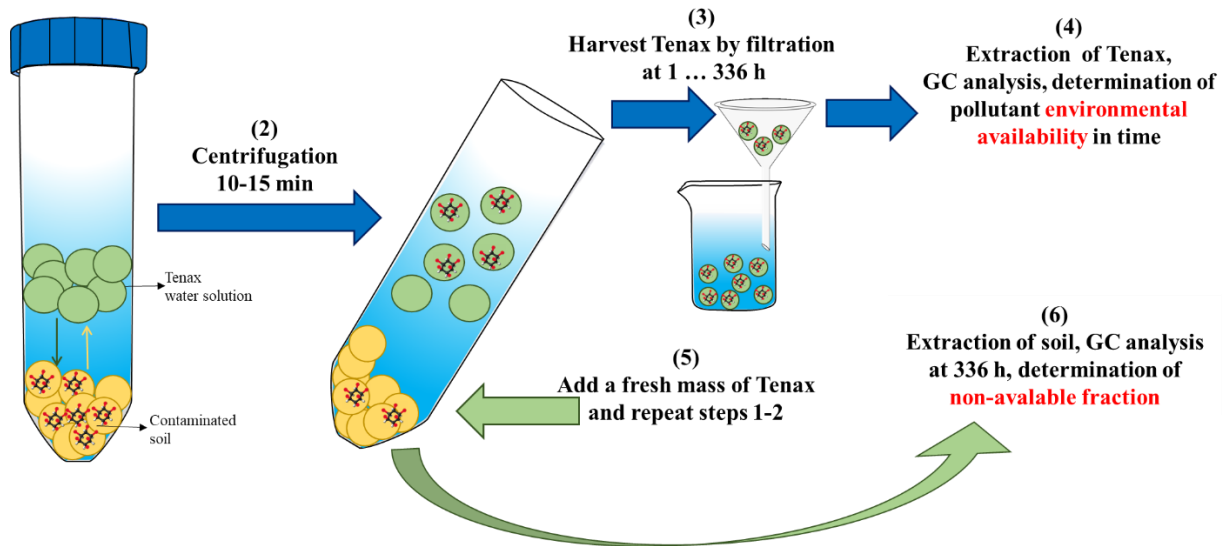


Figure 13 - Standard methodology of extraction based on the Tenax

Usually, when performing extraction on the basis of Tenax, the kinetics of desorption is investigated. Thus, the collection of Tenax granules after mixing and filtering is carried out in time, for example 1 hour, 2 hours, 4 hours ... 336 hours, and then sequential extraction is carried out. There is a three-component equation model (Eq. 1) that assumes first-order kinetics for each of the three compartments: desorption fraction of contaminant presented in aqueous phase (F_{aq}), rapidly desorption fraction (F_{rapid}), and slow desorption fraction (F_{slow}) (Cornelissen et al., 1997):

$$\frac{S_t}{S_0} = F_{aq} e^{-k_{aq}t} + F_{rapid} e^{-k_{rapid}t} + F_{slow} e^{-k_{slow}t} \quad (1)$$

where S_0 and S_t are the POP concentrations (μg) in the sample at the beginning (i.e. prior to desorption) and time t , respectively, and k_{aq} , k_{rapid} , and k_{slow} are the corresponding rate constants for the three desorption pools. However, it should be noted that desorption of POPs from soil is a continuum, and the parameters, such as F_{rapid} , F_{slow} , and F_{vslow} , are operationally defined to simplify the model application (Cornelissen et al., 1997).

Studies by Cornelissen et al., 1997 and Kukkonen et al., 2003 showed that Tenax extraction is most commonly used to determine F_{rapid} in soil samples. This is likely due to the fact that F_{rapid} is positively associated with POPs bioaccumulation and microbial degradation (in case of PAHs) (Braida et al., 2004; Cornelissen et al., 1997; Kraaij et al., 2002; Landrum et al., 2007; Leppänen et al., 2003). The main disadvantage of Tenax-based extraction is the need for long series of extractions to build the desorption kinetics for calculating F_{rapid} , which requires a lot of time, effort and therefore could be costly. However, some works (Cornelissen et al., 2001; Landrum et al., 2007; ten Hulscher et al., 2003) have studied desorption over a single time interval of 6 hours

(F_{6h}). At the same time, these studies noted that the ratio of F_{6h} to F_{rapid} has strong variations from 0.38 ± 0.25 to 10.26 ± 5.15 for PCBs, PAHs, chlorinated benzenes and DDT (Cornelissen et al., 2001; Landrum et al., 2007; ten Hulscher et al., 2003).

2.2 Bioaccessibility assays

The definition of bioaccessibility of soil borne POPs involves the use of *in vitro* methods for extracting chemicals from the gastrointestinal tract. The main principle of the methodology is to model the gastro-intestinal processes occurring in the body, which lead to the release of POPs from the soil matrix. It is clear that the digestive system of the body is a very complex system, therefore, methods for assessing bioaccessibility do not reproduce the conditions in the gastrointestinal tract but imitate key processes and their dynamics (Lu et al., 2021).

Methods for determining bioaccessibility *in vitro* include two main phases: gastric and intestinal (Figure 14). There are several parameters that are taken into account when developing a modeling methodology for a gastrointestinal model to simulate mobilization of soil borne POPs. These parameters include gastric and intestinal composition, pH, agitation, residence time, soil to solution ration, and food amendment.

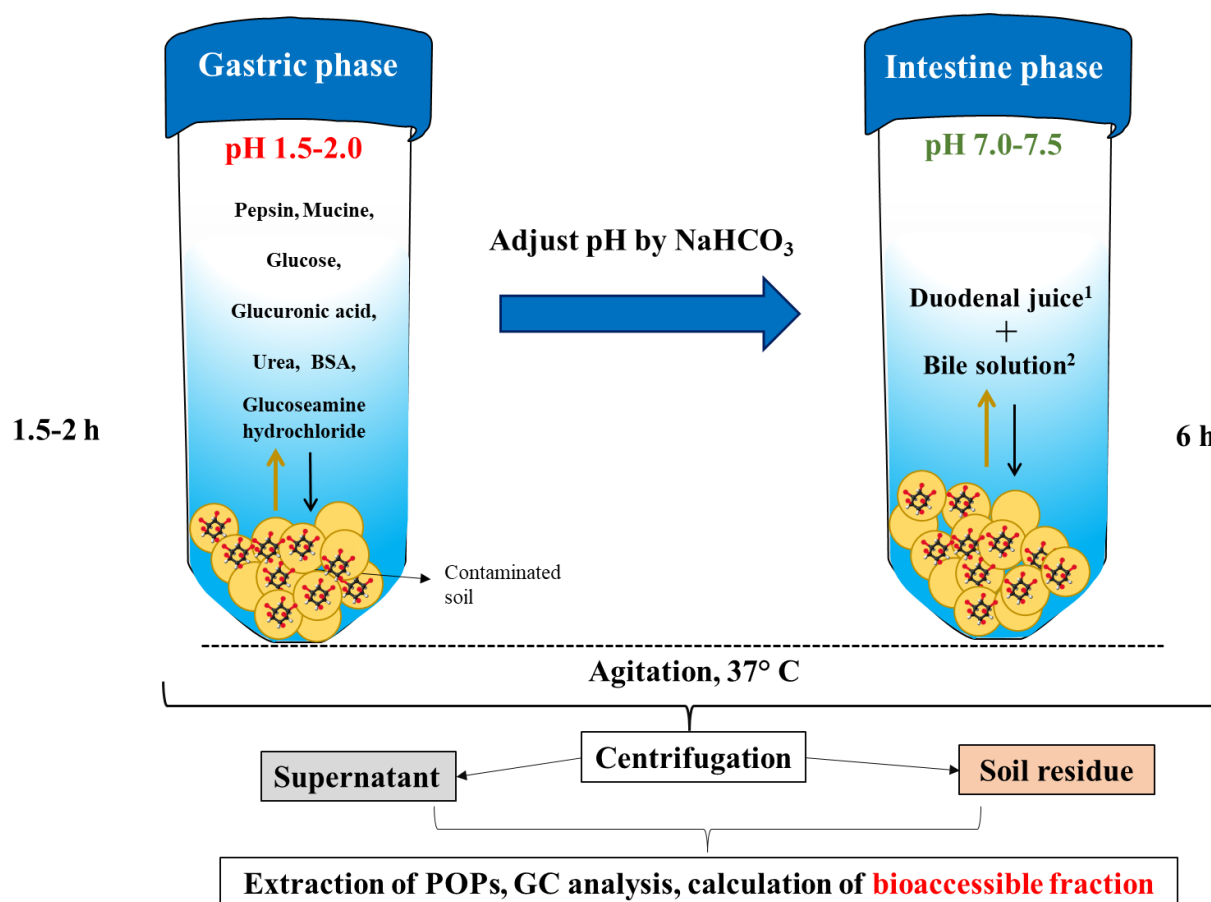


Figure 14 – Standard methodology to assess bioaccessibility of soil borne POPs

¹Duodenal juice composition: NaCl, NaHCO₃, KH₂PO₄, KCl, MgCl₂, urea, CaCl₂*2H₂O, BSA, porcine pancreatin, lipase;

²Bile solution: NaCl, NaHCO₃, KCl, urea, CaCl₂*2H₂O, BSA.

Composition of gastrointestinal patterns. The composition of gastric phase models can be simple, containing the main two components of gastric juice such as pepsin and mucin (Hack & Selenka, 1996; Scott & Dean, 2005; Wragg & Cave, 2003), and can also be complex, including, in addition to the above substances, many components such as glucose, glucuronic acid, urea, glucoseamine hydrochloride, bovine serum albumin (BSA), n-acetylneuraminic and oleic acids (Oomen et al., 2000, 2002; Ruby et al., 2002; Wittsiepe et al., 2001). The proportion and quantity of digestive substances also varies and is selected empirically for each target pollutant and specie. The gastric environment is characterized by the presence of the enzyme pepsin and glycosylated mucin proteins, which not only break down food in the body, but also increase the mobilization and solubility of POPs (Charman et al., 1997; Hack and Selenka, 1996) and thereby absorption into the intestinal environment.

An *in vitro* bioaccessibility model of the intestinal phase is characterized by the presence of bile and pancreatin. The latter, which is a mixture of amylase, lipase, trypsin and protease enzymes, hydrolyzes proteins to oligopeptides (trypsin), starch to oligosaccharides (amylase), triglycerides to fatty acids and glycerol (lipase) (Hack & Selenka, 1996; Wittsiepe et al., 2001). The gallbladder secretes bile into the duodenum during digestion to break down lipids. Bile with monoglycerides and fatty acids under the action of the lipase enzyme forms micelles, which in turn contribute to the mobilization of POPs in the intestine (Dean, 2007; Rostami & Juhasz, 2011). According to *in vitro* model experiments, porcine bile is most often used, since it is most similar in composition to human bile (Oomen et al., 2004).

pH values. The gastric media differs from the intestinal media in terms of pH. In most cases, in *in vitro* digestive systems, the pH is set based on the actual human or animal digestion environment. Thus, for example, gastric juice has an acidic environment from 1.5 to 2, and the intestinal environment is closer to neutral and varies from 7.0 to 7.5 (Figure 14). Consequently, most *in vitro* gastric and intestinal phase systems are performed at these time intervals (Collins et al., 2015; Rostami & Juhasz, 2011).

Residence time. The gastric emptying time takes 1-2 hours (for human), while it takes up to 6 hours for the chyme to pass from the beginning of the small intestine to the beginning of the large

intestine (Figure 14). Consequently, most models of the gastrointestinal tract adhere to the above residence time (Collins et al., 2015; Rostami & Juhasz, 2011).

The Soil:Solution ratio is the most critical in development of *in vitro* bioaccessibility study and may show the greatest impact on the bioavailable fraction of POPs. In review of Rostami and Juhasz, 2011 reported different ratios of soil to gastrointestinal solution depending on target POPs (i.e for PCDD/Fs 1:100, for PCBs 1:120).

Food amendments. Sometimes (optionally) food (for example lyophilized milk) is added to model experiments to evaluate and compare fasted and postprandial bioaccessibility of POPs (Hack and Selenka, 1996; Ruby M. et al., 1996). Such nutritional supplements can double the bioaccessibility of POPs (from 5-40% to 40-85%) (Hack and Selenka, 1996).

Temperature and agitation. The temperature is usually set at 37°C, as this is the physiological temperature of the human body. In addition, both models of the gastrointestinal tract are carried out with agitation by mixing on various shakers and incubators with a controller (Rostami and Juhasz, 2011).

3. *In vivo* tools

3.1 Bioavailability assays

Rodents and model farm animals such as chickens, goats and cows are widely used to assess POPs bioavailability in contaminated soil. The principle of the bioavailability method is to expose the animal by a fixed administrative dose of POPs (intravenously, but most often orally by adding to the daily feed) and determine the concentration of POPs in various tissues and organs (the so-called bioavailability endpoints) after a certain time. In the case of chlorine-containing POPs, blood is usually not examined, since POPs, unlike PAHs, are weakly metabolized in it, and therefore blood is a transport medium that quickly delivered POPs to more lipophilic target organs. POPs tend to bioaccumulate in liver, adipose tissue and muscle (Amutova et al., 2021; Huwe and Smith, 2005; Pirard and de Pauw, 2005; Piskorska-Pliszczynska et al., 2014; Traag et al., 2006; Wittsiepe et al., 2007). In addition, bioavailability studies could include matrices such as urine and faeces to estimate the non-bioavailable fraction of POP, i.e., the concentration of POPs in these matrices indicates the degree of elimination of substances from the body (Fries et al., 1989). Figure 15 showed the main steps conducted during the assessment of POPs bioavailability in contaminated soil for model farm animals.

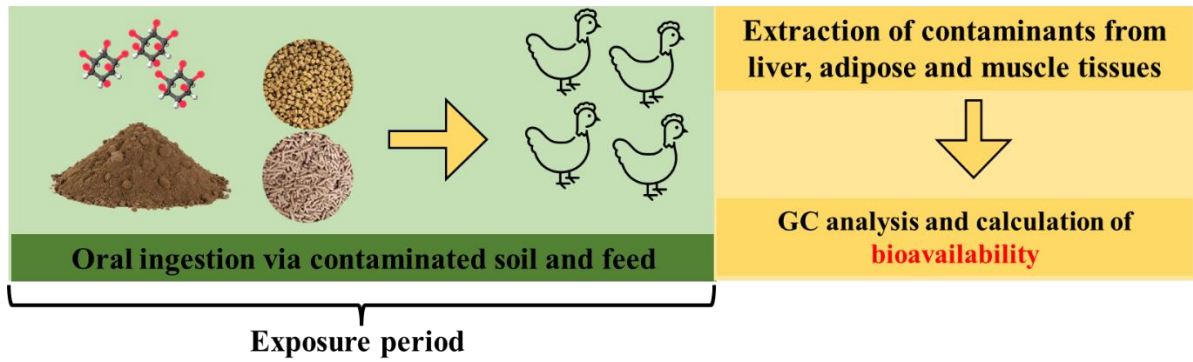


Figure 15 – Main steps of methodology of assessment of POP bioavailability in soil for experimental farm animals

The methodology includes soil preparation (homogenization, grinding to particle sizes less than 2mm) which is spiked with a known pollutant dose. This contaminated soil is introduced as an amendment in the daily diet of the treated animal. To determine the required exposure time and daily dose, the physiological parameters of the animal, such as age, weight, and, for some dairy animals, the lactation period are considered. For example, studies evaluating the bioavailability of PCDD/Fs in 6-week-old pigs with an exposure period of 28-30 days (Budinsky et al., 2008; Wittsiepe et al., 2007), determining the pesticide chlordecone in 2-month-old lambs for about 15 days (Jurjanz et al., 2014), PCBs on 35-day old pigs around 10 days of exposure (Delannoy et al., 2015). After exposure period all animals is slaughtered and target tissues such as liver, adipose and muscle tissues are collected. These tissues represented a bioavailability endpoints and therefore then extracted and analyzed by GC-MS (Figure 13). According to Wittsiepe et al., 2007 bioavailability could be expressed as the ratio of the mass of a pollutant in the tissue to the administered mass of the same pollutant from soil multiplied by 100% (eq.2):

$$b_{i,j} = \frac{m_{i,j}}{M_i} \times 100\% \quad (2)$$

$b_{i,j}$ – bioavailability of contaminant (i) in the tissues (j) in percent,

$m_{i,j}$ – mass of contaminant (i) in tissue (j) in pg,

M_i – mass of contaminant (i) administered to the animal by soil (pg).

For estimation of total bioavailability in the animal the following equation is used (eq.3):

$$B_i = \frac{\sum_j m_{i,j}}{M_i} \times 100\% \quad (3)$$

B_i – total bioavailability of pollutant (i) in the animal in percent,

$m_{i,j}$ – mass of contaminant (i) in tissue (j) in pg,

M_i – mass of contaminant (i) administered to the animal by soil (pg).

In case when study used soil and contaminated feed such as plant oil or solvent then relative bioavailability (RBA) could be compared between several ingested matrixes (Budinsky et al., 2008; Delannoy et al., 2015; Jurjanz et al., 2014). For relative bioavailability the equation 4 could be used:

$$b_{i,j} = \frac{b_{i,j \text{ Soil}}}{b_{i,j \text{ Feed}}} \times 100\%$$

or

$$B_i = \frac{B_{i \text{ Soil}}}{B_{i \text{ Feed}}} \times 100\%$$

$b_{i,j}$ – relative bioavailability of contaminant (i) in the tissues (j) in percent,

$b_{i,j \text{ soil}}$ - bioavailability of the contaminant (i) in the tissue (j) administered by soil in percent,

$b_{i,j \text{ feed}}$ bioavailability of the contaminant (i) in the tissue (j) administered by feed in percent,

B_i - relative total bioavailability of the contaminant (i) in the animal in percent,

$B_{i \text{ soil}}$ - total bioavailability of contaminant (i) in the animal administered by soil in percent,

$B_{i \text{ feed}}$ - total bioavailability of contaminant (i) in the animal administered by feed in percent.

The main advantage of *in vivo* POPs bioavailability studies involving experimental animals is the possibility of including this method in the assessment of human health effects. Although the time required to conduct animal trials, as well as cost and ethical concerns, are major drawbacks (Rostami & Juhasz, 2011).

3.2 Transfer rates and bioconcentration factors

Transfer rates (TR) and bioconcentration factor (BCF) are another efficient *in vivo* approaches for evaluating of POP transfer from ingested animal matrices to food products. Generally, these approaches used in the studies focusing on the food safety and risk assessment (Knutsen et al., 2018). Transfer rate (TR) is expressed transfer of pollutants to excreted animal product such as milk and eggs (Costera et al., 2006; Hoogenboom et al., 2006; McLachlan M. & Richter W., 1998) and bioconcentration factor estimate transfer of pollutants to different edible animal tissues such as liver, fat and muscle (Feil et al., 2000; Fernandes et al., 2011; Fries G., 1999; Hoogenboom et al., 2004; Huwe & Smith, 2005). The methodology is similar to the bioavailability assessment and consists in using farm animals as objects of exposure to a known dose of POPs. During the experiment and at the end of the exposure, the concentration of POPs in the excreted products (lactating animals or hens) is being monitored to assess the transfer rate. Also, after the end of the exposure period, slathering of experimental models is carried out to measure the concentrations of

POPs in the targeted tissues and organs and evaluate the BCF. Both parameters can be measured during one *in vivo* experiment.

According to Richter & McLachlan, 2001, the transfer rate is the ratio between the amount of POPs ingested and excreted in a food product (equation 5), and can only be calculated after the animal has reached a steady state:

$$TR_{\text{product}} = \frac{[\text{POP}]_{\text{Fat of product}} * \text{Daily fat excretion}}{[\text{POP}]_{\text{Diet}} * \text{Diet Intake}} * 100\% \quad (5)$$

Where $[\text{POP}]_{\text{fat of product}}$ is the concentration of studied POP in the fat of the food product (pg/g fat), $[\text{POP}]_{\text{Diet}}$ is the concentration of studied POP in the intake matter (soil or feed) (pg/g dry matter). Typically, due to lipophilicity, POPs concentration are expressed in relation to lipid content of milk or eggs.

The steady state is the physiological state of an animal during a continuous exposure to a fixed daily dose, leading to a concentration remaining stable in time (Casarett and Doull, 2008). Therefore, the exposure time for a given experimental animal should be long enough to reach the SS. Generally, exposure times in TR studies vary by animal species and POP family. For example, under controlled conditions, exposure periods to PCDD/Fs for dairy cows were 30, 49, 58 days (Fries G., 1999; Lorenzi et al., 2020; Slob et al., 1995, respectively), and for laying hens was 56 days (Hoogenboom et al., 2006). In contrast, the period of PCB exposure to SS in goats was 80 days, respectively (Ounnas et al., 2010). In addition, some studies carried out under the so-called field conditions imply on a sufficiently long-term exposure (Kerst et al., 2004; Schuler et al., 1997).

The choice of exposure time depends on the target POP and on the type of animal being studied. The half-life of the target compound would allow to predict the necessary exposure duration necessary to reach SS for a given animal species (mammals, birds) in respect to its animal production cycle. It is known that 3.3 half-lives of the considered POP could allow to achieve 90% of SS at the plateau (Holford N., 2017). Table 5 presents the half-life of some POPs in a given food products and in respect to animal production cycle and predicted exposure duration to achieve SS.

Table 5 – Parameters for prediction of exposure duration to achieve SS.

Half-life of the pollutant in animal specie	Animal production cycle	Predicted exposure duration to achieve SS
PCDD/Fs - 30 days - hen eggs	Laying hens \approx 1-2 years	99 = 30 x 3.3

PCDD/Fs - 40 days – cow/goat milk	Cows ≈ 6-10 years Goats up to 17 years	132 = 40 x 3.3
PCBs – 30 days - hen eggs and goat milk		99 = 30 x 3.3

Another critical factor in developing a method for assessing TR in farm animals is the choice of animal. Laying hens and dairy cows are more often used in many studies (Amutova et al., 2021). The experimental animals must be adults to exclude the factor of weight gain due to maturation and dilution of the administration dose of POPs during the exposure period, which in turn makes it problematic to achieve the SS state. In addition, test animals must be in the production cycle to assess the transfer of POPs to excreted products (eggs or milk).

Another tool for assessing the transfer of POPs in farm animals is the BCF, which is calculated as the ratio of the concentration of POPs in edible tissue (liver, fat or muscle) to the concentration of POPs in intake matters (soil, feed) (eq. 6):

$$BCF = \frac{[POP]_{tissue}}{[POP]_{intake}} \quad (6)$$

Where [POP]_{tissue} – concentration of POP in tissue (pg/g fat), [POP]_{intake} - concentration of POP in in feed (pg/g feed at 15% humidity) or in soil (pg/g dry matter).

The main difference between BCF and TR is the assessment of the transfer of POPs to organs and tissues, as well as the absence of the need to achieve SS (Amutova et al., 2021). The typical models used for estimation of BCF are meat-producing animals such as pigs (Fernandes et al., 2011; Rose et al., 2012; Spitaler et al., 2005; W. Traag et al., 2004), broilers (Parera et al., 2008; Traag et al., 2004), non-lactating animals (calves, yaks). In contrast to TR studies, BCF could be estimated on animals independently to its production type and age.

4. Differences between *in vivo* and *in vitro*

The main difference between *in vivo* and *in vitro* methods is the use of animals as models for assessing exposure of POPs in first case. In contrast, *in vitro* methods mimic some systems of organism. Both types of methods are an integral part for studying the processes of exposure, transport, absorption of POPs and are a fundamentally significant basis in both environmental risk assessment and human risk assessment. However, each type has its own features involving an advantages and disadvantages.

There are several factors by which *in vivo* and *in vitro* methods can be compared:

1. Extrapolation of the acquired knowledge to the human body. Studies conducted on model animals such as mammals (pigs, monkeys) most closely reflect the physiological processes associated with the impact of POPs on the human body. *In vitro* methods are represented an individual structures of animals or humans (for example, the gastrointestinal tract) that create certain environmental conditions and use chemical reagents, enzymes, proteins and other compounds. However, mimic digestive system *in vitro* are primitive systems compared to the complexity of the gastrointestinal tract with its microflora, mechanical processes, etc.

2. The ethical issue is a critical factor for *in vivo* methods and is an advantage for *in vitro* methods. So, at present, to conduct experiments in animals, very convincing evidence of the necessity and validity of the use of animals is needed.

3. Economic feasibility. This factor plays an important role in any scientific research in general. Therefore, it should be noted that the availability of published literature on POPs exposure on agricultural animals *in vivo* conditions is very limited, which is probably associated with high costs for the purchase and maintenance of animals. In this regard, *in vitro* methods will have an economic advantage, due to their relative simplicity and speed of implementation.

4. Correlation between *in vivo* and *in vitro* results. Data obtained by *in vivo* methods are important for validating *in vitro* results. *In vitro* correlation coefficients should ideally be close to *in vivo* tests, and the choice of the most appropriate *in vitro* model should be based on the objectives of the assay and consider the advantages and limitations offered by each model.

PART III: Sequestration as a strategy to reduce POPs transfer from soil to livestock food

The environmental problems associated with POPs make it necessary to develop and use strategies for the remediation of contaminated environmental matrices. Remediation technologies are numerous and varied, but can be classified into *in situ* and *ex situ* techniques. *Ex-situ* techniques include physically extracting of contaminated matrix and transfer it to another location to treatment. *In situ* techniques aim to eliminate pollution without removing soil or groundwater (Kuppusamy et al., 2016), i.e., on the place. Each of the *ex situ* (off place) and *in situ* (on place) techniques has its own advantages and disadvantages. The main advantage of *in situ* methods is that the contaminated matrix does not need to be removed or transported. The downside of *in situ* techniques is that they could be relatively less effective at removing contaminants than *ex situ* remediation options. Despite the high cost, *ex situ* treatment usually takes less time to achieve effective decontamination, is easy to control, and provides greater uniformity. After *ex situ* treatment, the decontaminated soils can be used for landscape purposes.

1. Place of a sequestration strategy among other remediation strategies

In the context of this study, remediation methods of soil contaminated with POPs are classified depending on the research methods. Generally, *in situ* and *ex situ* methods divided in three categories: biological, physical and chemical treatments (table 1). *In situ* and *ex situ* remediation technologies presented in table 6 are described in details including methodology, advantages and disadvantages in latest review papers (Castelo-Grande et al., 2010; Gomes et al., 2013; Kuppusamy et al., 2016; Murphy et al., 2006; Srivastava et al., 2019). In addition, practice integration on soil contaminated territories were also well reviewed by (Rubin and Burhan, 2006).

Table 6- *In situ* and *ex situ* remediation technologies used for POPs contaminated soil.

<i>In situ</i> remediation technologies for POPs contaminated soil		References
Biological treatment	Bio-remediation - a set of methods for soil decontamination using the metabolic potential of biological systems – microorganisms and plants usually for POPs. There are two main approaches of bioremediation: microbial degradation and	Abramowicz, 1995; Gomes et al., 2013

	phytoremediation. In the first case, microorganism potential is used which allow dechlorinating the target compounds to less toxic forms. In the second case, various forms of fast-growing plants are used for uptake the target POPs which supposed their migration from soil.	
Physical treatment	Capping or sequestration is an <i>in situ</i> remediation technique, where the sediment is covered with a clean material (cap) to prevent the POPs releases and being accumulated by biota. Activated carbon or biochar could be used as sequestration material in POP contaminated soil.	Josefsson et al., 2012; Murphy et al., 2006
Chemical treatment	Base-catalyzed decomposition (BCD) is a catalytic hydrogenation process which used in decontamination of POPs contaminated soils. The main principle is atoms of chlorine are removed from molecules and replaced by hydrogen atoms. Contaminated soil is mixed with sodium bicarbonate or sodium hydroxide and a carrier oil, which acts both as suspension medium and hydrogen donor.	Hu et al., 2011
Thermal treatment	Microwave energy can be used for soil remediation <i>in situ</i> , which could remove or immobilize contaminants through such mechanisms as thermal desorption, destruction, and vitrification	Abramovitch et al., 1998; Wu, 2008
<i>Ex situ</i> remediation technologies for POPs contaminated soil		
Biological treatment	Bioremediation using land farming performed in upper soil zone or biotreatment cells. POP contaminated soil is incorporated into the soil surface and periodically turned over to aerate the mixture.	Ghosh et al., 2003; L. Liu et al., 2007
Physical treatment	Thermal desorption utilizes direct or indirect heat to increase the volatility of POPs that are present in the solid matrix. Pollutants are vaporized and thus	J. Liu et al., 2019; Sato et al., 2010; C. Zhao et al.,

	migrate from the soil; a carrier gas transfers them to the off-gas treatment system	2019; Z. Zhao et al., 2016
Chemical treatment	Solvent extraction is an <i>ex situ</i> approach which involve utilization of organic solvent as extractant for separation of POPs from soil. Organic solvent is mixed with contaminated soil in extraction cell. After this mixture passed through the separator where POPs with solvent separated from soil media.	Majid et al., 2015 ; Nam et al., 2001

This chapter will focus mainly on application of *in situ* remediation technology based on physical treatment of soil contaminated with POPs. Briefly, *in situ* physical treatment is the amendment of an inert material directly to the contaminated soil (or water), which provides containment of the toxic substance rather than its depuration or removal (Cho et al., 2009). An amendment component that binding POPs in the soil can be different soil organic fractions such as potassium humate, humic acid silt, clay, as well as carbonaceous materials such as activated carbon (AC) or biochar (BC) (Rakowska et al., 2012). This type of remediation is called sequestration strategy and the amendment material which is supposed to immobilize pollutants defined as the sequestrant or the sequestration material. The latter interacted with the soil bound pollutants through the diffusion and adsorption mechanisms. This allows reducing pollutant bioavailability and therefore the risk of a further transfer (Brändli et al., 2008; Cho et al., 2009).

Amendment based on AC/BC has shown as a promising option for reclamation of soils contaminated not only non-organic (Bes and Mench, 2008) but also organic compounds such as POPs (Rakowska et al., 2012). In addition, there are several significant advantages to using AC in the remediation of contaminated soils: 1) as an *in-situ* method, it is more cost-effective and environmentally friendly (no problems with the transfer from one place to another) than *ex-situ* methods, 2) there are no releasing of new amounts of pollutants (compared to land farming or thermal desorption), 3) more efficient than in phytoremediation. Indeed, plants can only absorb a few percent of the pollutant and have a long growing period for the development of a reasonable plant biomass.

Economic benefits of AC based sequestration strategy depends on availability of a suitable form or raw material for AC production. Therefore, recently, the discovering of alternative carbonized materials has become a topical issue. Among some alternative options could be a biochars (Millward et al., 2005; Yu et al., 2009; Zimmerman et al., 2004) which is produced from various

plants and animal residual biomass. More details about the types, characteristics, and methods of production of sequestrant materials based on activated carbons and biochar is discussed in the next section.

2. Major mechanisms of sequestration based on AC/BCs

Sequestration of contaminated soil based on AC/BC is the introduction of an amendment in the form of AC/BC into the soil media in order to adsorb pollutants on the rich carbon-containing surface of AC or BC. The main effect of adsorption of POPs on the surface of AC/BC is a decrease their bioavailability, and thus a decrease its transport into the food chain. (Grgić et al., 2019; Morillo and Villaverde, 2017; Yehya et al., 2017). After the amendment, the AC/BC interact with POPs and soil microorganisms. After a certain contact time has elapsed, POPs are migrated from soil organic matter and start interacting with a functional group on the surface of the AC/BC and are adsorbed into its pores. The latter occurs as a result of mass transfer of pollutant molecules by interstitial water, which plays the role of a carrier (Figure 16).

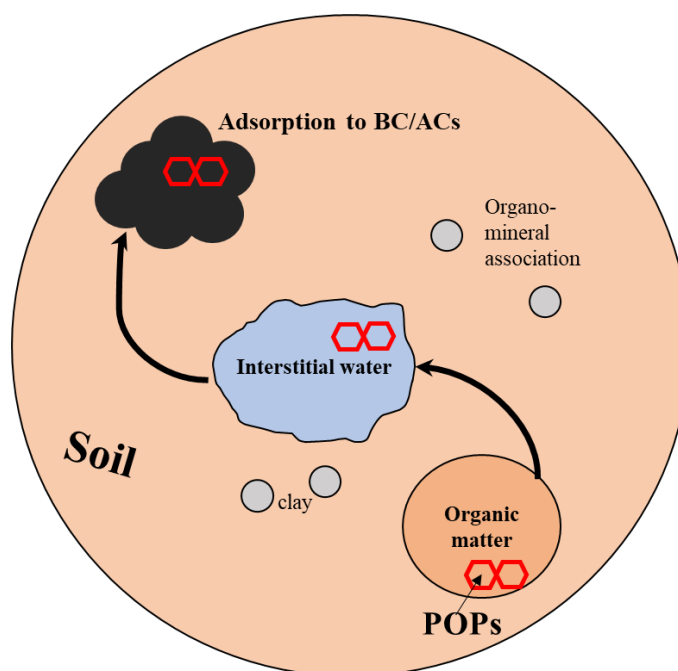


Figure 16 – Migration of POPs from soil organic matter to soil constituents

In addition, POPs can also undergo microbiological degradation, which is also stimulated by the addition of AC/BC. After some time, the concentration of POPs from soil interstitial water decreases, which also leads to a decrease in their bioavailability. A study by Guo et al., (2020) noted the beneficial effects of biochar amendments on soil quality characteristics. In addition, the

biochar amendment introduced minerals such as N, P, K, Ca, Mg and S, as well as biodegradable organic carbon, which in turn can serve as a microbial substrate.

Carbonaceous materials interact with POPs through several physical and chemical adsorption mechanisms (Figure 17). There are several interactions which included Van der Waals forces, universal electrostatic attraction between non-polar molecules (London dispersion forces) and between polar molecules (dipole-dipole forces) (Petrucci et al., 2010). Thus, Yang & Evans, 2007, reports that the Van der Waals forces generally weak but could increase if studied pollutants have a high molecular weight. Interaction via Van der Waals forces is characteristic of adsorbents with a low particle size.

ACs and BCs adsorbents have different functional groups, consisting of C, O, H, N and other mineral elements that interact with POPs and result to form H-bonds (or hydrogen bonds). Hydrogen bonding is a type of electrostatic interaction that is stronger than Van der Waals forces (Tan et al., 2015). Fidel et al., 2018 noted that the functional groups of the adsorbent can dissociate if the pH of the medium is greater than the pH zero net charge of AC/BC, thus making the surface of the adsorbent with a negative charge. Conversely, also, functional groups are protonated under conditions where the pH is less than pH zero net charge, resulting in a positively charged adsorbent surface. In general, the surface charges of the adsorbent allow polar and ionized POPs (eg pesticides) to be electrically attracted by their counter charges. This type of interaction is called electrostatic attraction and is usually stronger than hydrogen and Van der Waals forces. Enhanced electrostatic attraction can lead to specific surface interactions, i.e. when ionized POPs chemically react with the functional groups of the adsorbent and can be retained. Aromatic carbon atoms in carbonated materials may have excess p-electrons, while many organic molecules containing O, N, S, P, Cl and Br are electron-deficient. Thus, adsorbents based on AC / BC can interact with POPs through π - π electron donor-acceptor reactions (Guo et al., 2020).

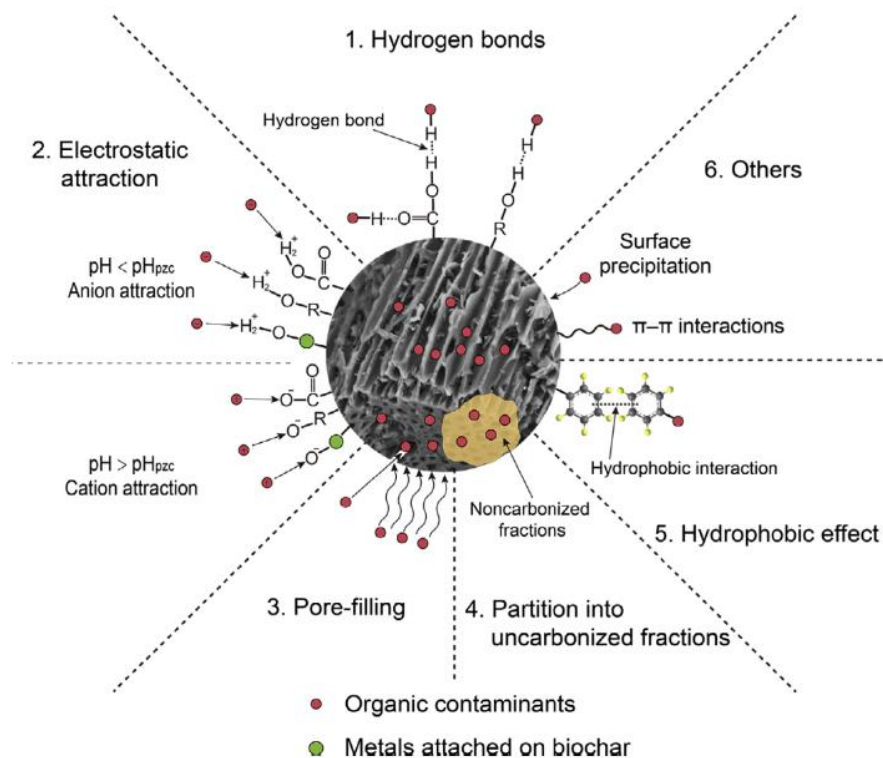


Figure 17- Major mechanisms through which activated carbon or biochar retain organic contaminants in soil. The graph was modified from (Tan et al., 2015).

AC/BC can adsorb non-ionic organic compounds through surface adsorption. Smaller pores have a higher surface energy; therefore, the sorption of organic pollutants primarily occurs in micropores (Uchimiya et al., 2010).

Pore filling (surface adsorption "in pores") is an important mechanism of adsorption of organic compounds on AC/BC (Figure 17). Studies show that the degree of surface adsorption is proportionally related to the specific surface area of coal and surface porosity, as well as aromaticity (Zhu et al., 2014), while the adsorption capacity of separation depends on the content of organic carbon of AC BC and the content of mineral ash (Chiou et al., 2015; Z. Zhao et al., 2019). The hydrophobic effect (preventing the contact of non-polar molecules and hydrophobic molecular fragments with water) also promotes the sorption of hydrophobic organic pollutants (Tan et al., 2015).

In addition, AC/BC may contain metals such as Fe, Al, Ca and Mg on their surface (Bian et al., 2014). Consequently, polar and ionized organic molecules can form complexes with metal ions and be deposited on the surface of the coal or deposited in the soil.

3. Sequestration materials

Application of carbon-rich sequestering materials such as activated carbon and biochar has been of interest in the past decades (Beesley et al., 2011; Rakowska et al., 2012; Wang et al., 2013) especially regarding POPs contaminated soil (Delannoy et al., 2015, 2018, 2020; Feidt et al., 2021; Ranguin et al., 2021). For example, such POPs as PAHs, PCBs and OCPs are strongly adsorbed into the organic matter of the soil (Cornelissen et al., 2005; Ghosh et al., 2003). The large adsorption potential of carbon-containing structures in contaminated soils has led to the targeted introduction of purified species of such structures as an amendment (for example, activated carbon or biochar) to soils and sediments to reduce the bioavailability of organic pollutants (Beesley et al., 2010; Zimmerman et al., 2004). The main properties that make these carbon-rich materials effective and economically available for binding POPs are a high porous structure, with a high carbon composition (up to 90%) on the one hand, and variety of raw materials, its availability and renewability.

Activated carbons (AC) are highly porous carbon-rich materials produced as result of pyrolysis of organic materials (from 500 ° C and above). AC could be produced from black coal, coal coke, petroleum coke, wood char, lignin, sawdust, peat, sludge, coconut shells, peach pits, fish residues, fertilizer waste, waste rubber tire (Brändli et al., 2008; Jeirani et al., 2017; Yin et al., 2007).

Biochar (BC) is a carbonaceous material, like activated carbon produced by combustion. But the main difference between BC and AC is raw materials. Huge variety of biomass may serve as the raw material for BC production (Wang and Wang, 2019). Biomass sources for biochar production could include:

- 1) agricultural crops and residuals (olive stones, coconut shell, bamboo, wheat, barley, rye, oat, maize, rice husk, rapeseed and sunflower,)
- 2) forestry crops and residuals (sawdust, and trees grown for biomass)
- 3) industrial residuals (lignin, Tara gum, sawdust)
- 4) animal residuals
- 5) sewage
- 6) municipal solid waste (food wastes, paper, wood trimmings and some textiles)

Biochar is not always exposed to high temperature treatment before being added as an amendment to the soil. Consequently, the structures of some biochars are often incompletely carbonized and can be composed of carbonaceous and amorphous organic matter in varying proportions (Chun et al., 2004).

Generally, there are several physicochemical properties that characterize and define AC/BC in relation to their adsorption and affinity to POPs. These properties include:

- 1) Textural characteristics
- 2) Chemical composition (functional groups)
- 3) pH, charge and hydrophobicity
- 4) Activation of AC/BCs
- 5) Modification of BCs

3.1. Textural properties

AC/BC has a carbon-rich porous structure. The structure consists of randomly spaced pores and cross-linked macromolecular particles, some of which are pseudo-graphite in nature, while others are amorphous particles (Jordi and Valero, 2015).

Porosity is one of the main physical properties of AC/BC. Pores can be divided into three groups according to the standard of the International Union of Pure and Applied Chemistry (IUPAC): micropores (<2nm), mesopores (2-50 nm) and macropores (>50 nm) (Figure 18) (Menéndez-Díaz and Martín-Gullón, 2006). Most of the surface of carbonized matrices consists of micropores (up to 90% of the total surface area). According to some literature, the presence of mesopores promotes better adsorption of pollutants such as POPs, due to the fact that mesopores provide the best conductivity to micropores. Macropores are also an important surface element, since they provide access to the inner parts of the meso and micropores (Bedia et al., 2018; Leng et al., 2021).

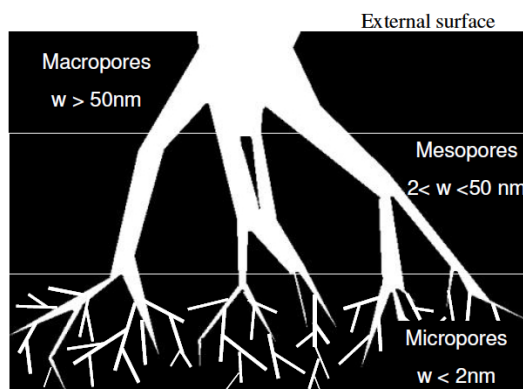


Figure 18- Pore network in AC/BC (derived from (Menéndez-Díaz and Martín-Gullón, 2006)

AC/BC are characterized by pore volume and specific surface area (SSA). The pore volume represents the space occupied by the pores (it can be from 0.1 to 2 cm³/g). Specific surface area of AC/BC is defined as the surface area of the solid particles divided by the mass of the solid particles and could achieve up to 2000 m²/g (Sing, 1982).

There are also 2 types of form of AC/BC: granular and powder. The granular AC/BC is made of pellet particles from 180 μm (80 mesh) (ASTM D2862-10, 2010). Powdered form is composed by particles of AC/BC less than 180 μm (ASTM D5158-98, 2005). Sequestration materials with a particle diameter from 75 to 300 μm are defined as fine granular AC/BC and is preferable used for retaining hydrophobic PCBs and PAHs (Hale et al., 2012, 2010; Zimmerman et al., 2005, 2004). However, some studies with OCPs reported mostly about applications of powdered BC (Table 7).

Table 7 - Different sequestration materials based on activated carbon (AC) and biochar (BC) applied for effective adsorption of POPs in soil, sediments and water (data derived from the published literature)

Sequestration material	Amendment rate (dry matter), %	Particle shape	Particle size, μm	Specific surface area (SSA), m^2/g	POPs family	Media	Reduction rate, %	Reference
AC TOG (coal)	3.4	granular	75-300 μm	938	PCBs, PAHs	Sediments	77 83	Zimmerman et al., 2004, 2005
AC F400 (coal)			420-1700 μm	1100				
AC TOG (coal)	-	granular	75-300 μm	938	PCBs	Sediments	-	Hale et al., 2010
AC GAC F400	-	granular	840-1000 μm	1070	Lindane, PCBs	Aqueous media	-	Sotelo, Ovejero, Delgado, & Martinez, 2002a, 2002b
AC ZJ-15 GAC modified with triolein	-	granular	n/a	791	Dieldrin, Endrin, Aldrin, Heptachlor or epoxide	Aqueous media	-	Ru et al., 2007
AC CAC	-	granular	250-2000 μm	n/a		Aqueous media	-	

AC Acacia etbaica		granular	n/a	n/a	Aldrin, Dieldrin, DDT			Gebrekidan et al., 2015	
AC CAC	0.5-10	granular	n/a	690	Lindane, HCB	Sediments	95 75	Grgić et al., 2019	
Pine bark BC	-	granular	125-300 μm	n/a	Lindane, HCB	Aqueous media	81 94	Ratola et al., 2003	
AC Palm date stone	-	granular	<1500 μm	1262	β -HCH, DDDs Heptachlor, Heptachlor or epoxide, Endrin	Aqueous media	-	Sahmarani et al., 2020	
Wheat straw BC	2	powdered	n/a	4.81	HCB	Soil	86	Song et al., 2012	
Digestate BC	-			357	α -HCH, β -HCH, γ -HCH, and δ -HCH	Aqueous media	-		Silvani et al., 2019
Tomato waste BC				7.3					
Durian shell BC				66.5					
Peanut shell BC	-	powdered	n/a	4.25	HCHs, DDTs,	Soil	From 47 to 60	Ali et al., 2019	
Sewage sludge BC				4.07	Chlordane, Aldrin,				
Soybean BC				2.63	Dieldrin, Endosulfans,				
Rice straw BC				2.21	Endrin, Heptachlor, Methoxychlor				

3.2. Chemical composition, pH, charge and hydrophobicity

The AC/BC surface is a basal plane with heterogeneous surface groups. Basically, such surface groups include oxygen-containing functional groups such as hydroxyl, carboxyl, phenol, lactone, lactol and quinone as well as inorganic ash. Most of the adsorption sites are located on the basal surface, which corresponds to 90% of the carbon surface (Franz et al., 2000). The AC/BC functional groups promote and accelerate adsorption of organic pollutants (Delgado et al., 2012; Franz et al., 2000). Functional groups, namely their proportional composition, mainly depends on the raw material and the method of coal activation (Vázquez-Santos et al., 2012; Yin et al., 2007).

High carbon matrices such as AC/BC are amphoteric substances, which mean they have both acidic and alkaline properties. In addition, mineral matter such as ash can affect the alkaline environment (Bansal and Goyal, 2005) . For example, if AC is placed in an aqueous medium, it develops a surface charge, which is created during the dissociation of functional groups. This charge directly depends on the medium in the aqueous solution and the characteristics of the carbon. If the pH of the aqueous solution is higher than AC, acid groups dissociate, leaving a negatively charged surface on AC. In the opposite situation, when the pH of activated carbon is higher than in the medium, then the adsorbent become a positively charged (Menéndez, 2018) Thus, the adsorption can be influenced by the charge and electrostatic forces of AC/BC and target substances (adsorbates).

Activated carbon and biochar are lipophilic, i.e., they are not insoluble in the water. The presence of acidic, alkaline and neutral functional groups allows AC/BC to bind water molecules using hydrogen bonds. This, in turn, can cause an increase in hydrophilicity due to the bond between water and oxygen atoms on the carbon surface (Bansal and Goyal, 2005)

3.3. Production of carbonaceous sequestrants

To produce activated carbon, carbon-enriched materials go through a so-called activation process based on physical and/or chemical treatment (Figure 19) (Bedia et al., 2020; Yin et al., 2007; Zhang et al., 2008).

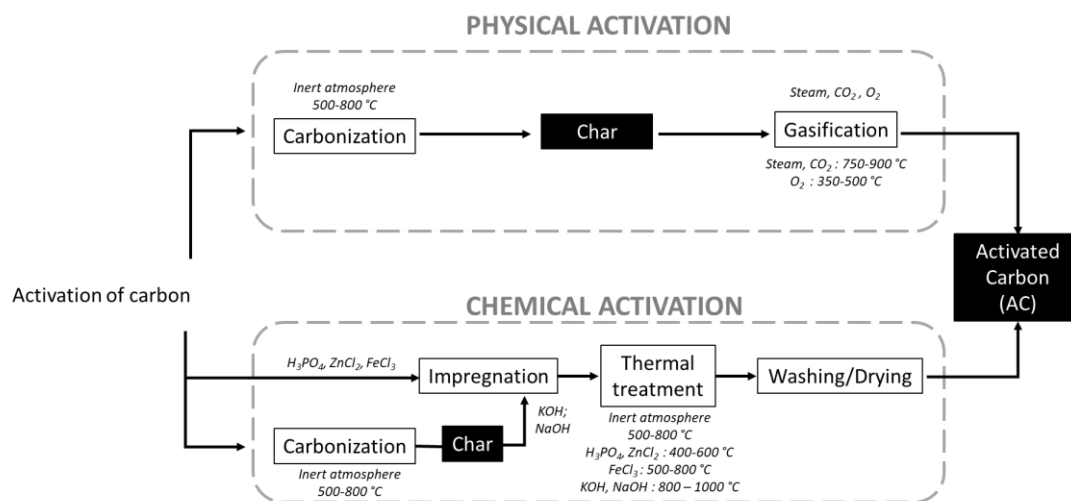


Figure 19- Carbon activation methods adapted from study of Bedia et al., 2018

Physical activation of carbon consists of two stages: pyrolysis at a temperature of 500-800°C and gasification. Pyrolysis or carbonization of carbon takes place in conditions where there is no oxygen or almost no oxygen, to avoid the ignition of the carbonaceous substance. The process removes heteroatoms, releases volatile compounds, and ultimately form a char with high carbon content but low porosity. The second stage (gasification) consists of selectively removing the most reactive carbon atoms through controlled gasification reactions that create a high porosity of the activated carbon. Water steam, CO₂ or O₂ (air) is used as gasification agent. Gasification temperature can vary from 700 to 900° C when using water steam or CO₂, and from 300 to 450° C when using more reactive O₂ (Bedia et al., 2020).

Physical activation of carbon increases the surface area and porosity responsible for the retention of organic pollutants (Brändli et al., 2008). Indeed, recent reviews (Ambaye et al., 2021; Leng et al., 2021; S. Li et al., 2017) studied AC/BCs noted that activation temperature play a very important role in the formation of different pore sizes. Sometimes too high temperature (above 700° C) negatively impacts on amount of oxygen-containing functional groups (Leng et al., 2021) which could be problematic for adsorption of non-organic compounds such as heavy metals. However, the high temperature activation (up to 700° C) is allowed to produce a large surface with a high amount of mesopores which are generally favourable for enhancing adsorption of organic compounds such as POPs (Y. M. Cho et al., 2009b; Cooney, 1999; Jeirani et al., 2017; Ranguin et al., 2021). Therefore, optimal activation temperature should be chosen with caution and experimentally approved for a given pollutant.

Chemical activation of carbon usually performed using chemical reagents including salts, acids and bases. Chemical activation consists of three stages, including one thermal. The first step is to

impregnation of the carbonated material with an activating chemical agent. The agents could be a FeCl_3 , ZnCl_2 , H_3PO_4 , NaOH , or KOH . These chemicals significantly reduce the formation of gums, volatiles and unwanted products that can form during the carbonization step. Impregnation with chemical agents can take place using several ways (Bedia et al., 2020, 2018), for example, mixing of coal in an aqueous solution with a chemical agent (mentioned above). An important parameter at this stage is the mass ratio between the chemical reagent and the coal (impregnation coefficient). After impregnation, the second stage is heat treatment in an inert atmosphere. The treatment temperature depends on the chemical agent. At this stage, the processes of depolymerization, dehydration and condensation take place, which lead to a higher carbon yield than during physical activation, due to the limitation of the formation of resins and volatile substances (Bedia et al., 2018). The third stage is washing of chemicals and by-products and drying (Bedia et al., 2020). After chemical activation, AC presents a higher specific surface area and a greater number of mesopores than after physical activation. In addition, chemical activation occurs at lower temperatures and takes a shorter activation time (Ahmadpour and Do, 1996; Lozano-Castelló et al., 2001). However, despite these advantages, the mechanisms of chemical activation remain not fully studied and mainly depend on the raw materials of carbon.

Biochar production is based on two processes: carbonization and hydrothermal carbonization (Figure 20). The first method involves a standard process of carbonization, when the biomass is heated in an inert atmosphere to temperatures from 500 to 800° C and kept at the required temperature for a certain time. Then the biomass is cooled to room temperature. In this case, as in the activation of coal, due to an increase in the carbonization temperature, an increase in the surface area and porosity of biochar occurs. Too high temperatures (more than 900° C), on the contrary, cause a decrease in these parameters, mainly due to the melting of biochar ash, which, as a result, leads to the expansion and adhesion of pores, significant structural rearrangements of the surface, such as destruction of micropores and carbon structure (Burhenne et al., 2013; Chen et al., 2012; Fu et al., 2009).

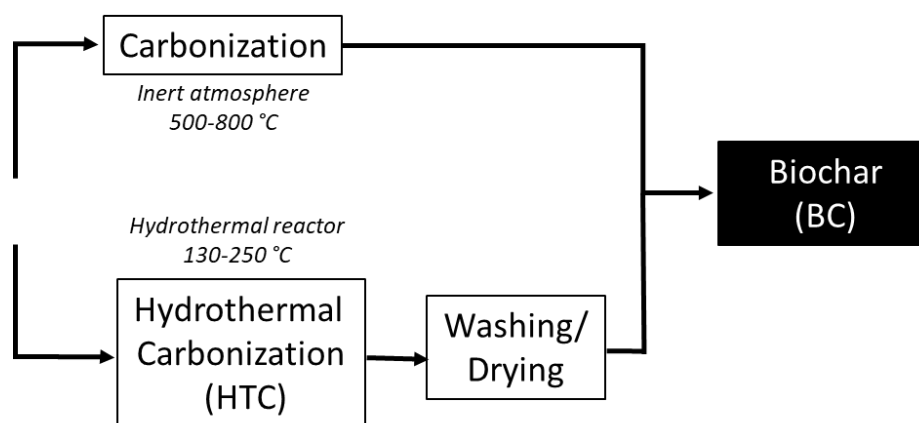


Figure 20 - Biochar production methods adapted from study of Bedia et al., 2018

The biochar carbonization process also affects the formation of functional groups on the surface, which is also a parameter responsible for the adsorption capacity. The ratio of atoms H/C and O/C in the raw material can vary in the ranges of 1.4-1.8 and 0.55-0.75, respectively, which confirms the predominance of aliphatic groups (Kim et al., 2012) . When biochar is activated, these ratios decrease, especially at high temperature conditions (Fu et al., 2009; Xin et al., 2015).

In addition to activation by standard carbonization, there is also a second method, in particular, the hydrothermal carbonization of biochar (Lucian et al., 2018; Sevilla and Fuertes, 2009). The method consists in placing raw materials in an aqueous medium in a closed chamber and holding at a temperature of 130 to 250° C for 2 to 24 hours. This method has significant advantages over conventional carbonization. Firstly, the main advantage is the low operating temperature, and secondly, the absence of a drying stage, which reduces energy consumption and, consequently, the cost of the method (Funke and Ziegler, 2010).

3.4 Modification of biochars

In addition to the production of biochar, there is also the concept of modification. Biochar modification is an additional process carried out after production, which consists in changing the chemical composition of the biochar surface due to the binding of various heteroatoms (nitrogen, phosphorus, sulfur, metal oxides with various chemical reagents) (Bedia et al., 2018; Wang and Wang, 2019). The modification allows to significantly increase the adsorption capacity, in particular, porosity and hydrophobic surface, which is especially important in the context of POPs retention. Usually, biochar obtained using classical approach does not have a high porosity, having a moderate or low surface area, a limited number of functional groups, which limits their practical application. The main types of biochar modifications include acidic, alkaline, oxidizing modifications, and modification with metal salts and oxides.

Hydrochloric acid (Peng et al., 2016; Rajapaksha et al., 2016), sulfuric acid (Yakout et al., 2015), nitric acid (Li Y. et al., 2014), phosphoric acid (Taha et al., 2014; Zhou et al., 2017), oxalic acid and citric acid (Feng et al., 2013; Lonappan et al., 2020) widely applied in acidic modification of biochars. This method reduces the ash content, increases the hydrophobicity and total surface of biochar, and graft carboxyl groups.

Alkaline substances that are used to modify biochar include potassium hydroxide and sodium hydroxide. These alkalis can also significantly increase the total surface area, as well as graft oxygen-containing functional groups (Cazetta et al., 2011; X. Jin et al., 2014). Oxidizing agents such as hydrogen peroxide can cause the same modifications (Huff and Lee, 2016; Xue et al., 2012).

In addition, modification based on metal salts and oxides is used to influence on adsorption and magnetism characteristics of biochar. This modification method is relevant for the adsorption of cations or anions. Using metal salts or oxides, it is possible to change the charge of the surface of the coal from positive to negative (and vice versa), which increases its adsorption capacity. In addition, this modification makes it possible to increase the magnetic properties of biochar, which facilitates its recirculation during the purification of an aqueous medium (Wang et al., 2015).

Thus, the increase in the adsorption capacity of biochars due to modification depends on such important factors as the concentration and type of reagent, raw materials, and preparation conditions.

4. Mechanical aspects of POPs sequestration based on AC/BCs

The mechanism underlying the sequestration of POPs using AC/BC in soil is adsorption. Therefore, first adsorption definition and tools for its estimation will be investigated. Adsorption could be defined as a process in which molecules (adsorbates) are retained on the surface of solid porous materials (adsorbents). From the point of view of physics, it's a mass transfer based on interactions between adsorbent and adsorbates, adsorbates and their initial media (water or soil). The reverse process of adsorption is desorption, i.e. the process of releasing adsorbates from the surface of the adsorbent into the environment. Desorption is caused by changes in adsorbate concentration, temperature and pH of the environment media.

One of the main parameters of adsorption is the adsorption amount (or q), which is defined as a mass of the target compound adsorbed per unit of adsorbed mass. There are 2 scientific concepts for assessing adsorption:

- 1) Adsorption equilibrium
- 2) Adsorption kinetics

Adsorption equilibrium is a concept that allows to estimate the effect of concentration of target compound and adsorption temperature on an adsorbed amount (Bedia et al., 2018). Usually, adsorption equilibrium is considered at a constant temperature and is expressed as an adsorption isotherm (eq.1).

$$q = f(C); T = \text{constant} (1)$$

where C is the concentration of target compound (adsorbate) in the medium (in case of water unit could be $\mu\text{g/L}$, in case of soil $\mu\text{g/kg}$ dry matter).

The adsorption kinetics allow studying the change in the concentration of the adsorbate at different contact times, also at a constant temperature (eq. 2).

$$q = f(t); T = \text{constant} (2)$$

where t is a time.

In addition, there is such a concept as the rate of adsorption, which regulates the process of mass transfer from the medium (water, soil) to the surface of the adsorbent (Worch E., 2012).

4.1 Adsorption Equilibrium

The study of adsorption equilibrium is important for assessment the adsorption process, in particular, the choice of the optimal adsorbent and the conditions for the sequestration process. The basis of the equilibrium is the adsorbate-adsorbent interaction, temperature and pH of the medium, as well as the presence of competition between adsorbates. To obtain curves of adsorption equilibrium in laboratory conditions, a series of experiments (batches) are usually carried out at a fixed temperature, and calculations are made to obtain an equilibrium isotherm (Wang et al., 2020). Usually, the experiment is carried out in bottles filled with a solution volume (V) containing a known concentration of the target substance (adsorbate), or so-called initial concentration (C_0). Then, the mass of adsorbent (m) is added to each bottle and the samples are placed on a shaker for mixing. This procedure is carried out in order to achieve the equilibrium plateau. However, preliminary to determine the equilibrium time it is necessary to perform another batch of experiments called kinetic adsorption. For this, stirring is carried out from several hours to several days, experimentally determining the optimal contact time to achieve equilibrium (kinetic adsorption). So, for example, in studies of El-Kady et al., 2013; Gebrekidan et al., 2015; Jeirani et al., 2017; Olivella et al., 2013; Ru et al., 2007 with some POPs, equilibrium times were found from

2 to 10 hours. After reaching equilibrium, the concentration of the adsorbate (C_e) in the solution is determined by various extraction methods (Avino and Russo, 2018; Foreman et al., 1995; Muir and Sverko, 2006; Ozcan et al., 2011; Samsidar et al., 2018; Veningerova et al., 1997). Thus, the amount of adsorbed compounds can be determined using the equation below (eq. 4):

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (4)$$

where q_e - adsorbed amount of compound (g), C_0 -initial concentration of compound and C_e – equilibrium concentration of compound ($\mu\text{g/L}$), V - aqueous solution (L) and m – mass of adsorbent (g).

Currently, there is no unified isothermal equation that considers all experimental equilibrium curves. The most commonly used adsorption isotherm models are those described by the researchers Langmuir, 1918 and Freundlich, 1907 which were named after them.

The Langmuir equation is linear and has the following form (eq. 5):

$$q = \frac{q_m * b * C_e}{1 + b * C_e} \quad (5)$$

where q_m is the saturation capacity and has the same unit of measurement as the adsorbed substance (adsorbent loading) (usually in mg/g or mmol/g), b is the reciprocal of the concentration. To determine the parameters q_m and b , it is necessary to plot the dependence of C_{eq}/q (Y-axis) and C_{eq} (X-axis). This model allows to estimate that adsorption occurs through a monolayer coating of the surface of the adsorbent with the energy homogeneity of the adsorption sites (Bedia et al., 2018).

Freundlich isotherm has the following equation (6):

$$q = K \times C^n \quad (6)$$

where K is the coefficient of adsorption, indicating the strength of adsorption. Higher K values are associated with higher adsorption. The n is a parameter of the energetic inhomogeneity of the adsorbent surface, and also determines the curvature of the isotherm. Values of n less than 1 give a concave isotherm, equal to 1 corresponds to a linear isotherm, and for n greater than 1, the isotherm will be convex (Figure 21).

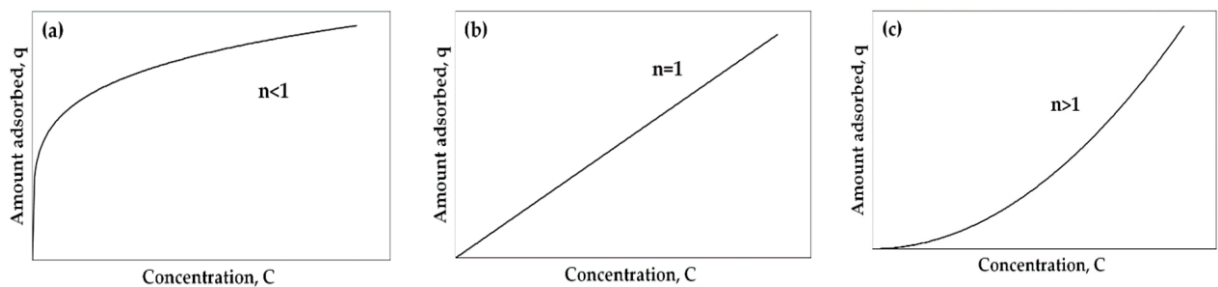


Figure 21- Freundlich isotherm type depending on the value n (a) $n < 1$, (b) $n = 1$, (c) $n > 1$

The n parameter can be any value. For example, Freundlich isotherms with $n < 1$ show high adsorbent loading at low adsorbate concentrations. Therefore, such an isotherm can be considered a favorable, and vice versa, an unfavorable isotherm for $n > 1$. The Freundlich isotherm is not suitable for describing the linear range at very low adsorbate concentrations, nor can it describe the saturation effect at very high concentrations. On the contrary, the average concentrations are very well suited for this model. In addition, the Freundlich isotherm is widely used to model activated carbon adsorption and therefore used as a standard model for prediction of multi-adsorption (Bedia et al., 2018; Worch E., 2012).

4.2 Adsorption Kinetic

The adsorption process with porous carbonized adsorbents takes time to reach equilibrium due to the resistance to mass transfer. The adsorption kinetics is the change in the amount of adsorbed molecules over time. In this case, an important indicator is the rate of adsorption on porous adsorbents. The rate of adsorption depends on the diffusion (penetration and distribution) of the target substances through the external surface of the adsorbent into its pores. Thus, adsorption consists of 4 sequential processes:

- 1) Diffusion of the adsorbate (target substance) from the liquid phase into the hydrodynamic boundary layer surrounding the adsorbent particles;
- 2) Diffusion through this layer to the external surface of the adsorbent (external diffusion)
- 3) Diffusion through the pores of the adsorbent (internal diffusion);
- 4) Energy interaction between adsorbate and adsorption sites.

The first and fourth processes are very fast. The second and third processes determine the rate of adsorption. To determine which process controls the rate of adsorption, it is necessary to take into account that external diffusion is dependent of the hydrodynamic conditions. Therefore, increasing the stirring rate could positively impact on the adsorption rate. It is important to take into account that the size of the adsorbent particles affects both external and internal diffusion, and, accordingly, leads to a change in the accessible surface area and diffusion paths. The internal diffusion mechanism is regulated by the efficiency of diffusion over pore volume and surface diffusion (Bedia et al., 2018; Worch E., 2012).

There are several models of adsorption kinetics. Some models assume that adsorption is the rate-limiting step in the adsorption process. Other models suggest that diffusion is a rate-limiting step. Therefore, fitting the experimental data to the models makes it possible to determine the adsorption mechanism.

To obtain the curves of kinetic adsorption $C = f(t)$, it is necessary to observe the change in the concentration of the adsorbate over time in a solution (V) with a known mass of the adsorbent (m). Fitting of the kinetic curve to different kinetic models of adsorption makes it possible to determine the mass transfer coefficients.

The traditional diffusion model is the pore volume and surface diffusion model (PVSDM) (Leyva-Ramos and Geankoplis, 1984). It is a complex diffusion model that considers adsorption, external mass transfer, and internal partial diffusion. It is assumed that inwardly partial diffusion occurs both due to diffusion in the pore volume and due to surface diffusion. The main conditions are constant temperature, spherical adsorbent particles and insignificant transfer of adsorbate molecules into the pores. Thus, the values of the effective diffusion coefficient over the pore volume (D_p) and the effective surface diffusion coefficient (D_s) will be constant, and the adsorption rate on the active centre will be instantaneous. The equations of the PVSDM model are presented in several works (Leyva-Ramos and Geankoplis, 1984; Worch E., 2012), and are distinguished by an complex mathematically structure, consisting of several equations. Thus, this has led to the integration of several simple models based on the kinetics of chemical reactions. The works of recent decades on the study of the kinetics of adsorption of various compounds (Feng et al., 2013; Li Y. et al., 2014; Zhou et al., 2017), including POPs (Ambaye et al., 2021; Jeirani et al., 2017; Ru et al., 2007) on carbon-containing materials, are increasingly used pseudo-first and pseudo-second order models, and the Elovich equation.

The pseudo-first order model has the following equation (eq. 7):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

where q_e and q_t (both in $\text{mg} \cdot \text{g}^{-1}$) are the absorption by the adsorbent at equilibrium and time t , respectively, and k_1 (min^{-1}) is a pseudo-first order rate constant. The solution to this equation with the initial condition $t = 0; q = 0$ and $t = t; q = q_t$ gives the following equation (eq. 8):

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1 * t \quad \text{or} \quad q_t = q_e * [1 - \exp(-k_1 * t)] \quad (8)$$

Various studies of the adsorption of pollutants from the liquid phase have argued that this model is the most suitable for adsorption kinetics.

A pseudo second order model (Ho and Mckay, 1999) can be expressed as follows (eq. 9):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

where k_2 is a pseudo second order rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). Integration of the above equation with the initial condition $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ gives (eq. 10):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 * t \quad (10)$$

Or alternatively (eq.11):

$$q_t = \frac{t}{\left(\frac{1}{h_0}\right) - \left(\frac{1}{q_e}\right)}; \quad h_0 = k_2 * q_e^2 \quad (11)$$

where h_0 ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) - initial adsorption rate. This model has also been successfully applied to the adsorption of various compounds from aqueous solution.

Elovich model (Bedia et al., 2018) was described by the following equation 12:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q} \quad (12)$$

where α ($\text{mg} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$) is a constant associated to chemisorption rate and β ($\text{g} \cdot \text{mg}^{-1}$) is a constant related to the extent of surface coverage. If $\alpha\beta t \gg 1$, and with the initial condition of $q = 0$ at $t = 0$ and $q = q$ at $t = t$, the solution is given by equation 13:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \quad (13)$$

β can be directly obtained from the slope of the plot of q_t versus $\ln(t)$ and α can be calculated from the intercept of the same plot once β is known.

4.3 POPs adsorption in soil

Soil is a complex heterogeneous environmental matrix containing mineral and organic materials with living, dead and decaying biological components. Interaction of POPs and soil are influenced by pollutant properties and its ability to be adsorbed or not. In addition, soil properties such as organic matter are also very important parameters which impact on the adsorption of POPs.

It is known that soil represents a powerful reservoir of organic pollutants. This is induced by the presence of soil organic matter. Generally, soil can contain from 2 to 60% of organic matter, which in turn can include up to 58% carbon atoms. Soil organic matter is a heterogeneous mixture of proteins, polysaccharides, lipids, humic substances, kerogen and black carbon (Mechlińska et al., 2009). In addition, soil organic matter composed of 2 groups of substances: humic and non-humic components (Anderson & Schoneau, 2007). The latter group may include peptides, amino acids and sugars. Up to 80% of soil organic matter consists of the humic group of substances. This group of substances includes humin, humic and fulvic acids. The humic group is characterized by color

(yellow to black), high molecular weight not to be susceptible to mineralization (Hayes et al., 2017).

Humin plays an important role on the adsorption of POPs (Piccolo A., 1996). Hydrophobic POPs have an affinity for the hydrophobic fraction of organic matter, i.e., humin or some of its fractions. The humin content varies greatly in soils and can be from 10% in spodosol and over 60% in vertisol (Andreux F., 1996). Consequently, the higher the humin content in the soil, the more strongly such soil can accumulate POPs (Tremolada et al., 2012). Many studies reported that adsorption of POPs into soil is associated with soil organic matter content (Chianese et al., 2020; Doick et al., 2005; Tremolada et al., 2012). Indeed, the published literature data agreed that POPs such as OCPs (Ahmad et al., 2001; Devi et al., 2013; C. Zhao et al., 2013), as well as PCBs and PAHs (Chiou et al., 2015; Doick et al., 2005c; Kohl and Rice, 1998) are particularly accumulate in soil enriched with organic matter.

According to studies (Cousins et al., 1999; Krauss et al., 1999; Moeckel et al., 2008), POPs are mainly found in the soil in the surface layers due to the distribution of organic matter. However, POPs can be transported to different depths in arable soils that are usually periodically plowed and cultivated (Armitage et al., 2006). It should also be noted that vegetation can act as a filter for the soil and accumulate POPs from the ambient air, thus reducing transport to the soil. Thus, forest soils have higher levels of POPs contamination than soils with herbaceous vegetation (Tremolada et al., 2008). Consequently, the above elements can influence the level of POPs pollution, surpassing the impact of soil organic matter. In addition, sometimes soils with the same organic matter content may also exhibit different POPs adsorption potential and could not be used as an indicator for prediction of POP contamination level. For instance, soils which were located close to pollution sources (Meijer et al., 2003), soils that have undergone temperature fluctuations depending on latitude (Meijer et al., 2002), altitude (Ribes et al., 2002), or seasons (Guazzoni et al., 2011).

The soil binding process of POPs is complex because of the large variety of competing components such as microorganisms, mesofauna (worms) and plants. These components compete for the absorption of lipophilic contaminants.

On the other hand, POPs with low to moderate adsorption capacity remain bioavailable. There are organisms which could interact with the soil include microorganisms, worms, plants (roots) and livestock. Bioavailable POPs can pollute water, air, forage plants, livestock and move on to the food chain. Main determinant of bioavailability is chemical aging in soil (Alexander M, 2000).

Chemical aging in soil is the movement of chemicals from the surface of soil particles into less accessible sites with time (Reid et al., 2000). Aging leads to three types of POPs desorption: “fast”, “slow” and “very slow”. POP molecules which are rapidly desorbing, can be adsorbed on the surface and interact with water in the pores of the soil, therefore they easily become bioavailable. However, the slow and very slow desorbed fraction of POPs are strongly bound in soil micropores, which makes them inaccessible even to microorganisms (Semple et al., 2007). Thus, the processes of adsorption and desorption are key factors that determine the ability of POPs to be bioavailable.

5. Methodological aspects of AC/BC amendment to soil

The main parameters that impact on the sequestration of POPs in soil using AC / BC are mixing, contact time, adsorbent characteristics, adsorbent concentration and pollutant concentration (Hilber and Bucheli, 2010).

The way in which the AC / BC amendment is applied to the soil and mixing is a key factor influencing the effectiveness of a pollutant sequestration strategy. First, mixing the amendment and soil should lead to a uniform distribution, which in turn stimulates contact between the pollutant molecules, AC / BC particles, and soil particles. The better the contact, the faster the equilibration of POPs between the soil and the AC / BC occurs (Rakowska et al., 2012; Werner et al., 2005). For this, an aqueous solution with AC / BC is used, which is added to the contaminated soil. Secondly, mixing should be minimally invasive and exclude (even temporary) increase of pollutants exposure on the environment. Homogenization (or mixing) is carried out under laboratory conditions using a rotary shaker, or by shaking incubators. However, quite often the researchers did not bother to describe in detail how they carried out the procedure of the soil amendment. In this case, it is necessary to take into account contact (or exposure) time between amendment and soil. Thus, the exposure time of coal for soils contaminated with PCDD / Fs, PCBs and some OCPs ranges from several hours to several months (Chai et al., 2012; Guo et al., 2020; Hilber and Bucheli, 2010).

The concentration of the AC / BC amendment is also an important parameter in the development of a method for sequestering POPs in soil. The amendment concentration usually could be achieved empirically under laboratory conditions, taking into account also the concentration of organic pollutants in the soil. Typically, the concentration of AC or BC ranges from 0.1 to 3.5% (Denyes et al., 2013; Hilber and Bucheli, 2010). The literature reports that the larger the AC/BC dose and the contact time, the more efficient the sequestration of organic pollutants is (Jeirani et al., 2017). However, this does not mean that large amounts of amendment can be added to the

contaminated soil unreasonably. It is known that AC/BC has a fairly strong environmental stability due to the presence of condensed aromatic carbon, hence there is no knowledge of its long-term effect on soil quality (Guo et al., 2020). According to Singh & Singh, 2017 the mean residence time of biochar in the natural soil environment was estimated at 90–1,600 years. It is necessary to select the sequestration parameters in the way to not to disturb the soil balance and its fertility in one side, and maintaining the effect of POPs retention and reducing their bioavailability for other links of the food chain in another side.

6. Intermediate conclusions

Therefore, based on this review of the strategy for sequestering POPs in soil, several conclusions can be drawn:

1) The sequestration strategy is a relatively new way of remediation of contaminated soils, which will reduce the transfer of POPs by their strong adsorption on the surface of AC / BC, long-term retention and reducing their bioavailability. Therefore, this will allow them to reduce or, at best, prevent the transfer of pollutants, for example, to farm animals, and then to the food products they produce.

2) The wide variety of cheap and locally produced raw materials for the production of AC and BC based sequestration materials makes the sequestration strategy economically and environmentally friendly.

3) Different characteristics of AC/BC played an important role in adsorption of POPs. Among them: specific surface area, porosity, and functional groups.

4) Validation the strategy *in situ* requires a preliminary *in vitro* study which supposed to investigate the main parameters of sequestration strategy: contact time (or aging), concentration of AC/BC, equilibrium and kinetic adsorption. These parameters could be used as a basis for integration this promising strategy *in situ* on contaminated soil.

CONCLUSION OF THE BIBLIOGRAPHIC SYNTHESIS

Literature synthesis showed that contamination of soil by chlorinated POPs such as PCDD/Fs, PCBs and OCPs could possess a high risk for humans as soil represents a carrier of these chemicals for food producing animals. POPs deposited on upper layer of soil and could be stored in this matrix for a very long period (from decades to centuries). This is explained by their physical and chemical properties as well as soil organic matter, which could strongly bind them. Livestock especially free-range animals on daily basis could ingest soil in different proportions together with vegetation which in case of contamination context represent a serious consequence to produce insecure food of animal origin.

This bibliographic synthesis showed that different carbonaceous materials such as AC/BCs can adsorb POPs reducing its availability in soil and bioavailability for animals (liver, fat and muscle). As consequence this effect led to limitation of POP transfer from soil to livestock animals. The considered tests for assessing pollutant environmental availability, bioavailability (relative and absolute) can be effectively used to study the sequestration strategy based on AC/BC, i.e. using them as soil amendment.

Validation the strategy *in situ* requires a preliminary *in vitro* study which supposed to investigate the main parameters of sequestration strategy: contact time (or aging), concentration of AC/BC, equilibrium and kinetic adsorption. These parameters could be used as a basis for integration this promising strategy *in situ* on contaminated soil. This is briefly shown in Figure 22.

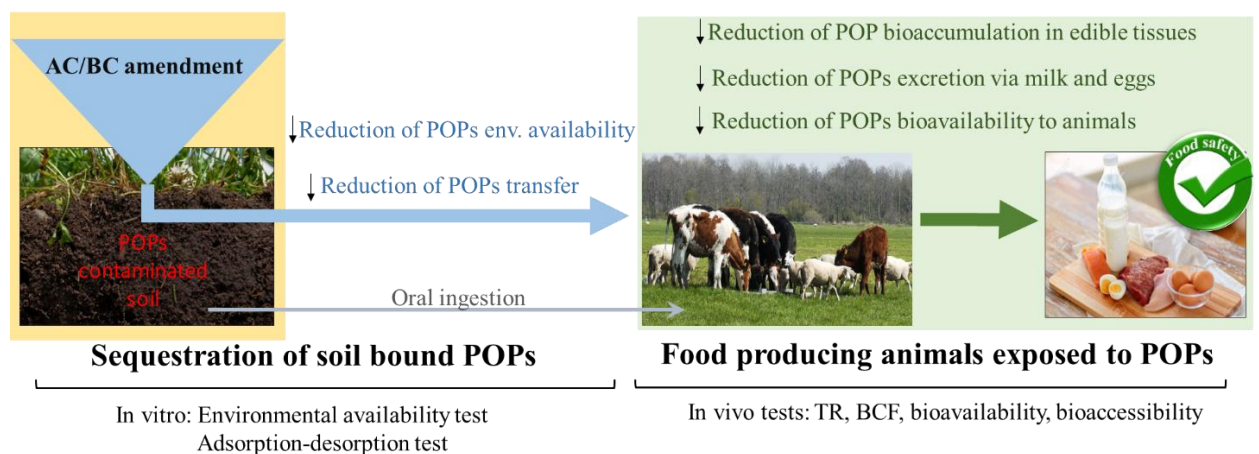


Figure 22 – General scheme of main idea of the work.

Indications: AC- activated carbon, BC-biochar, TR - transfer rate, BCF- bioconcentration factor.

ORIENTATION OF THESIS WORK

The main hypothesis of the current work was to find and explore the strategies which could firstly limit POPs availability in environment and secondly to reduce their transfer from soil to the food producing animals. Taking into account the interests of the Kazakh-French relations when performing this work within the framework of a double doctoral program, the OCPs family was chosen as representatives of the POPs. Storage of these obsolete and forbidden pesticides represents a common emerging question in a several countries, including France and Kazakhstan, which was justified the study of their behavior in soil. Among the selected OCPs were DDT and metabolites, HCH isomers and CLD. Historically contaminated regions were selected for sampling contaminated soils which were integrated in building *in vivo* and *in vitro* model experiments. In addition, locally produced carbonaceous adsorbents from France and Kazakhstan were also investigated. Thus, this work composed of 1 meta-analysis and 3 experimental studies.

Meta-analysis of 41 articles with a very different experimental or case studies was performed to better understand the transfer of different POP families (including PCDD/Fs, PCBs, OCPs and PBDEs) in different food of animal origin. A consolidated methodology was created to discriminate the current knowledge about distribution and accumulation of different POPs in animal liver, fat and muscle tissue and their excretion into milk and eggs. In addition, meta-analysis showed that TRs and BCFs could be a very valuable tools to describe and assess contaminant's transfer to animals and their subsequent food-products. They allow to predict maximum POP levels when the exposure context (ingest dose of POPs) is accurately known and play by consequence a major role in risk assessments dealing with food contaminations. Data base which was created using published literature showed that the most toxic POPs (tetra-to hexachlorinated dioxins and furans, highly chlorinated PCBs, especially congener 126, as well as DDT) are highly transferred to the most consumed food products such as eggs, milk, and to a lesser extent also meat. Therefore, further experiments were focused on studies of application of different carbonaceous materials (AC/BCs), which could be serious candidates to sequestrate POPs.

First experiment was conducted to investigate an adsorption behavior and linked it to physico-chemical properties of several sequestration materials (SMs) which could be a potential candidate to sequestrate OCPs and being applied as sequestrants in remediation of contaminated soil or water in perspective. The current study explored adsorption of OCPs with different hydrophobic nature, on 4 contrasted porous adsorbents (ACs and BCs) and 5 different basic substances of soil organic matter (SOM) in aqueous media using kinetics and isotherm batch studies with emphasis on

relationship between adsorption capabilities and physico-chemical properties. The results of this experiment identified several SMs that were used in the further experiments to reduce the environmental availability of OCPs in soil and bioavailability in animal edible tissues.

The second experiment was performed *in vitro* and was aimed to study 2 ACs and 1 BC for the ability to reduce environmental availability in two historically OCP-contaminated soils. Two parameters were investigated such as amendment rate and granulometry of SMs. This study showed that AC/BCs with 2% amendment rate could reduce up to 90% of environmental availability of DDT and metabolites in soil which was heavily contaminated. A clear effect of SM granulometry was also observed, i.e., the finer the particles (<150 µm) and higher the amendment rate (2% dry matter) the better the sequestration of the target pollutants.

Finally, the last experiment was focused on study of sequestration potential of two contrasted ACs by an *in vivo* study to efficiently retain CLD during digestive processes of piglets when provided either via feed incorporation or via soil amendment. Results of this study showed that the most effective way to perform sequestration to limit POPs contamination in animals (and their body tissues) is performing an AC/BC amendment to the soil rather than to incorporate it in the animal feed. The bioavailability reduction coefficient of CLD reached up to 86% in the liver and fat of exposed piglets when AC were added to contaminated soil.

The thesis work is summarized in the table 1.

Table 8 - Experimental scheme of the experiments carried out during the thesis work.

Experimental part	Type of the study	Contaminant	Target matrix	Sequestration materials	Testing methods
I	Meta-analysis	PCDD/Fs, PCBs, OCPs, PBDEs	Feed Soil	-	TR, BCF
II	Experiment (<i>in vitro</i>)	DDTs, HCHs, CLDs	Aqueous media	2 ACs: DARCO, Shubarkol 2 BCs: Oak tree, Japanese knotweed 5 SOMs*: Humic acid, fulvic acid, raw peat, potassium humate and raw brown coal (Shoptkyol)	Kinetic adsorption, Isotherm adsorption
III	Experiment (<i>in vitro</i>)	DDTs, HCHs, CLDs	Soil	2 ACs: DARCO, ORBO 1 BC: Sargassum	Environmental availability test
IV	Experiment (<i>in vivo</i>)	CLD	Feed Soil	2 ACs: DARCO, ORBO	Bioavailability test

*SOM - Soil organic matter

CHAPTER 2: EXPERIMENTATION

PART I: Assessment of the transfer of different families of POPs to food of animal origin

This chapter considered as meta-analysis which was published in a peer-review journal «Chemosphere» with title «Transfer of persistent organic pollutants in food of animal origin - Meta-analysis of published data» in the frame of this PhD thesis (Amutova et al., 2021).

1. Introduction

Free-range agricultural animals ingest various environmental matrices as vegetation frequently used as feed, but also water or even soil. Several studies have reported that ruminants would consume in normal grazing conditions up to 10% of soil in daily dry matter intake (Collas et al., 2019; Healy, 1968; Jurjanz et al., 2012) and even up to 30% in the worst conditions as winter grazing (Abrahams and Steigmajer, 2003). Poultry also ingest soil along pecking contaminated feed from the ground. In unbalanced feeding conditions, the soil intake in laying hens may reach up to 23% (Jondreville et al., 2010).

During such soil intake, persistent organic pollutants (POPs) deposited on the upper soil can be ingested by livestock (Fries, 1982; Jones et al., 1989; Stevens & Gerbec, 1988) and transferred into their subsequent food products. Previous studies have demonstrated that contaminated soil is the main source of exposure to pollutants for livestock, especially when soil is contaminated by lipophilic POPs, such as polychlorinated biphenyls (PCBs), dioxins and furans (PCDD/Fs) (Diletti et al., 2014), or organochlorinated pesticides (OCPs) (Tao et al., 2009). Some studies have reported transfers of OCPs and PCBs to livestock after atmospheric deposition leading to contamination of water, soil and vegetation (Pan et al., 2014) by regular floods (Abrahams and Steigmajer, 2003; Rose et al., 2012) and others. Subsequently, POPs can be transferred to food of animal origin, such as milk, meat and eggs. As a result, consumption of such contaminated food would be a possible route of POP exposure for humans (Mclachlan et al., 1990), and the correct quantification of the POP transfer from contaminated environmental matter to food products is essential for a reliable risk assessment.

Nevertheless, considerable variations can be found between reported transfers among different studies as they are based on different contamination matrices, doses, and duration of exposure. However, such data are required to realize a risk assessment of food production systems. The aim of this paper was to derive and summarize current literature data on the transfer of different classes of POPs to edible tissues and food of animal origin. A consolidated methodology was used to

discriminate the current knowledge about distribution and accumulation of PCDD/Fs, PCBs, PBDEs and OCPs in animal liver, fat and muscle tissue and their excretion into milk and eggs. At the end, this synthesis aims to improve monitoring system for livestock farming in contaminated.

2. Materials and methods

A database was created using peer-reviewed research articles reporting the transfer of POPs from ingested environmental matrices to edible tissues in different animal species (Table 9). Then, the transfer was evaluated by bioconcentration factors and transfer rates to characterize respectively the distribution of pollutants in tissues or the excretion of POPs via milk or eggs.

2.1. Building-up the database

In total, forty-one peer-reviewed articles reporting transfer of different POPs were browsed by Google Scholar through queries comprising the following keywords:

Excretion OR mass-balance OR carry-over rate OR transfer rate OR biotransfer AND (PCDD/F OR PCB OR OCP OR PBDE) AND ((milk AND ((cow OR cattle) OR (Goat OR Caprine))) OR (hens OR pig)).

Transfer was quantified in two different concepts: as transfer rate (TR) when the target was excreted milk or eggs or as a bioconcentration factor (BCF) when transfer was measured via the enrichment in body tissues such as liver, muscles, or body fat. Nevertheless, we did not integrate data of biotransfer factors (BTF), i.e., a ratio between tissue concentration and ingested amount of the studied POP. Although this approach would have several advantages, as the ingested amounts of all contaminated materials over the whole exposure period are required. These data are often missing due to field conditions and therefore not available for a risk assessment. As the concepts of TR and BCF were not used homogeneously in the literature, we firstly defined them.

The TR corresponds to the ratio between ingested and excreted amounts of the pollutant (equation (1)) which can be calculated after reaching steady state (Richter & McLachlan, 2001) and expressed as a percentage:

$$\text{COR}_{\text{product}} = \frac{[\text{pollutant}]_{\text{Fat of product}} * \text{Daily fat excretion}}{[\text{pollutant}]_{\text{Diet}} * \text{Diet Intake}} * 100\% \quad (1)$$

The $[\text{pollutant}]_{\text{fat of product}}$ corresponds to the concentration of pollutant in the fat of the food product (pg/g fat) and $[\text{pollutant}]_{\text{Diet}}$ to its concentration in the intake matrix feed or in soil (pg/g dry matter).

Table 9 - Studies extracted from the literature, validation of the methodologic criteria and the decision of their integration in the data set.

№	Reference	Studied compounds	Exposure media	Category of animals	Exposure (days)	SS ¹	Parameters ²	Intake			Edible tissues			Integration ⁵
								C ³	<LQ ⁴	Q ³	C ³	<LQ ⁴	Q ³	
1	Aulakh et al., 2006	OCPs	Feed	Laying hens	Field exposure	(✓)	(BCF)	✓	-	Q ³	✓	-	✓	✓
							(TR)							✓
2	Brambilla et al., 2008	PCDD/Fs	Minerals	Dairy cows	28	(X)	TR	X	-	✓	X	-	✓	X (exposure < half-live)
3	Costera et al., 2006	PCDD/Fs, PCBs	Hay	Dairy goats	70	✓	TR	✓	-	✓	✓	-	✓	✓
4	Diletti et al., 2014	PCDD/Fs, PCBs	Feed	dairy buffaloes	100	✓	TR	✓	-	✓	✓	2 PCDD/Fs congeners out of 17	X	✓
5	Feil et al., 2000	PCDD/Fs	Feed	Cattle (calves)	120	✓	BCF	✓	-	✓	✓	8 congeners out of 17	-	X (C wet basis, 8 congeners <LQs)
6	Fernandes et al., 2011	PCDD/Fs, dl-PCBs	Feed	Pigs	81-179	-	BTF	X	-	X	X	-	X	X (BTF, no reported C)
				Sheep (non lact. ewes)	48-153	-	BTF	X	-	X	X	-	X	
				Broilers, Laying hens	28-250	-	BTF	X	-	X	X	-	X	
7	Fournier et al., 2013	iPCBs	Corn silage	goats	39	✓	MISS	✓	-	✓	X	-	✓	X (no reported C in milk)

8	Fries G., 1999	PCDD/Fs	PCP-treated Wood and feed	dairy cows	58	✓	TR	✓	-	✓	✓	-	✓	✓
9	Fries et al., 2002	PCDD/Fs	Feed	dairy cows	58	✓	TR	✗	3 congeners out of 17	✓	✗	3 congeners out of 17	✗	✓
10	Hoogenboom et al., 2004	PCDD/Fs PCBs	Feed	Broilers	7	✗	BCF	✓	-	✓	✓	3 PCDD/Fs congeners out of 17	✗	✓
		PCDD/Fs PCBs	Feed	Pigs	7	✗	BCF	✓	-	✓	✓	3 PCDD/Fs congeners out of 17	✗	✓
11	Hoogenboom et al., 2006	PCDD/Fs	Feed	Laying hens	56	✓	TR	✓	-	✓	✓	-	✓	✓
12	Hoogenboom et al., 2015a	PCDD/Fs	Maize silage	dairy cows	33	(✗)	TR	✓	-	✓	✓	9 congeners out of 17	✓	✗ (exposure < half-live)
		PCDD/Fs	Sugar beet	dairy cows	33	(✗)	TR	✓	-	✓	✓	9 congeners out of 17	✓	✗ (exposure < half-live)
		PCBs	Maize silage	dairy cows	33	(✓)	TR	✓	7 congeners out of 12	✓	✓	4 congeners out of 12	✓	✓
		PCBs	Sugar beet	dairy cows	33	(✓)	TR	✓	8 congeners out of 12	✓	✓	4 congeners out of 12	✓	✓
13	Hoogenboom et al., 2015b	PCDD/Fs, PCBs	Grass	Lamb	113	(✓)	(BCF)	✓	1 congener out of 17	✓	✓	2 congeners out of 17	✗	✓
14		PCDD/Fs	Mineral Mix			✓	TR	✓		✓	✓	-	✓	✗

	Huwe & Smith, 2005	dl-PCBs		dairy cows	Averaged between 17 to 38		BCF		3 congeners out of 17					(exposure < half-live)
														✓
15	Kerst et al., 2004	dl-PCBs	Grass	dairy cows	Field exposure	(✓)	TR	✓	-	✓	✓	-	✓	✓
16	Kierkegaard et al., 2009	PBDE	Feed	dairy cows	90	✓	(BCF)	(✓)	-	✓	(✓)	-	✓	✓
17	Lorenzi et al., 2020	PCDD/Fs, dl-PCBs, Indicator PCBs	Feed	dairy cows	49	✓	TR	✓	-	✓	✓	-	✓	✓
18	Mclachlan et al., 1990	PCDD/Fs	Feed	dairy cows	35	✗	TR	✗	-	✓	✗	-	✓	✗ (exposure < half-live)
19	Mclachlan & Richter, 1998	PCDD/Fs	Feed	dairy cows	84	(✓)	TR	✓	-	✓	✗	4 congeners out of 17	✓	✓
		PCDD/Fs	Feed	dairy cows	23	(✗)	TR	✓	-	✓	✗	2 congeners out of 17	✓	✗ (exposure < half-live)
20	Malisch, 2000	PCDD/Fs	Citrus pulp	dairy cows	180	(✓)	TR	✗	-	✓	✓	1 congener out of 17	✗	✓
21	Olling et al., 1991	PCDD/Fs	Intraruminally dose in olive oil	dairy cows	1 (single dose)	✗	TR	✗	-	✓	✓	-	✓	✗ (Single dose exposure)
22	Ounnas et al., 2010	PCBs (dl & mono-	Soil	goats	80	✓	TR BCF	✓	-	✓	✓	-	✓	✓

		ortho), PBDE												
23	Pan et al., 2014	OCPs iPCBs	Grass	yak	Field exposure	(√)	(BCF)	√	-	×	√	-	×	√
24	Parera et al., 2008	PCDD/Fs	Feed	Broilers	39	-	(BCF)	√	-	√	√	2 congeners out of 17	-	√
25	Petreas' et al., 1991	PCDD/Fs	Soil	Laying hens	178	√	BTF	√	2 congeners out of 17	(√)	√	-	(√)	×
							(TR)							√
26	Pirard & de Pauw, 2005	PCDD/Fs, dl-PCBs	Feed	Laying hens	54	√	BCF	√	1 PCDD/Fs congener out of 17	(√)	√	1 PCDD/Fs congener out of 17	(√)	√
							(TR)							√
27	Pirard & de Pauw, 2006	PCDD/Fs,	Feed	Laying hens	98	√	BCF	√	-	(√)	√	2 congeners out of 17	(√)	√
							(TR)							√
28	Piskorska- Pliszczynska et al., 2014	PCDD/Fs	Soil	Laying hens	Field exposure	(√)	(BCF)	√	-	(√)	√	-	√	√
29	Rose et al., 2012	PCDD/Fs dl-PCBs,	Feed	pigs	Field exposure	(√)	(BCF)	√	10 PCDD/Fs out of 17 congeners	×	√	10 PCDD/Fs congeners out of 17	√	×
		iPCBs, Mono-ortho					MISS							√
30	Schuler et al., 1997	PCDD/Fs	Grass	dairy cows	Field exposure	(√)	TR	√	-	×	√	-	√	√

31	Shen et al., 2012	PCDD/Fs, dl-PCB	Soybean oil	pigs	91	(X)	MISS	X	-	X	✓	-	-	X (no reported intake C)
32	Shih et al., 2009	PCDD/Fs	Feed	ducks	41	✓	BCF	✓	-	(✓)	✓	-	(✓)	✓
							(TR)							✓
33	Slob et al., 1995	PCDD/Fs	Fly ash	dairy cows	1	X	BA	✓	-	✓	✓	2 PCDD/Fs congeners out of 17	✓	X Single dose exposure
		PCDD/Fs, dl-PCB	Grass	dairy cows	30	✓	TR	✓	-	✓	✓	2 PCDD/Fs congeners out of 17	✓	X (no SS)
34	Spitaler et al., 2005	PCDD/Fs	Feed	pigs	126	(✓)	(BCF)	✓	-	✓	✓	5 congeners out of 17	✓	✓
35	Tao et al., 2009	OCPs	Feed	hens	Field exposure	(✓)	(BCF)	✓	-	X	✓	-	X	✓
36	Thomas et al., 1999	Indicator PCBs, Mono-ortho PCBs	Feed	dairy cows	128	✓	TR	X	-	✓	X	-	✓	✓
37	Thorpe et al., 2001	PCDD/Fs	Gelatin capsule	Cattle (heifers)	28	(X)	MISS	(X)	-	X	✓	-	X	X (no reported C in feed)
		PCBs (iPCBs, mono-ortho)												
38		PCDD/Fs PCBs	Feed	Laying hens	7	X	(TR)	✓	-	✓	✓	2 PCDD/Fs congeners out of 17	✓	X (no SS)

	Traag et al., 2006	PCDD/Fs PCBs	Feed	Laying hens	7	X	(BCF)	✓	-	✓	✓	4 PCDD/Fs congeners out of 17	✓	✓
39	Tuinstra et al., n.d.	PCDD/Fs	Feed	dairy cows	105-119	(✓)	MISS	✓	-	✓	X	-	X	X (no reported C in milk)
40	Watanabe et al., 2010	PCDD/Fs, PCBs	Dust & soil	pigs	Field exposure	X	MISS	X	-	X	✓	3 PCDD/Fs congeners out of 17	X	X (no reported C in feed)
41	Wittsiepe et al., 2007	PCDD/Fs	Soil	Minipigs, 56-78 days	28	X	MISS	✓	-	✓	✓	4 congeners out of 17	-	X (no reported C in feed)
		PCDD/Fs	feed			X	MISS	✓	-	✓	✓	1 congener out of 17;	-	X (no reported C in feed)

Bold mean integrated article in our dataset

¹ Statement of steady state (SS) given by the authors or in brackets when statement was made by us.

² TR- transfer rate, BCF – bioconcentration factor, BA- bioavailability, BTF- biotransfer factor. MISS – missing data. Values of the parameters taken from the authors or in brackets when re-calculated by us.

³ C – concentrations, Q-quantities where ✓ = given in the article; (✓) = Recalculated; X= not available

⁴ Compounds that below limit of quantification (LQ)

⁵ Decision of integration (✓) or not (X) the given study in our dataset

Due to their lipophilicity, POP concentrations are commonly expressed in relation to fat content needing therefore information about fat mass of milk or eggs. Pollutants can also be accumulated in body tissues and reach concentrations higher than in the exposure matrix. The extent of this accumulation is expressed as the ratio between the concentrations in intake (i.e., feed or dry soil) and the studied body tissue (equation (2)).

$$\text{BCF} = \frac{[\text{pollutant}]_{\text{tissue}}}{[\text{pollutant}]_{\text{intake}}} \quad (2)$$

In this equation, [pollutant] tissue corresponds to the pollutant concentration in the tissues (pg/g fat) and [pollutant]feed to its concentration in feed (pg/g feed at 15% wet content) or in soil (pg/g dry matter).

2.2. Selection criterion of articles in the dataset

A calculation of transfer rate was conditioned by the duration of exposure which would allow the considered compound to reach in the tissue of the exposed animal a stable concentration of steady state (Huwe & Smith, 2005; Ounnas et al., 2010). Casarett & Doull, 2008 defined the steady state as the physiological state of an animal during a continuous exposure to a fixed daily dose, leading to a concentration remaining stable in time. Therefore, the compound specific exposure duration is the key parameter to achieve a steady state plateau.

We considered that steady state conditions have been reached when authors reported it clearly in their article. If not, we evaluated the exposure duration in comparison to the half-life of the considered compound in the given animal type (mammalians versus birds) in respect to its life expectancy. For example, half-life of PCDD/Fs in hen eggs is 30 days (Petreas et al., 1991), but would be more than 40 days in cow milk (Huwe & Smith, 2005; Olling et al., 1991) and goat milk (Costera et al., 2006). Contrarily, half-life of PCBs in hen eggs and goat milk of only 30 days has been confirmed by averaged results of Hoogenboom et al., 2015a and Costera et al., 2006 respectively. Indeed, half-life of the target compound would allow to predict the necessary exposure duration to reach steady state (Holford, 2012) : 50% of the steady state concentration would be reached after one half-life and 87,6% after three half-lives. We fixed an acceptable level of steady state at 90% of the plateau corresponding to 3.3 half-lives of the considered compound. The study of Hoogenboom et al., 2006 on laying hens reported the transfer of different POPs in eggs after exposure durations of 56 days, declared as “close to steady state plateau”. By acceptance, this study has been integrated in the dataset. Furthermore, some studies have reported exposure due to a field contamination (i.e. long-time exposure of several weeks, often several months) for dairy cows (Kerst et al., 2004; Schuler et al., 1997) or laying hens (Aulakh et al.,

2006; Piskorska-Pliszczynska et al., 2014). These studies were also integrated in our dataset considering that these animals had probably be exposed long enough to the studied compounds that makes the achievement of a steady state plateau likely.

In contrast to transfer studies into milk or eggs, the achievement of a steady state was not a selection criterion to integrate studies reporting BCFs. Indeed, the target animals were generally meat-producing categories such as pigs, broilers or, lambs. Their rapid increase in body mass will constantly redistribute target substances in tissues that makes the achievement of a stable concentration nearly impossible. In other words, the steady state could only be achieved in adults with a stable body weight. Therefore, we compared BCFs between two groups of animals: firstly, excreting adults (lactating mammals or laying birds) or secondly, rapidly growing young animals, generally raised for meat production. Then comparisons were carried out on BCFs issued from the same study: either the different congeners within the same tissue or the different tissues for given congener. Finally, the interpretation of BCFs will distinguish short time exposure (≤ 7 days) but no single dose and chronic exposure (clearly more than 7 days).

Except some minor adaptations of the expression (i.e. equations (1) and (2)), we used generally TRs and BCFs as they were indicated in the article. In absence of reported TR or BCFs we calculated them ourselves using the data reported in the article. However, some studies needed some zootechnical hypothesis to calculate TRs or BCFs:

1) Some studies have reported only concentrations in feed and tissues (Hoogenboom et al., 2015a; Huwe & Smith, 2005; Kierkegaard et al., 2009; Parera et al., 2008; Tao et al., 2009; Traag et al., 2006) that we used to calculate BCFs.

2) In absence of any specification in the article, we evaluated the daily feed intake of laying hens as 110g (studies of Petreas et al., 1991; Pirard & de Pauw, 2005). If missing, the output of very lipophilic POPs by laying hens has been evaluated on the basis of a standard egg (55g containing 27% lipids in the yolk) enhancing a fat excretion of 5.4g per egg. The laying productivity in intensive free-range rearing conditions of 6 eggs per week was supposed leading to an average daily fat excretion of 4.6 g/day via egg laying. In addition, Petreas et al., 1991 reported TRs of PCDD/Fs in eggs in a study where 10% of contaminated soil was integrated in the feed. Therefore, we considered a global intake of 99g of feed and 11g of (contaminated) soil to establish the global intake concentration of the contaminants.

3) Shih et al., 2009 investigated the transfer of PCDD/Fs into eggs of laying ducks. The contaminants were issued from dust of which 0,6% was integrated in their feed. According to Bley & Bessei, 2008, a daily feed intake of 200 g was supposed and then the daily dust intake would

represent 1.2 g. The fat excretion in duck eggs has been supposed to be 7.5g daily (laying productivity of 90% for eggs of 66g containing 8.3g of yolk fat; (Kaewmanee et al., 2009).

4) The field study of Piskorska-Pliszczynska et al., 2014 considered soil as the only source of PCDD/Fs. Aiming to obtain a reliable concentration in the global intake for BCF calculations, we divided the ingested amounts of contaminants by an estimated amount of ingested matter, i.e. 90 g of feed and 20 g of soil in free range laying hens as reported by Jondreville C., 2010.

5) The study on yaks (Pan et al., 2014) allowed calculations of BCFs between grass and the tissues muscle and liver considering grass as the only exposure source. Nevertheless, notable differences in POP concentrations had been shown between summer and winter samples. Therefore, the average concentration in tissues has been used. In absence of consolidated data about feed intake or milk yields of these yaks, we renounced to calculate TRs in milk.

6) Aulakh et al., 2006 presented an original field study reporting concentration of different OCPs in feed, eggs and muscles of hens. TR to eggs was calculated using the same feed intake and egg composition than previously presented. The calculation of BCFs in hen muscle was based on a fat content of 10% in the fresh matter according to Kaewkot et al., 2019.

Thus, Table 9 shows the complete list of extracted articles, the studied compounds, species, exposure duration and the integration choices. Thirteen research papers out of 41 have not been integrated and 2 only partly, mainly due to a too short exposure duration of the animals (in case of TRs), which not allowed to achieve steady state conditions (Brambilla et al., 2008; Huwe & Smith, 2005; Mclachlan et al., 1990; Olling et al., 1991; Slob et al., 1995; Traag et al., 2006). In addition, there are missing intake and/or tissue concentrations for calculation of BCFs in the studies of Fernandes et al., 2011; Fournier et al., 2013; Shen et al., 2012; Thorpe et al., 2001; Tuinstra et al., 1992; Watanabe et al., 2010; Wittsiepe et al., 2007. Finally, the studies of Feil et al., 2000 and Rose et al., 2012 reported transfer of PCDD/Fs and PCBs from feeds but the concentrations of the studied POPs are generally under the limit of quantification.

2.3. Data analysis

2.3.1. Transfer rates

After extraction of TRs values from the relevant studies, a mean and a SD were calculated for each congener in a given product (i.e. milk or egg). Based on these values, the transfer was classified in four levels depending on the TR:

- high transfer when $TR > 25\%$;
- medium transfer for TRs between 10 and 25%;
- low transfer when TR is between 0.5 and up to 10% and

- no significant transfer was considered when TRs were <0.5%.

The comparison between the different congeners of PCDD/Fs (Table 10) and PCBs (Table 11) was based on the one hand on the differences between mean TRs weighed by the associated SDs and on the other hand on the attributed transfer levels.

Additionally, two separate principal component analysis (PCA) were carried out respectively for milk and eggs using the software XLSTAT 2020 (Addinsoft Corp., New York, USA) to illustrate the link between TRs and some chemical characteristics of the PCB congeners (Log K_{ow} , MW, number of chlorines Cln, ortho-substitution) (Figure 1). The variable TR being the variable to be explained was added as a supplementary variable (Penny and Jolliffe, 2001).

2.3.2. Bioconcentration factors

The BCFs derived from the relevant papers were summarized in tables depending on the chemical family (i.e. PCDD/PCDFs, PCBs, PBDEs and OCPs). Within each table, the BCFs per congener and tissue were listed. Tissues were inventoried in the tables in a decreasing order of mean BCFs over all integrated studies.

Then, BCFs for PCDD/Fs were divided in two animal categories and presented separately:

- Adult animals with depuration excretion (i.e. lactating mammals or laying birds) (Table 12 grouping the data issued from the studies of Huwe & Smith, 2005; Pirard & de Pauw, 2005, 2006; Piskorska-Pliszczynska et al., 2014; Shih et al., 2009; Traag et al., 2006.

- Rapidly growing young animals, generally raised for meat purposes (broilers, pigs and lambs) (Table 13) grouping data from the studies of Hoogenboom et al., 2004; Hoogenboom et al., 2015; Parera et al., 2008; Spitaler et al., 2005.

The size of the dataset for PCBs, PBDEs or OCPs did not allow such a distinction for the presentation of their data. BCFs for PCBs were grouped in one synthetic table (Table 14) for both groups of animals. Nevertheless, the mention of the animal type and the duration allowed the comparison of BCFs between tissues or between congeners. Finally, sparser data of PBDEs (2 studies) and OCPs (3 studies) were simply listed by tissues and by congeners in a synthetic table (respectively 15 and 16). By the way, the analysis of PBDEs was restricted by numerous tissue concentrations under the LQ.

A statistical comparison of BCFs appeared irrelevant due to the differences between the grouped studies, especially on exposure duration and doses. Therefore, the comparisons were built on the

hierarchy of the distribution within a given study on the one hand between the different congeners and on the other hand between the different tissues to generalize pathways of bioconcentration mechanisms.

3. Results

3.1 Transfer into milk and eggs (TRs)

3.1.1 PCDD/Fs

The TRs of PCDD/F congeners (means and standard deviations) into milk and eggs were presented together with the associated transfer levels, their toxicity (TEF) as well as their chemical characteristics Cl_n , $\log K_{ow}$ and MW in Table 10.

Generally, all studied PCDD/Fs congeners were transferred to milk or eggs at a very variable degree. Unfortunately, the most toxic compounds (i.e. TCDD and 1,2,3,7,8-PeCDD) showed the highest transfer to these food products with over 26% and over 35% for milk and eggs respectively (Table 10).

Table 10 - Transfer of PCDD/Fs in milk and eggs expressed as TR (mean and SD) and transfer level, depending on the congener, its chemical characteristics (number of chlorines (Cl_n), Log of the partition coefficient octanol/water ($\log K_{ow}$), molecular weight (MW)) and Toxic Equivalency Factors (TEF).

Compound	TEF (WHO ₀₅)	Chemical characteristics			Transfer to milk		Transfer to chicken eggs		Transfer to duck eggs TR ⁵ , %
		Cl_n	$\log K_{ow}$ ¹	MW	TR ² , % (n=8)	Level ³	TR ⁴ , % (n=4)	Level	
2,3,7,8-TCDD	1.0	4	6.6	322	34.0 ± 6.3	H	39.1 ± 12.6	H	2.0
1,2,3,7,8 -PeCDD	1.0	5	7.2	340	26.7 ± 7.1	H	35.8 ± 12.2	H	3.4
1,2,3,4,7,8-HxCDD	0.1	6	7.6	391	17.8 ± 8.0	M	43.3 ± 16.5	H	2.3
1,2,3,6,7,8-HxCDD	0.1	6	7.6	391	22.7 ± 7.1	M	40.6 ± 14.4	H	3.0
1,2,3,7,8,9-HxCDD	0.1	6	7.6	391	13.2 ± 3.4	M	29.1 ± 12.4	H	1.3
1,2,3,4,6,7,8-HpCDD	0.01	7	8.0	425	4.1 ± 1.3	L	16.2 ± 6.2	M	1.1
OCDD	0.0003	8	8.4	460	1.2 ± 0.8	L	6.8 ± 4.8	L	1.0
2,3,7,8-TCDF	0.1	4	6.5	306	3.4 ± 2.9	L	39.1 ± 16.8	H	6.4
1,2,3,7,8-PeCDF	0.03	5	7.0	340	4.9 ± 4.5	L	38.0 ± 7.4	H	4.5
2,3,4,7,8-PeCDF	0.3	5	7.1	340	35.6 ± 14.8	H	40.0 ± 10.1	H	4.8
1,2,3,4,7,8-HxCDF	0.1	6	7.5	375	19.3 ± 8.9	M	39.8 ± 13.0	H	2.5
1,2,3,6,7,8-HxCDF	0.1	6	7.6	375	17.7 ± 6.0	M	37.3 ± 16.1	H	2.4
1,2,3,7,8,9-HxCDF	0.1	6	7.7	375	10.7 ± 7.0	M	25.6 ± 13.0	H	1.9
2,3,4,6,7,8-HxCDF	0.1	6	7.6	375	11.6 ± 8.7	M	23.0 ± 16.5	M	0.8
1,2,3,4,6,7,8-HpCDF	0.01	7	8.0	409	3.1 ± 1.1	L	16.6 ± 10.7	M	0.7
1,2,3,4,7,8,9-HpCDF	0.01	7	8.2	409	4.6 ± 1.3	L	17.8 ± 8.7	M	1.1
OCDF	0.0003	8	8.6	443	1.0 ± 1.3	L	4.0 ± 2.5	L	0.1

¹ $\log K_{ow}$ for PCDDs and PCDFs were taken from Chen et al., 2001 and Covers & Krop, 1998 respectively.

² Means and SD of TRs to milk were calculated using the data reported in studies Costera et al., 2006; Diletti et al., 2014; Fries G., 1999; Fries G. et al., 2002; Lorenzi et al., 2020; Malisch R., 2000; Mclachlan M. & Richter W., 1998; Schuler et al., 1997.

³ Level: H- high (bold), M- medium, L-low

⁴ Means and SD of TRs to eggs were calculated using the data of the 2 treatments reported by Hoogenboom et al., 2006; Petreas et al., 1991; Pirard & de Pauw, 2005, 2006.

⁵ Transfer to duck eggs based on Shih et al., 2009, level of transfer is low for all congeners.

Generally, all studied PCDD/Fs congeners were transferred to milk or eggs at a very variable degree. Unfortunately, the most toxic compounds (i.e. TCDD and 1,2,3,7,8-PeCDD) showed the highest transfer to these food products with over 26% and over 35% for milk and eggs respectively (Table 10). Hexachlorinated dioxins had a medium transfer level to milk (13-23%) but were highly transferred to eggs (29-43%). Hepta- and octachlorinated dioxins were generally transferred at a low level, but always less in milk (<4%) than in eggs (7-16%) (Table 10). Also, for PCDFs, transfer to eggs is generally higher than to milk. Tetra- and pentachlorinated furans had highest TR levels in eggs (i.e. 38%-40%) but not in milk where only 2,3,4,7,8-PeCDF had a TRs of over 35%. Nevertheless, this pentachlorinated furan was transferred very differently to milk depending on studies resulting in an important SD (Table 10). As for dioxins, hexachlorinated furans showed medium TRs to milk (11-19%) in contrast to systematic high transfer levels to egg (23-40%).

3.1.2 Polychlorinated biphenyls

TRs (means and SD) and transfer levels (high, medium and low) in Table 11 together with their characteristics: TEF (WHO05), Cl_n, log K_{ow}, substitution type and MW.

The transfer levels to eggs were classified generally as high except the di-ortho congeners 52 and 101. Except these latest, all congeners were transferred at over 30% to eggs and reached the highest TRs of 74 or 80% respectively for the PCBs 123 and 167. The analysis of transfer to milk was built on a quite solid dataset of, depending on the congener, three to six studies (Table 11) even if some TRs to milk were associated to high SD. This generally reflect a study effect and therefore warrants a cautious generalization (for ex. congeners 28, 52, 77,105 and 118). Except PCB 123, the most lipophilic congeners (i.e. log K_{ow} > 6.5) presented high TRs to milk of over 40% (Table 11). By the way, low or medium transferred congeners were characterised by lower MW and number of chlorination, again except PCB 123.

Nine out of 12 dioxin-like PCBs were classified as highly transferred in both food products. A special attention should be paid to the congeners presenting the highest TEFs: 126 and 169, which

appeared to be highly transferred to milk and eggs with average TRs of respectively 39% and 40%. Two dioxin-like, non-ortho congeners (77 and 81) showed high transfer levels in the egg study (>30%) but much lower transfer to milk (<13%) (Table 11). Only two non-dioxin like congeners (52 and 101) presented generally low transfer levels to milk and eggs (around 5%).

Table 11 - Transfer of PCBs in milk and eggs expressed as TR (mean and SD) and transfer level, depending on the congener, its Toxic Equivalency Factors (TEF) and its chemical characteristics number of chlorines (Cl_n), Log of the partition coefficient octanol/water (log K_{ow}), molecular weight (MW) and the substitution.

PCB No	TEF (WHO ₀₅)	Chemical characteristics				Transfer to milk			Transfer to hen eggs		
		Cl _n	Log K _{ow} ¹	MW	Substitution type	TR ² , %	level	n	TR ³ , %	level	n
28	nd	3	5.6	257	mono-ortho	9.4 ± 12.8	medium	7	40.5 ± 3.5	high	2
52	nd	3	5.8	292	di-ortho	3.8 ± 5.4	low	6	4.5 ± 0.7	low	2
77	0.0001	4	6.4	292	non-ortho	5.5 ± 4.3	low	7	32.6 ± 25.9	high	3
81	0.0003	4	6.4	292	non-ortho	12.5 ± 6.0	medium	6	30.2 ± 17.8	high	3
101	nd	5	6.3	326	di-ortho	4.8 ± 1.3	low	6	5.0	low	2
105	0.00003	5	6.6	326	mono-ortho	50.0 ± 33.4	high	4	49.0 ± 4.2	high	2
114	0.00003	5	6.6	326	mono-ortho	51.8 ± 16.2	high	6	51.5 ± 0.7	high	2
118	0.00003	5	6.7	326	mono-ortho	77.8 ± 45.1	high	5	50.0 ± 2.8	high	2
123	0.00003	5	6.7	326	mono-ortho	22.2 ± 10.6	medium	6	74.0 ± 5.7	high	2
126	0.1	5	7.0	326	non-ortho	40.2 ± 11.4	high	5	37.7 ± 19.6	high	3
138	nd	6	6.7	361	di-ortho	46.1 ± 19.0	high	6	52.5 ± 2.1	high	2
153	nd	6	6.8	361	di-ortho	54.1 ± 25.1	high	4	59.0 ± 2.8	high	2
156	0.00003	6	7.1	361	mono-ortho	64.1 ± 26.3	high	3	56.5 ± 2.1	high	2
157	0.00003	6	7.1	361	mono-ortho	50.5 ± 21.5	high	3	58.0 ± 9.9	high	2
167	0.00003	6	7.2	361	mono-ortho	58.1 ± 25.3	high	3	80.0 ± 5.7	high	2
169	0.03	6	7.5	361	non-ortho	40.3 ± 8.0	high	4	39.5 ± 19.9	high	3
180	nd	7	7.2	395	di-ortho	51.8 ± 17.7	high	3	50.0 ± 12.7	high	2
189	0.00003	7	7.6	395	mono-ortho	38.0 ± 23.2	high	3	61.0	high	2

Bold mean high TRs

¹ Log K_{ow} taken from Zhou et al., 2005.

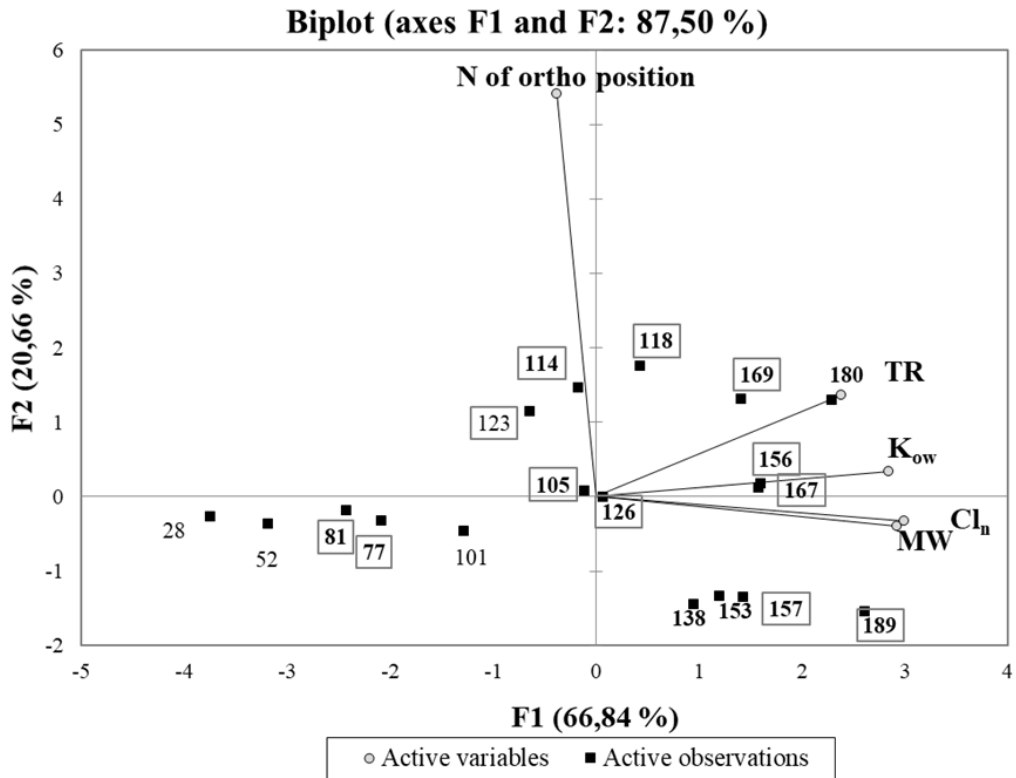
² Means and SD of TRs to milk were calculated using the data reported in studies (Costera et al., 2006; Diletti et al., 2014; Hoogenboom et al., 2015a; Kerst et al., 2004; Lorenzi et al., 2020; Ounnas et al., 2010b; Thomas et al., 1999).

³ Means and SD of TRs to

The PCA of the transfer of PCBs in milk (Figure 23A) and eggs (Figure 23B) confirmed the relationship of the transfer degree to the chemical characteristics of the congener. The first axis (F1) was mainly composed by MW, number of chlorination and lipophilicity (i.e. log K_{ow}) explained 57.3% and 70.7% of the variation of TRs respectively to milk and eggs. The second axis (F2) was represented by the substitution type and explained 20.1% and 24.7% of TR variations respectively for milk and eggs. Indeed, the first two axes of PCA explained much better the variability of the transfer into eggs (95%) than this of the transfer into milk (77%). This analysis fitted generally well for 13 out of 18 congeners except PCB 28, PCB 52, PCB 77, PCB 81 and PCB 169. Pearson's correlation coefficient of MW (0.640 and 0.520), log K_{ow} (0.618 and 0.578) and number of chlorine atoms (0.660 and 0.586) were significantly (P < 0.05) correlated with TRs into milk and eggs, respectively. Contrarily, the correlation between the TRs and the position of the ortho substitutions was not significant with Pearson's coefficient of only 0.058 and -0.048

respectively for milk and eggs (Figure 23A and Figure 23B).

A



B

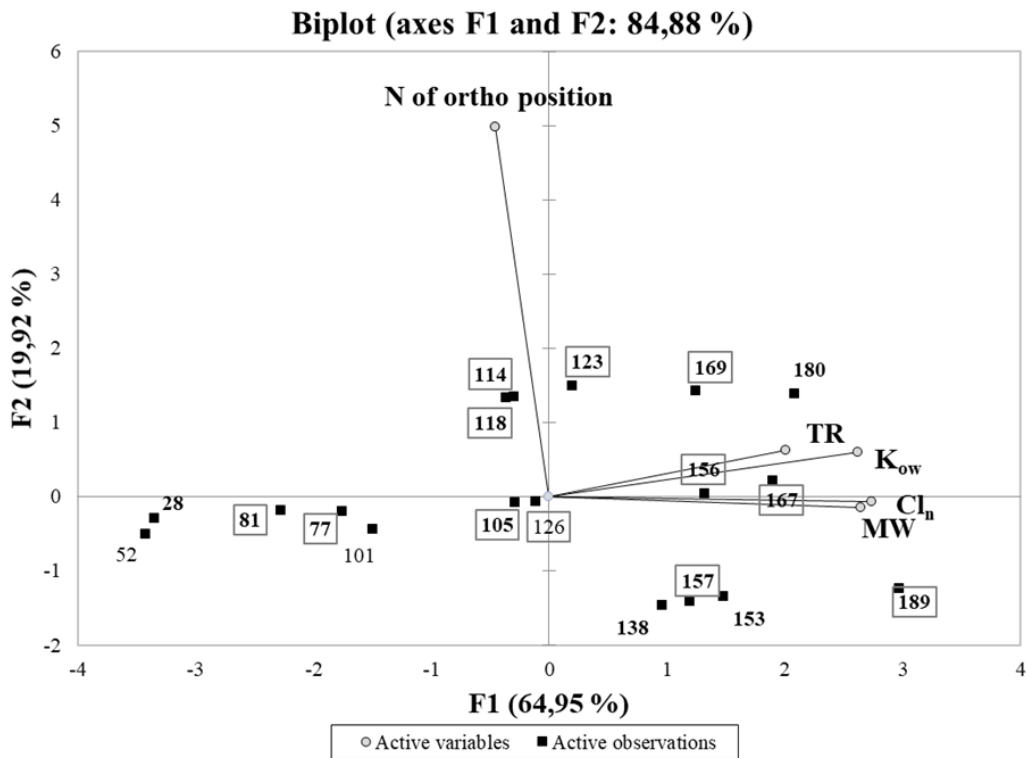


Figure 23 - Factorial plan (F1, F2) of PCA applied on mean TRs of PCBs for milk (A) and eggs (B), chlorine substitution at none, mono and di-ortho position, number of chlorines (Cl_n), molecular weight (M.W), n-Octanol/Water Partition Coefficient (K_{ow}). Indication: Numbers

correspond to the PCB isomers. Framed congeners are dioxin-like PCBs. Bold PCBs are the high excreted congeners with the ranges 40-78% and 41-80% for milk and eggs respectively.

3.2 Transfer to tissues (BCFs)

3.2.1 PCDD/Fs

BCFs of PCDD/Fs in different tissues were presented separately for excreting adult animals (Table 12, six studies) and rapidly growing animals (Table 13, four studies) and indicated by the shades of grey the four bioconcentration degrees (as described previously).

Despite the difficulties to compare the data of both tables (i.e. differences between the types of animals and their metabolism), bioconcentration in adult animals (Table 12) seemed higher than in rapidly growing animals (Table 13). This tendency appeared especially when BCFs in liver, fat and muscles were compared. The short time study on adults (Traag et al., 2006 in Table 12) showed clearly lower BCFs contrarily to the short time study on rapidly growing animals (Hoogenboom et al., 2004 in Table 13) whose BCFs did not really stand out in comparison to the chronic exposure studies. In addition, the highest BCFs of PCDD/Fs were extracted from studies with a field exposure. As previously observed for TRs to excretion products, BCFs in liver and kidney of birds (i.e. hens) seemed higher than in (dairy) cows, even if few data issued from very different studies incite to compare these data very carefully.

Generally, PCDDs were bioconcentrated in all studied tissues of excreting adult animals but to a very variable extent. Therefore, it seemed difficult to establish a clear hierarchy between tissues, even if BCFs in liver seemed slightly higher (except the short time study) and muscles had a slight tendency of lower BCFs (Table 12). These large variations seemed to reflect a study effect. The bioconcentration of furans in the studied tissues looks similar. The comparison of the BCFs of the different congeners does not indicate clear differences. Indeed, the hierarchical order of congeners seemed to change from one study to another, and the lower TRs reported for hepta- and octachlorinated PCDD/Fs were not clearly confirmed for the BCFs.

In rapidly growing animals (Table 13) notable BCFs were reported only in liver and did hardly exceed 1 in the other tissues (different fats and muscles). Unfortunately, several tissues were confounded with an effect of studies and even of species but bioconcentration in fat (abdominal and kidney) seemed to vary around 1 and dropped under 1 (i.e. no clear bioconcentration) in different muscles (Table 13). In these animals, BCFs of hepta- and octachlorinated congeners were lower than in less chlorinated ones, especially hexachlorinated PCDD/Fs (Table 13).

Table 12 - BCFs of PCDD/Fs of different tissues in milk-egg producing animals derived from literature and classified in hierarchical order. Colors signification: dark grey – high level of BCF (over 25), grey – medium level of BCF (over 10 to 25), light grey – low level of BCF (overpass 1 and lower 10), white – no bioconcentration (BCF<1).

Tissue	Study ¹	Exposure (days)	PCDDs							PCDFs									
			2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9 - HxCDD	1,2,3,4,6,7,8 - HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8 - PeCDF	2,3,4,7,8 - PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF
Liver	A (hens)	Field	20	45	74	106	113	134	34	32	36	87	14	18	0.3	90	21	10	28
	B (hens)	54	43	36	72	85	41	52	36	27	25	35	80	57	54	40	29	32	LQ
	C(hens)	98	LQ	9	6	6	4	1	0.3	13	10	9	5	4	2	4	1	1	LQ
	D (hens)	7	LQ	1	2	10	9	8	33	0.3	0.2	0.4	1	1	LQ	LQ	2	2	20
	F (cows)	27	11	20	29	20	9	11	3	1	1	103	43	49	LQ	43	19	21	3
Ovary	A (hens)	Field	6	23	56	82	78	48	10	19	13	29	21	25	21	25	9	LQ	LQ
Serum	B (hens)	54	24	36	26	29	18	7	73	6	12	38	8	14	0.7	36	13	5	10
Abdominal fat	A (hens)	Field	8	27	28	43	38	13	2	7	11	38	4	7	1	16	4	2	2
	B (hens)	54	20	19	17	16	8	4	LQ	15	10	32	15	15	13	10	3	5	LQ
	C(hens)	98	n.d.	9	7	7	4	1	n.d.	13	10	9	5	5	2	3	0.4	1	n.d.
	D (hens)	7	2	1	1	LQ	LQ	0.1	0.2	2	1	1	1	1	LQ	0.5	0.1	0.2	0.1
Kidney	B (hens)	54	24	25	22	16	11	7	11	20	11	21	19	18	16	12	6	6	LQ
	F (cows)	27	2	2	2	2	0.4	0.2	0.04	0.1	0.1	2	1	1	LQ	0.4	0.1	0.1	0.01
Heart	B (hens)	54	21	18	16	14	8	2	LQ	13	8	16	10	11	11	8	2	4	LQ
Muscles	A (hens)	Field	5	14	11	40	28	12	3	6	15	33	4	6	1	11	4	2	4
	B (hens)	54	18	17	15	11	6	2	LQ	13	9	14	10	11	9	8	2	3	LQ
	C (hens)	98	LQ	9	7	6	4	3	3	11	8	7	4	3	1	2	1	1	1
	E (ducks)	41	19	12	5	6	1	0.4	0.4	30	7	11	2	2	1	1	LQ	1	LQ
Meat	F (cows)	27	2	2	1	1	LQ	0.1	0.03	LQ	LQ	1	0.5	0.4	LQ	0.3	0.1	LQ	LQ

¹ 1 – studies: **Study A** - Piskorska-Pliszczynska et al., 2014, **study B** - Pirard & de Pauw, 2005, **study C** - Pirard & de Pauw, 2006, **study D** - Traag et al., 2006, **study E** - Shih et al., 2009 (laying ducks), **study F**- Huwe & Smith, 2005 (dairy cows).

LQ – values lower than limit of quantification. All BCFs in tissues on lipid weight basis

Table 13 - BCFs of PCDD/Fs of different tissues in meat producing animals derived from literature and classified in hierarchical order. Colors signification: dark grey – high level of BCF (over 25), grey – medium level of BCF (over 10 to 25), light grey – low level of BCF (overpass 1 and lower 10), white – no bioconcentration (BCF<1).

Tissue	Study ¹	Exposure (days)	PCDDs						PCDFs										
			2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF
Liver	A (lamb)	113	11	20	29	20	9	11	3	1	1	103	43	49	LQ	43	19	21	3
	B (broilers)	39	21	14	16	14	16	13	5	17	15	13	18	16	14	16	7	10	2
Abdominal fat	C (broilers)	7	3	2	2	3	1	LQ	1	2	2	2	1	1	LQ	1	0.3	0.4	LQ
	C (pigs)	7	1	1	1	1	0.3	1	1	0.1	LQ	1	1	1	LQ	0.3	0.4	0.2	LQ
Kidney fat	A (lamb)	113	2	2	2	2	0.4	0.2	0.04	0.1	0.1	2	1	1	LQ	0.4	0.1	0.1	0.01
Muscle	A (lamb)	113	2	2	1	1	LQ	0.14	0.03	LQ	LQ	1	0.5	0.4	LQ	0.3	0.1	LQ	LQ
Belly	D (pigs)	126	0.1	0.1	0.2	0.1	0.03	0.2	0.2	0.01	0.005	0.1	0.2	0.1	n.d.	0.1	0.1	0.1	0.01
Fore-end	D (pigs)	126	0.03	0.02	0.05	0.03	n.d.	0.06	0.07	n.d.	0.03	0.04	0.04	0.02	0.03	n.d.	0.03	n.d.	0.01
Loin	D (pigs)	125	0.03	0.03	0.05	0.03	0.01	0.06	0.01	LQ	LQ	0.03	0.05	0.02	n.d.	0.02	0.04	0.02	0.001

¹ Studies: **Study A** - Hoogenboom et al., 2015b, **Study B** - Parera et al., 2008, **Study C** - Hoogenboom et al., 2004, **Study D**- Spitaler et al., 2005

LQ – values lower than limit of quantification.

All BCFs in tissues on lipid weight basis

3.2.2 Polychlorinated biphenyls

Dataset for the bioconcentration of PCBs in different tissues were derived from six studies which differed widely by the type of exposed animals and by the exposure durations (Table 14). Therefore, comparisons and generalizations were complicated despite the interesting size of the dataset.

Mainly low BCFs (i.e. <10) have been shown in short time studies (Hoogenboom et al., 2004; Traag W. et al., 2006) or studies on excreting adult animals (Huwe & Smith, 2005; Ounnas et al., 2010; Pirard & de Pauw, 2005). Only chronic exposure study on growing sheep (Hoogenboom et al., 2015b) reported medium or high BCFs in liver and in abdominal fat (Table 14).

The hierarchy between PCB congeners within a same tissue of a given study seemed clearer: The strongest bioconcentration was shown for congener 126, but also for some higher congeners (i.e. more chlorinated and more lipophilic) 138, 153, 156, 157, 169 and 180. Low but significant bioconcentration (i.e. BCFs up to 10) was revealed for a second group of congeners (77, 81, 105, 118 and probably 123). Finally, no or only low bioconcentrations (BCFs ≤ 1) were revealed for PCBs 28, 52, 101, 114, and 189. The chronic exposure study on growing lambs (Hoogenboom et al., 2015) reported another interesting result: no ($<LOQ$) or very low bioconcentration were observed for PCBs 28, 52, 77, 81, 101, 114, and 123 in liver and fat, whereas medium to high BCFs were found for congeners 126 and 138 only in liver, but for PCBs 153, 156, 157, 167, 169 and 180 in both tissues.

Table 14 - BCFs of PCBs of different tissues in food producing animals derived from literature and classified in hierarchical order. Colors signification: dark grey – high level of BCF (over 25), grey – medium level of BCF (over 10 to 25), light grey – low level of BCF (overpass 1 and lower 10), white – no bioconcentration (BCF<1).

Tissue	Study ¹	Exposure (days)	PCB congener																	
			28	52	77	81	101	105	114	118	123	126	138	153	156	157	167	169	180	189
Liver	A (hens)	54			2	3					8						7			
	B (hens)	7		0	0.2	0.2	0	0	0	0	0.4	0	0	0	0	0	1	0	0	
	C (cows)	17-38								21							5			
	D (goats)	80			1			3		3	3	23	10		4	5	5			
	E (sheep)	113	1	LQ	0.1	5	0.4	6	LQ	4	LQ	46	27	62	9	15	4	26	25	LQ
Serum	A (hens)	54			2	8					15								16	
Abdominal fat	A (hens)	54			1	4					11								10	
	B (hens)	7	0.5	0.2	2	2	0.4	1	1	1	2	2	2	1	1	1	1	1	2	1
	D (goats)	80			0.4			3		6	1	4	4		6	6	7			
	E (lamb)	113	1	LQ	0.1	1	0.3	5	LQ	4	LQ	2	3	16	14	18	4	13	14	LQ
	F (broilers)	7	1	1	2	3	1	3	2	2	4	2	2	2	3	3	3	3	2	2
	F (pigs)	7	0.2	1	0.1		1	1	1	1		1	1	1	1	1	1	1	1	1
Muscle	A (hens)	54			6	10					10								11	
	E (lamb)	113	1	LQ	0.2	1	LQ	3	LQ	3	LQ	2	2	8	8	11	3	8	7	LQ
Heart	A (hens)	54			2	4					6								7	
Kidney	A (hens)	54			3	4					8								8	

¹ Studies: Study A - Pirard and De Pauw 2005; Study B - Traag et al.,2006; Study C - Huwe et al.,2005; Study D- Ounnas et al., 2010; Study E – Hoogenboom et al., 2015 (b); Study F - Hoogenboom et al.,2004;.

LQ – values lower than limit of quantification.

All BCFs in tissues on lipid weight basis

3.2.3 Polybrominated diphenyl ethers (PBDEs)

Bioconcentration factors of PBDEs were derived from studies on lactating cows (Kierkegaard et al., 2009) or lactating goats (Ounnas et al., 2010) and presented in Table 15. Generally, bioconcentration of PBDEs seemed limited and never exceed 10. Moreover, several congeners (BDE 28, 49, 66 and 85) were not bioconcentrated and only BDEs 47, 153 and 154 reached a notable but low level of BCFs of 6-7 (Table 15). As previously noted for PCBs, the BCFs of PBDEs also increased with the lipophilicity (i.e. log K_{ow}) of the congeners.

Table 15 - Comparison of bromination (Br_n), molecular weight (MW), Log of partition coefficient octanol-water (Log K_{ow}) and bioconcentration factors of PBDEs of different tissues in cows (A) and goats (B). Colors signification: dark grey – high level of BCF (over 25), grey – medium level of BCF (over 10 to 25), light grey – low level of BCF (overpass 1 and lower 10), white – no bioconcentration (BCF<1).

Study ¹	Chemical characteristics			Tissues					
	MW	Br_n	Log k_{ow} ²	Liver		Heart	Fat		Kidney
				A	B	A	A	B	A
BDE 28	407	3	5.9	1		1	1		0.4
BDE 47	486	4	6.8	9	5	6	5	2	2
BDE 49	486	4	6.3	LQ		LQ	0.4		LQ
BDE 66	486	4	6.3	LQ		LQ	1		LQ
BDE 85	565	5	7.4	LQ		LQ	2		LQ
BDE 99	565	5	7.3	4	3	4	4	2	LQ
BDE 100	565	5	7.2	LQ		LQ	6		LQ
BDE 153	644	6	7.9	5		6	10		3
BDE 154	644	6	7.8	9		6	7		5

¹ Study A - Kierkegaard et al. 2009, study B - Ounnas et al. 2010

² Log k_{ow} derived from Braekevelt et al. 2003 except for BDEs 49 and 66 which were derived from [Kierkegaard et al. 2007](#).

LQ – values lower than limit of quantification.³ All BCFs in tissues on lipid weight basis

3.2.4 Organochlorinated pesticides (OCPs)

Bioconcentrations of dichlorodiphenyltrichloroethane (DDT) and its metabolites as well as hexachlorocyclohexane (HCH) isomers in edible chicken tissues (Aulakh et al., 2006; Tao et al., 2009) and in yak tissues (Pan et al., 2014) were presented in Table 16.

BCFs of DDT ranked up to 50. Indeed, one of the most persistent organochlorine pesticide p,p'-DDT demonstrated high BCFs in all studied chicken tissues: stomach (50), skin (36), liver (18) and muscle (17). However, even the DDT metabolites DDD and DDE presented low to medium levels of bioconcentration (Table 16). Values from the study on lactating yaks were very low (<1). It is not clear if this study effect can be attributed to this specie or the experimental conditions.

Similar results were obtained for HCHs which bioconcentration ranked from low to high depending on the congener and the considered tissue. Bioconcentration was highest for β -HCH (between 3 and 34). In contrast, accumulation of γ -HCH (i.e. lindane) seemed limited with BCFs, which did not overpass 3 in all studied tissues. Except γ -HCH, BCFs in liver were clearly higher than in the gizzard, in which the three other isomers were more bioconcentrated than in skin and muscle. Contrarily, bioconcentration of γ -HCH varied few between the studied tissues (Table 16).

Recalculated TRs of DDT to eggs seemed to indicate high transfer of both OCPs as previously stated for PCDD/Fs and PCBs.

Table 16 - Bioconcentration factors of DDT and HCH isomers in different tissues of chicken (1: Tao et al. 2009; 2:Auklakh et al. 2006) or yak (Pan et al 2014). Colors signification: dark grey – high level of BCF (over 25), grey – medium level of BCF (over 10 to 25), light grey – low level of BCF (overpass 1 and lower 10), white – no bioconcentration (BCF<1).

Compound	stomach (gizzard)		liver			skin		muscle		eggs TR 2
	Chicken 1	Chicken 1	yak	Chicken 1	Chicken 1	Chicken 2	yak			
DDT and its metabolites										
p,p'-DDT	50	18	0.3	36	17	1.5	0.5	14		
o,p'-DDT	10	24	na	6	6	nd	na	15		
p,p'-DDE	14	5	0.5	4	6	7	0.4	58		
o,p'-DDE	5	20	na	6	5	3	na	35		
p,p'-DDD	14	9	nd	5	4	2	nd	54		
o,p'-DDD	10	11	na	13	5	2	na	19		
HCH isomers										
α -HCH	5	21	0.3	5	2	0.3	0.3	6		
β -HCH	21	34	28	12	12	3	2.2	32		
γ -HCH	3	2	0.5	3	2	1	0.9	22		
δ -HCH	2	8	na	1	1	nd	na			

na: not analysed

nd: not detected

All BCFs in tissues on lipid weight basis

4. Discussion

4.1 Methodological considerations of the concepts of TR and BCF

TRs and BCFs are both valuable concepts to describe contaminant transfer into food products. Nevertheless, their meaningfulness is conditioned by several parameters. The main limit in transfer studies of POPs in vivo consists in the completion of steady state. Firstly, this commonly accepted condition (see also Material and Methods) was difficult to calculate accurately as the preciseness of modeled curves depends on the number and spacing of the experimental points. Besides the aspect of costs of numerous analysis, any approximation in the measurement of very low concentrations of POPs in the studied tissue would considerably increase the confidence interval around the asymptote of the logarithmic enrichment curve. Therefore, numerous authors calculated

the necessary time of exposure via the half-life of the target compound but experiments were generally based on a group of congeners whereas the half-life can vary considerably between the different congeners of the same family. Indeed, half-lives have been estimated for PCDD/Fs at several weeks (7 weeks) in laying hens (Traag et al., 2004) and cows (50 days) (Firestone et al., 1979b). Olling et al. (1991) estimated half-life for PCDD/Fs ranging from 40 ± 7.7 days for 2,3,7,8-TCDD to 34 ± 13 days for 1,2,3,4,6,7,8-HpCD. PCBs presented also different half-lives according to their chlorination: half-life of PCB 101 in lactating goats were reported at <4 days whereas PCB 180 showed half-life greater than 8 days (Fournier et al., 2013). Sum of PBDEs presented half-lives of 58 days in dairy cows (Fries and Marrow, 1975). Half-life of DDT in egg yolk was estimated to be of 7.6 days (Furusawa and Morita, 2001). Finally, the half-life time should be compatible with the life expectancy of the studied animal: easy to respect for animals such as laying hens (around 1 year), goats and cows (approximately 5 years), but very complicated in chicken which are generally farmed only 2 months for producing meat. Thus, the determination of the minimal exposure time will be always a subjective compromise but should target to approach as good as possible the steady state conditions in the studied animal. This motivated our initial condition to require an exposure time of around 50 days when PCDD/Fs were studied in long life cattle but accepted quite shorter exposure times for PCBs. The achievement of steady state seems impossible when tissue enrichment was studied, i.e. BCF approaches. In rapidly growing animals, the tissue enrichment by the compound intake would be permanently diluted by the body mass gain. In adults with more or less stable body weight, excretions like milk or eggs would at least slow down the achievement of steady state. Therefore, the comparison of bioconcentration between different studies, using different animals with different metabolic status, seems too difficult. Bioconcentration hierarchy can be drawn out between congeners or tissues within the same study (same exposure dose and duration, same animals) and then, these hierarchic orders between congeners or tissues can be compared. Another aspect, especially for BCFs, consisted in the comparison to the concentration in the intake matrix, generally feed. Nevertheless, it is possible that other ingested matrices as soil, water or contaminated vegetable cover would also be contaminated and leading to an underestimation of the real exposure concentration. Finally, the statistical power depends on the number of available data. Indeed, the analysis of the PCDD/Fs transfer to milk built on 8 studies seems quite solid contrarily to the OCP transfer where the small number of data makes it rather a first exploratory approach.

Accepting these minimal requirements, the concepts of TRs and BCFs are very useful to hierarchize the extent of transfer between different tissues or also between different compounds. Such a ranking is very useful to give recommendations in risk assessments. Indeed, full interdiction

of any food produced in contaminated areas makes local people completely dependent from importations while targeting only the most hazardous tissues of the contaminated animals would allow reducing significantly the consumer's exposure but maintaining local food supply.

4.2 Transfer mechanisms

Transfer of POPs to organs and excreted product results from a succession of physiological steps: Absorption, Metabolization, Distribution and Excretion.

Absorption is driven by (i) the physiological characteristics i.e. the animal species and (ii) the chemicals properties of the molecule. Absorption of POPs is the first key process determining the transfer of persistent compounds to livestock. Studied compounds were mainly absorbed in the intestine by crossing the epithelium wall, most of the studied compounds by a transcellular route (entering the intestinal epithelial cell by crossing the plasma membrane) (Kelly et al., 2004; Sanford, 1992). From a mechanistically point of view, lipophilic compounds are mostly transported in micelles formed by excreted bile salts and lipids present in the chyme (Kelly et al., 2004). These micelles containing lipophilic POPs, crossed an aqueous thin layer covering the intestinal wall, conceptualized and referred as the Unstirred Water Layer, before crossing intestinal epithelium cells (Kelly et al., 2004) and subsequently reaching blood or lymph streams. As these mechanisms involved aqueous phase and amphiphilic micelles, lipophilicity appears as a key characteristic explaining this absorption efficiency (Drouillard and Norstrom, 2003; Kelly et al., 2004; McLachlan, 1993). For different species like dairy cows (McLachlan, 1993) and birds (Drouillard & Norstrom, 2003), this efficiency is higher for medium lipophilic molecules and decrease after a threshold value of the partition coefficient K_{ow} . This threshold and the extent of the reduction appears to be species-dependent (Kelly et al., 2004). In birds, models illustrate a very high absorption efficiency (close to 100%) of ingested dose until a log of K_{ow} of 8.0, then a slow reduction of efficiency appears for higher K_{ow} mainly explained by the ultimate Unstirred Water Layer. Indeed, this aqueous layer constitutes a physical limitation to solubilization of the most lipophilic compounds. Concerning dairy cow, and due to its particular polygastric digestive system, absorption efficiency of lipids is lower (80%) and the efficiency threshold is attained for lower K_{ow} (7.0) (McLachlan, 1993). Then a drastic reduction of absorption efficiency occurs for more lipophilic compounds: absorption efficiency is lower than 35% for molecules displaying K_{ow} of 8.0 (McLachlan, 1993). These elements are in line with the present results for highly chlorinated dioxins: TRs and BCFs displaying lower values than less lipophilic compounds of the same chemical family. In addition, a greater transfer reduction was obtained in milk compared to eggs,

highlighting the potential difference of absorption between species for the highest lipophilic compound, especially for PCDD/Fs.

Metabolization of molecules can take place in distinct phases: in the intestinal lumen, in the liver, in the endothelial cells of blood vessels and in the deposition organs. The hepatic metabolism was the most investigated path of biotransformation of the studied compounds. The BCFs in liver were globally higher than in other organs which may result from a high first pass effect (i.e. xenobiotic metabolism occurring after absorption and before the reach of systemic circulation) for these molecules or a specific sites of binding notably enzyme binding (Ohtake et al., 2007). If few data were obtained for reared animals such as dairy cows, laying hens or chickens, some studies highlighted the specific role of monooxygenase enzymes cytochrome (like CYP1A2 and CYP1A1) and AhR (aryl hydrocarbon receptor) which could explain these high concentrations in the liver (Casarett and Doull, 2008; Kuroki et al., 1986). It should also be noticed that the metabolization rate was found or suspected low for the majority of studied compounds: as shown for PCDD/Fs (Adolphs et al., 2013), PBDEs (Kohli et al., 1978), PCBs (Lutz et al., 1977; Matthews and Dedrick, 2003), DDTs (Casarett and Doull, 2008). Congeners within each POP family present distinct metabolization rates as proven for PCBs for which substitution appeared as a main factor of variation (McLachlan, 1993). However, HCH metabolization appears extensive (ATSDR, 2005) which seems in line with the reduced levels of BCFs found in chicken muscles compared to hepatic tissues. If few data are available concerning PBDE metabolization, debromination of PBDEs was suspected in dairy cows (Kierkegaard et al., 2007) as it was shown elsewhere in fish (Stapleton et al., 2003) and rats (Mörck et al., 2003) , without a proper demonstration of its existence, extent nor specific mechanism.

The **distribution** of POPs to organs is realized through blood. Different blood constituents such as lipoproteins (HDL, VLDL, IDL, LDL) and albumins are known to vehicles POPs (Casarett and Doull, 2008; Delannoy et al., 2020; Soine et al., 2009). Distribution of these lipophilic POPs result in preferential accumulation of lipophilic POPs in lipid-rich organs. Found results illustrated this fact for the most lipophilic congeners (i.e. $\log K_{ow} > 7.2$) as levels present in muscle tissue, kidneys or heart are generally lower than in adipose tissue, and ovary follicles. Concerning milk and eggs, it is already known that lactating and laying involve a remobilization of POPs from adipose tissue stock to milk and eggs (Fournier et al., 2012; Gobas et al., 2003; Kierkegaard et al., 2007).

Excretion of PCDD/Fs, PCBs, PBDEs, HCH and DDT isomers may be realized through several routes: fecal egestion, bile and urinary excretion represent secondary routes whereas milk and egg

excretion constitute the major ones. The importance of excreted food product in the excretion of lipophilic compounds is related to the co-excretion of fat along egg or milk. This explains that most of Quantitative Structure Activity Relationships model to predict milk and egg excretion implements log of K_{ow} (Gobas et al., 2003). These elements are in line with these data and could illustrate the differences found in terms of BCFs: highest BCF were found for PCDD/Fs, DDT and HCH (highest K_{ow}), then PCB (medium K_{ow}) and the lowest for PBDEs (low K_{ow}).

4.3 Toxicity and implications in food safety

Lipophilic POPs are not only highly transferred to edible products such as milk, eggs, meat and offal, but even more, these food products present higher POPs exposure sources than the animal feed carrying them. In this context, PCDD/Fs appeared as the most problematic compound family regarding, notably, their reprotoxicity and carcinogenic potential along their high potency to transfer in animal food products. Indeed, BCFs higher than 10 and TRs over 33% were found for all congeners except the highest chlorinated ones, also known to be less toxic. HCH isomers present, notably, neurotoxicity, reprotoxicity and hepatotoxicity. Similarly, the most toxic congeners (γ -HCH and β -HCH) appeared also to be the most transferred to food of animal origin (Table 8, ATSDR, 2005). Concerning DDT and its ortho and para metabolites DDE and DDD similar patterns of toxicity were reported by (ATSDR, 2019), notably neurodevelopmental toxicity, reprotoxicity and hepatotoxicity. BCFs over 10 illustrated their potency to bioconcentrate.

Finally, neurotoxicity, reprotoxicity and endocrine disruption were also reported for PBDEs (ATSDR, 2017), with higher toxicity for less brominated compounds. BDE 47 appears to be the most problematic congener in terms of food safety as it is one of the most transferred to food product and presents high toxicity. Health effects associated to PCB exposure in humans and/or animals include hepatic, thyroid, dermal and ocular changes, immunological and neurodevelopmental alterations, reduced birth weight, reproductive toxicity, and cancer (ATSDR, 2000). They present also the highest TRs emphasizing their high potency to be transferred into milk and eggs.

5. Conclusions

The understanding of POP transfer into food of animal origin is a huge field of investigation necessary to ensure food safety and therefore the sustainability of livestock productions. Through the present meta-analysis of many but very different experimental or case studies, a better understanding of the transfer of POPs was attempted. Thus, TRs and BCFs are shown to be valuable tools to describe and assess contaminant's transfer to animals and their subsequent food-

products. They allow to predict maximum POP levels when the exposure context (ingest dose of POPs) is accurately known, and play by consequence a major role in risk assessments dealing with food contaminations. However, to derive them, a careful attention must be paid to the duration of animals exposure in order to reach conditions as close as possible to steady state. For lipophilic elements such as POPs the duration could be challenging and numerous valuable articles could not reach this appropriate length. Nevertheless, selected literature provides helpful insight concerning POPs behavior and to expected levels in edible products. Lipophilicity tend to these POPs to be excreted or accumulated in fatty tissues. Unfortunately, the most toxic POPs (tetra-to hexachlorinated dioxins and furans, highly chlorinated PCBs, especially congener 126, as well as DDT) are highly transferred to the most consumed food products such as eggs, milk, and to a lesser extent also meat. The bioconcentration of these pollutants could threaten the animal rearing system. This risk must be considered in free-range rearing systems and especially when the surrounding environment of the system is contaminated.

PART II: Adsorption of organochlorinated pesticides on different organic sequestrants – adsorption kinetic and adsorption isotherm study

This chapter explored adsorption of OCPs with different hydrophobic natures, on 4 contrasted porous adsorbents (ACs and BCs) and 5 different basic substances of soil organic matter (SOM) in aqueous media using kinetics and isotherm study with emphasis on relationship between adsorption capabilities and physico-chemical properties.

1. Introduction

Organochlorine pesticides (OCPs) are highly toxic synthetic chemicals, which have been classified as persistent organic pollutants (POPs) (Stockholm Convention, 2019). These pesticides have been used due to their effectiveness against pests and insects in agricultural crops up to the 1970s in the agriculture (ATSDR, 2021, 2020, 2019, 2005) but have been withdrawal due to their toxic adverse effects on health such as cancer, but also different disorders of the reproductive, nervous and hormonal systems (Gomaa et al., 2008; X. Jin et al., 2014; X. T. Jin et al., 2014). In addition, OCPs characterized by their high persistency in the environment, especially in soil, as this media is a powerful reservoir of different contaminants. The OCP half-lives in soil varied from 60 days to 15 years (Jayaraj et al., 2016). In this context, soil is a huge storage reservoir for many POPs, and at the same time it's the key element in many food chains as well as its play an important role for water management systems. Therefore, soil could be the main vector for the transfer of POPs to agricultural animals, and, accordingly, to the food products they produce (meat, milk, eggs) (Amutova et al., 2021; MacLachlan and Bhula, 2009; Maervoet et al., 2004; Weber et al., 2018). This pathway is the highest exposure way of human to POPs because of their high persistence in soil and highest bioaccumulation ability, which would create a great health risk for people consuming contaminated food. Therefore, the presence of OCPs in the environment represents a global problem and its transfer appears to be a key physiological mechanism explaining the subsequent contamination of biota, food and, ultimately, humans (Feidt et al., 2021).

A direct impact on this transfer could reduce contamination of the entire food chain. One possible strategy to reduce this transfer of organic contaminants is to sequester it in environmental carrier-matrix (soil or water) using activated carbon (AC) or biochar (BC). Application of carbon-rich mineral materials such as AC or BC has been efficiently used in sequestration of inorganic and

organic pollutants in environmental matrices (Beesley et al., 2011; Delannoy et al., 2020b, 2018; Feidt et al., 2021; Rakowska et al., 2012). This technique is based on adsorption processes and therefore provides retention of the toxic substance rather than its depuration or removal (Cho et al., 2009). The main effect of AC/BC based sequestration strategies is immobilization and reducing of pollutant bioavailability and therefore lowered risk of the transfer (Brändli et al., 2008; Cho et al., 2009). The main properties making these carbon-rich materials efficient and economically achievable for binding POPs are a highly porous structure, elevated carbon contents (up to 90%) on the one hand, and variety of raw materials, its availability and renewability on the other hand.

Therefore, the aim of the study was to investigate an adsorption behavior and physico-chemical properties of several sequestration materials (SMs) which could be a potential candidate to sequester OCPs and being applied as sequestrants in remediation of contaminated soil or water in perspective. The current study explored adsorption of OCPs with different hydrophobic nature, on 4 contrasted porous adsorbents (ACs and BCs) and 5 different basic substances of soil organic matter (SOM) in aqueous media using kinetics and isotherm batch studies with emphasis on relationship between adsorption capabilities and physico-chemical properties.

2. Materials and methods

Nine OCPs with different hydrophobic properties, α -HCH, β -HCH, γ -HCH, δ -HCH (log K_{ow} 3.8-4.1) chlordecone (log K_{ow} 4.5), 2,4-DDD, 4,4-DDE, 4,4-DDD 4,4-DDT (6.5-6.9) were selected to investigate the adsorption behavior of nine adsorbents (AC DARCO, AC Shubarkol, BC oak tree, BC Japanese knotweed, peat, potassium humate, humic acid, fulvic acid and black coal Shoptkol). Assessment of adsorption was based on 2 batch studies:

1) *Adsorption kinetic* study, which allows one to determine the time needed to reach equilibrium between OCPs and adsorbents. This study was performed at Scientific and Research Enterprise Antigen Co (Almaty, Kazakhstan).

2) *Adsorption isotherm* study, which allows determining OCPs adsorption behavior for different SM at equilibrium in constant time and temperature. The current experiment was carried out at UR AFPA (Université de Lorraine, Nancy, France).

2.1 Chemical reagents and other consumables

Analytical standards of OCPs included α -HCH, β -HCH, γ -HCH, δ -HCH, chlordecone (Dr. Ehrenstorfer GmbH, Augsburg, Germany), 2,4'-DDD, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT (Sigma

Aldrich, St Louis, USA) were used in the experiments. In addition, ^{13}C -labeled β -HCH analytical standard (Dr. Ehrenstorfer GmbH, Augsburg, Germany) was used as internal standard.

Organic solvents such as n-hexane, dichloromethane and acetone were GC grade (Sigma Aldrich, St Louis, USA). Magnesium sulphate used as a desiccant was >99% (Sigma Aldrich, St Louis, USA).

Laboratory glassware used throughout the experiment was rinsed with deionized water and calcined in a muffle furnace at 500 ° C for 24.

2.2 Production and acquisition of sequestration materials

Sequestration materials involved two groups of adsorbents:

1) Porous adsorbents: AC DARCO®, AC Shubarkol, BC Japanese knotweed and BC oak tree.

2) Non-porous adsorbents: peat, humic acid, fulvic acid, potassium humate and lignite Shoptkyol.

Activated carbon DARCO® (CAS № 7440-44-0) and humic acid (CAS № 1415-93-6) represented a commercial product purchased from Sigma-Aldrich (St Louis, USA). Peat is also a commercial product of Florentaise Truffaut (Paris, France).

Fulvic acid, potassium humate, AC Shubarkol, and lignite Shoptkyol represented locally produced Kazakhstani adsorbents, which were obtained from the Institute of Coal Chemistry and Technologies (ICCT, Nur-Sultan, Kazakhstan), which specializes in the production of carbonaceous materials. Shoptkyol and AC Shubarkol are samples of brown coal (lignite) from the Kazakhstani deposits "Shoptkyol" (51°17'46" N, 75°47'00" E) and "Shubarkol" (48°58'32" N, 68°47'28" E) that have produced up to 20 million tons per year since the end of the 19th century.

BC Japanese knotweed and BC oak tree were produced by the CarboFrance company (Montiers-sur-Saulx, France). Biochar oak tree (*Quercus ilex*) was integrated in the current list due to its promising results in reducing CLD bioavailability in soil (Yehya, 2017). Japanese knotweed (*Reynoutria japonica*) classified as a pest and invasive species in many countries which are characterized by extremely fast growth and distribution, gaining advantages over native species and threatening entire ecosystems (Cottet et al., 2015). This plant typically has a high biomass yield. Therefore, the collection of this biomass could be an interesting alternative in application as an initial source for BC production and its integration in the sequestration strategy.

2.3 Characterization of sequestration materials

Origin sources, acquisition, and production conditions, as well as adsorption characteristics (BET surface area, total pore volume, elemental composition, functional groups) of studied SMs presented in tables 18-20. The characteristics of AC DARCO and BC Oak tree were derived from available literature and indicated as footnotes in table 18.

Elemental composition of the SMs was tested using X-ray photoelectron spectrometry (XPS) analysis which was performed on a Kratos Axis Ultra (Kratos Analytical, U.K.) in the LCPME laboratory (LCPME, Vandoeuvre-lès-Nancy, France). The spectrometer is equipped with a monochromatic Al K α source (1486.6 eV). All spectra were recorded at a 90° take-off angle, with an analyzed area of about 0.7 × 0.3 mm. Survey spectra were acquired with 1.0 eV step and 160 eV analyzer pass energy. The high-resolution regions were acquired with 0.1 eV step (0.05 eV for O 1s and C 1s) and 20 eV pass energy. A neutralizer was used to perform the recording to compensate charge effects. Curves were fitted using a Gaussian/Lorentzian (70/30) peak shape after Shirley's background subtraction and using CasaXPS software. The carbon C 1s is calibrated at 284.8 eV for C-C and C-H bonds.

Morphological characterization was studied by scanning electron microscope coupled with energy dispersive X-ray (SEM/EDX) was also performed in the LCPME laboratory (LCPME, Vandoeuvre-lès-Nancy, France). Results of SEM analysis presented in Figure 26.

Specific surface areas (SSA) and porosity of studied AC/BCs were determined at the LIEC laboratory (LIEC, Vandœuvre-les-Nancy, France). The measurements were performed based on nitrogen adsorption-desorption volumetry at 77K. Nitrogen adsorption-desorption isotherms were recorded on a Belsorp max II (MicrotracBEL Corp.) which were equipped with a turbomolecular pumping unit which ensures a residual vacuum of 10⁻⁵ Pa. The device is equipped with 4 ports including 3 ports for samples and a reference port. Each sample port has 3 pressure sensors covering different ranges: 133 kPa (1000 Torr), 1.33 kPa (10 Torr), 0.0133 kPa (0.1 Torr).

After outgassing the samples at 30°C during 12 h under a residual vacuum of 10⁻⁵ Pa, nitrogen adsorption-desorption isotherms (i.e., volume of nitrogen adsorbed at 77K vs relative pressure P/P₀, where P is the equilibrium pressure of the adsorbing gas and P₀ is the vapour saturation pressure) were performed using a step-by-step method in the interval of relative pressures, P/P₀, up to 0.98. All experiments were carried out with ultra-pure nitrogen (>99.9995%, supplied by Air Liquide).

The Brunauer-Emmet-Teller (BET) method was used to estimate the SSA, using a 16.3 Å cross-sectional area of nitrogen molecules (Brunauer et al., 1938).

The De Boer method (or t-plot, Lippens and de Boer, 1965) was carried out to determine **microporous volume** and **external surface area**. Micropore filling happens at low and very low relative pressure values, and then includes the domain of the monolayer adsorption on the external surface. To be able to distinguish adsorption onto the external surface from adsorption into the micropores (pore size < Å), the experimental isotherm is compared to a reference curve obtained for a non-porous solid, with chemical features and energetic constant as close as possible to the studied matrix.

2.4 Adsorption of OCPs by sequestration materials

2.4.1 Batch adsorption kinetic and adsorption isotherm study

Preparation of OCPs working solution

For the experiment, each pesticide analytical standard was in powder form. The appropriate masses of each pesticide were weighted and used for the preparation of their mixture with a concentration of 100 mg/L in acetone (OCPs stock solution). This mixture was used for preparation of calibration standards (in n-hexane) for quantification of OCPs in extracts and for preparation of an aqueous working solution for batch adsorption experiments.

The aqueous working solution was prepared by dissolving the OCP stock solution (100 mg/L) in 5 L flask in DI water to achieve a concentration of 50 µg/L for each single congener. The resulting solution was mixed manually for 2-3 min and remained under the fume hood for 24 hours for stabilization.

Kinetic adsorption study

Design of kinetic adsorption experiment shown on Figure 24.

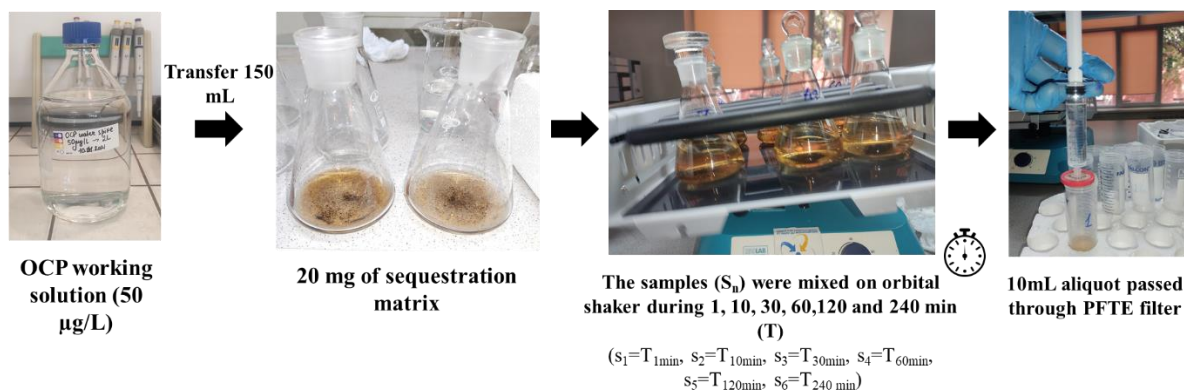


Figure 24 – Design of the kinetic experiment

Twenty mg of sequestration matrix was distributed in six 250 mL flat bottom flasks. Each flask corresponded to a contact time after which collection of aliquots is performed. 150 mL of aqueous working solution from OCPs was added to each flask and closed with a glass cap. The samples were mixed in a 3D orbital shaker (Isolab, Germany) at ambient temperature. Then, aliquot of 10 mL was collected after contact time of 1 min, 10 min, 30 min, 60 min, 120 min and 240 min using 10-mL disposable plastic syringe. The samples were filtered using 0.45µm PFTE syringe filter and collected in 50 mL centrifuge tubes. The filter and syringe were rinsed by 2-3 mL of dichlormetane:hexane (1:1) and combined with the sample.

The control samples of this experiment (without addition of sequestration material) consisted of a working solution of 10 mL of OCP that was transferred to a 50 mL centrifuge tube. All samples were performed in 2 replicates and then extracted and analyzed by GS-MS as described below.

Adsorption isotherm study

Design of the adsorption isotherm experiment is presented in Figure 25.

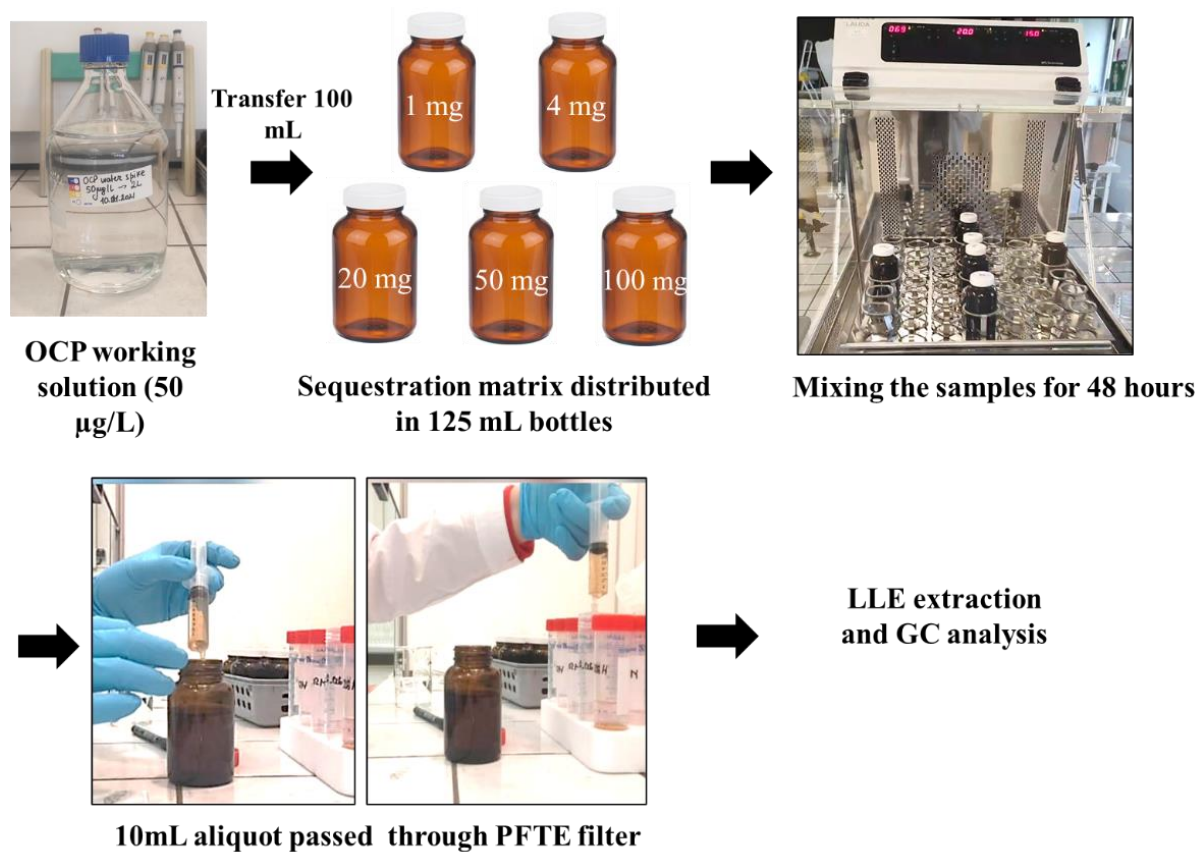


Figure 25 – Design of the study of adsorption equilibrium

Sequestration material with masses of 1, 4, 20, 50, and 100 mg was transferred to five 125 mL amber bottles. Then 100 mL of OCPs working solution was added in each bottle. Samples were incubated for 48 hours at room temperature by stirring (150 rpm) in an incubator with a laboratory shaker VS 150 OI (Lauda, France). Finally, an aliquot of 10 mL was filtered using 0.45µm PFTE syringe filter and collected in 50 mL centrifuge tubes for further extraction and GC analysis.

Control samples were incubated 48 hours under the same conditions. All samples were prepared in 2 replicates and then extracted and analyzed by GS-MS as described below.

2.4.2 Liquid-liquid extraction (LLE)

The extraction procedure was in accordance with Fosu-Mensah et al., 2016. Samples were extracted by adding a 15 mL of dichlormethane:hexane (1:1) and vortexed 3 min. The samples were then centrifugated at 5000 rpm at 4 ° C for 5 min. The supernatant was collected and passed through the paper filter with magnesium sulfate (0,5 g) directly to a 125 mL evaporation glass tube. The LLE procedure is repeated twice. The combined filtrate was evaporated at 60 °C under vacuum conditions of up to 1-1,5 mL (BUCHI MultivaporTM P-6 Parallel Evaporator).

Prior extraction of samples achieved through isotherm experiment, 50 μ L of ^{13}C -labeled β -HCH (10 $\mu\text{g}/\text{mL}$) was added as internal standard for accurate quantification.

2.4.3 GC analysis

The determination of OCPs in the samples was carried out using a GC-MS (7890B, Agilent Technologies) at Antigen Co (Almaty, Kazakhstan) and GC-MS (5975C, Agilent Technologies) at URAFPA (Nancy, France) respectively for kinetic adsorption and equilibrium adsorption samples. Briefly, the mass spectrometer was set at a resolution of 10,000, in electron ionization mode (70 eV electron energy). Single Ion Monitoring (SIM) was used to record the most abundant signals (table 17). Injection temperature and injection volume were 270 $^{\circ}\text{C}$ and 1 μL , respectively. The injection mode was splitless.

Table 17 – Main target ions (m/z) and retention time (RT) of OCPs used in GC-MS analysis

No	Name of the OCP	m/z	RT, min (HP-5ms Ultra Inert capillary column)	RT, min (DB-5 MS capillary column)
1	2,4 -DDD	235	-	15.49
2	4,4 -DDD	235	11.25	16.33
3	4,4- DDT	235	13.22	-
4	4,4 -DDE	246	9.54	15.34
5	α -HCH	183	4.99	9.64
6	β -HCH	183	5.29	10.28
7	γ -HCH	183	-	10.44
8	δ -HCH	183	5.62	11.14
9	Chlordecone	272	12.09	16.8
10	^{13}C -labelled β -HCH (IS)	186,9	-	10.27

The chromatographic parameters of the GC system performed for the analysis of the kinetic adsorption samples were the HP-5ms Ultra Inert capillary column (30 m x 250 μm x 0.25 μm) (Agilent Technologies) was used for the separation of the OCPs. Gas chromatograph oven was set up at 120 $^{\circ}\text{C}$ (1 min) and then gradually increasing to 220 $^{\circ}\text{C}$ at 40 $^{\circ}\text{C}/\text{min}$ (13 min). The total analysis time was 16,5 min. Signals were integrated using Mass Hunter (B 07.05.2479).

The chromatographic parameters of the GC system performed for the analysis of equilibrium adsorption samples involved a DB-5 MS capillary column (30m \times 250 μm \times 0.25 μm) (Agilent Technologies). The gas chromatograph was programmed as follows: 100 $^{\circ}\text{C}$ for 1 min, 190 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ for 1 min, and 280 $^{\circ}\text{C}$ for 3 min. The total analysis time was 25.5 min. Signals were integrated using GC Chem Station software.

2.4.4 Data analysis

2.4.4.1 Quality control

Analysis of adsorption kinetic and equilibrium was performed in 2 replicates and included blank samples represented OCP aqueous solution without the presence of an adsorbent. Calibration of GC-MS system was performed regularly before analysis of samples using analytical standards of individually dissolved OCPs in n-hexane. Samples of equilibrium adsorption were quantified using internal standard (^{13}C -labelled β -HCH). In addition, n-hexane was used as equipment blank and was introduced between two samples on the analytical tray to avoid cross-contamination.

2.4.4.2 Quantification

The concentrations of pesticides (C) in the samples were calculated using i) internal calibration method using a ^{13}C -labelled β -HCH as an internal standard (IS) for equilibrium study and ii) external calibration method applied for kinetic study.

Calibration solutions with concentrations 50, 100, 250, 500 and 1000 $\mu\text{g/L}$ for each OCP and the addition of 50 μL of internal standard (10 $\mu\text{g/mL}$) were prepared in 1 mL of n-hexane and injected into GC-MS. Each calibration solution was realized in duplicate. The ratio of peak areas of OCPs to peak areas of IS ($A_{\text{OCP}}/A_{\text{IS}}$) in the calibration samples was obtained to build the calibration curves.

External calibration applied on kinetic samples was performed in the same concentration range and in the same solvent as previously mentioned (without addition of IS). Peak areas of each OCPs in calibration samples and kinetic samples were obtained using GC-MS integrator.

The parameters of linear equations of calibration such as relative response factor (RRF) and R^2 were used for further calculation of studied OCP concentration in the adsorption samples.

Equilibrium sample processing was based on deriving the ratio of peak area studied pesticide to peak area of IS ($AS_{\text{OCP}}/AS_{\text{IS}}$).

The concentration (C) of the studied OCPs was calculated according to the equations 1 and 2 respectively for equilibrium and kinetic adsorption samples:

$$C = \left(\frac{AS_{\text{OCP}}}{AS_{\text{IS}}} \right) \frac{1}{RRF} \quad (1)$$

Where, $AS_{\text{OCP}}/AS_{\text{IS}}$ – ratio of the peak area of pesticide to the peak area of IS in the sample, RRF – relative response factor of the calibration curve.

$$C = \left(\frac{AS}{RRF} \right) \quad (2)$$

Where AS - peak areas of pesticide in the sample, RRF – relative response factor of calibration curve.

Using the OCP concentration before and after adsorbent treatment, the efficiency of adsorption by sequestration materials was calculated using equation 3:

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_i} \times 100\% \quad (3)$$

Where C_i - initial concentration of pesticide in the aqueous solution (which corresponds to 50 $\mu\text{g/L}$), C_e - concentration of pesticide remaining after adsorption ($\mu\text{g/L}$).

The absorbed quantity of OCPs per 1 g of sequestration matrix (q_e) was evaluated based on equation 4:

$$q_e = \frac{C_i - C_e}{m} \times V \quad (4)$$

Where V is the volume of the aqueous solution (L), m is the mass of the sequestration matrix (g).

2.4.4.3 Statistical treatment

Equilibrium in kinetic study was evaluated when adsorption becomes stable in time and reaches a plateau. Adsorption efficiency of OCPs on SMs which revealed no observable growth after 2 hours was set as criteria of achievement of the plateau.

Equilibrium adsorption data were fitted to the Freundlich isotherm model (Freundlich, 1907) to characterize the adsorption behavior of OCPs. Freundlich isotherm is an empirical adsorption isotherm model for heterogeneous adsorbent surfaces that have been well validated for hydrophobic organic pollutants (Gebrekidan et al., 2015; Kupryianchyk et al., 2016; Olivella et al., 2011; Ru et al., 2007; Silvani et al., 2019). Linear form of the Freundlich model is represented by equation 5:

$$\log q_e = \log K_F + \left(\frac{1}{n} \right) \log C_e \quad (5)$$

where K_F [$(\mu\text{g/g (g/L)})$] and $1/n$ are Freundlich constants related to the adsorption capacity of the adsorbents and the surface heterogeneity, respectively. To determine the Freundlich constants, log

q_e plotted against $\log C_e$, and data are analyzed by linear regression. Intercept equals to $\log K_F$ and K_F is antilogarithm of intercept. Slope is equal to $1/n$.

Linear regression analysis and ANOVA test was performed by using OriginPro 2018 (ver. b9.5.1.195, OriginLab Corporation, Northampton, MA, USA). The Pearson correlation tests (XLSTAT, 2022, Addinsoft, New York, USA) were performed for adsorption capacities (table 23) or adsorption intensities (table 25) between OCP couples.

For better understanding adsorption behavior of studied OCPs on SMs, two principal component analysis (PCA) were carried out to explore relationship between physico-chemical characteristics and adsorption capacities resulted by Freundlich isotherm model (table 23).

First PCA (not shown) was built to define the main SMs properties which would significantly impact on the adsorption process between OCPs-SMs couples. Thus, adsorption capacities of OCPs-SMs couples were explained by BET SSA and porosity (table 18), mineral elements (table 19) and functional groups (table 20). Results of the PCA were presented as squared cosines to show correlation between K_F of OCPs-SMs couples, porosity, mineral elements and functional groups of SMs (table 27).

Afterwards, agglomerative hierarchical clustering (AHC) was done in regard to mineral elements and functional groups of SMs (Figure 29) to simplify the global view. Results of the SMs classification were integrated into second PCA (Figure 30). Second PCA represented a dispersion composed of 2 plots with quantitative variables (i.e., K_F of OCPs-SMs couples and porosity) and qualitative variables (i.e., SM classes depending on mineral elements and functional groups). Missing values in PCA were set as zero.

3. Results and Discussion

3.1 Characterization of SMs

Generally, the studied SMs divided on porous (AC/BCs) and non-porous (peat, potassium humate, humic acid, fulvic acid and brown coal Shoptkol) sequestration materials. Porous carbonaceous matrices demonstrated by a set of different textural characteristics as shown by the specific surface areas (SSA) ranging from 144 to 794 m^2/g (Table 18). Activated carbons (AC1, AC2) displayed the highest SSAs (between 723 and 794 m^2/g) and biochars (BC1 and BC2) the lowest (144 and 196 m^2/g , respectively). The higher SSAs could be associated with high temperatures used during productions of studied AC/BCs.

Results of element composition presented in table 19 showed that ACs (AC1, AC2) and BCs (BC1, BC2) are mainly composed of carbon (C) and oxygen (O). The carbon concentrations in these matrices are generally higher compared to the other non-porous organic materials. This could be explained by application of the high temperature's treatment during the production of studied AC/BCs. The highest concentrations of C with more than 90% were found in AC1 and BC1. However, AC2 (72%) and BC2 (85%) with a less carbon content showed a presence of minerals such as potassium (K), calcium (Ca) and chlorine (Cl).

Non-porous organic matrices are differed by its richer element composition (including K, Ca and Cl) compared to the studied AC/BCs. Among the richest by mineral composition was fulvic acid (SOM3) which composed of Cl, K, Fe, Al, N, Cr and Ca (Table 19).

Table 18 - Origin and physico-chemical characterization of sequestration materials

Sequestration Materials	Type	Origin	Production	BET method		t-plot method		
				Surface area (m ² /g)	Total surface (m ² /g)	Microporous surface (m ² /g)	Non-microporous surface (m ² /g)	Mesoporous volume (cm ³ /g)
DARCO	AC1	Lignite ^a	n/s	793.8 ± 14.5 ^b	829.9 ^b	486.8 ^b	382.1 ^b	-
Shubarkol	AC2	Lignite ^b	900°C ^b	722.8 ± 5.4	744.0	314.1	450	0.30
Oak tree	BC1	<i>Quercus ilex</i> ^c	500°C ^c	144.4 ± 7.8 ^c	-	76.6 ^c	79.0 ^c	-
Japanese knotweed	BC2	<i>Reynoutria japonica</i> ^d	700°C ^d	190.0 ± 7.2	198.5	99.3	105.6	0.08
Peat	SOM1	<i>Sphagnaceae</i> ^d	n/s	na	na	na	na	na
Humic acid	SOM2	Humic acid ^e	Soil extract ^e	na	na	na	na	na
Fulvic acid	SOM3	Fulvic acid ^e	Humate extract ^e	na	na	na	na	na
Potassium humate	SOM4	Potassium humate ^e	Lignite ^e	na	na	na	na	na
Shoptokol	SOM5	Lignite ^c	n/s	4.55 ± 0.8	-	-	-	0.01

Abbreviations: AC-activated carbon, BC- biochar, SOM- soil organic matter.

Indications: na- not applicable, n/s- not specified.

a – specified in supplementary material provided by Sigma-Aldrich (St Louis, USA).

b – data derived from Yermagambet et al., 2020

c – data derived from Yehya S., 2017

d – data derived from el-Wanny et al. 2022

e – data derived from Yermagambet et al., 2019a

f – data derived from Yermagambet B, 2019b

Ratio of oxygen to carbon (O/C) indicated the typical polarity, i.e., abundance of polar oxygen functional groups on the AC/BC surface. Results showed that O/C ratio of studied SMs varied between 0.04 and 0.65. The most polar surface had SOM5 and the most non-polar AC1 (Table 19).

Table 19 - Atomic concentration (%) of the chemical elements presented for studied sequestration matrices.

Sequestration materials	O (1s)	C (1s)	O/C (1s)	K (2p)	Ca (2p)	Cl (2p)	Na (1s)	Fe (2p)	Cr (2p)	N (1s)	Al (2s)	Si (2p)
AC1	4.2	95.8	0.04	-	-	-	-	-	-	-	-	-
AC2	22.5	72.2	0.31	-	-	0.4	-	-	-	-	1.2	1.5
BC1	9.8	90.2	0.11	-	-	-	-	-	-	-	-	-
BC2	12.8	84.8	0.15	0.9	1.1	0.3	-	-	-	-	-	-
SOM1	19.3	78.9	0.24	-	-	-	-	-	-	1.8	-	-
SOM2	18.3	77.1	0.23	-	0.3	1.8	2.5	-	-	-	-	-
SOM3	20.3	61.0	0.33	2.8	0.7	9.7	-	1.7	0.8	1.6	1.4	-
SOM4	23.8	66.0	0.36	8.9	-	0.6	-	-	-	-	-	0.6
SOM5	32.4	51.4	0.65	13.6	-	2.6	-	-	-	-	-	-

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2-Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

Table 20 – Surface functional groups (peak area, %) of studied SMs

SMs	C _{Sp2}	C-C/C-H	C=C	C-O	C=O	-O-C=O
AC1	74.0	20.5	-	5.4	-	-
AC2	-	25.1	64.1	7.6	-	3.2
BC1	-	15.7	72.3	8.4	-	3.6
BC2	69.8	16.1	-	9.13	-	4.9
SOM1	-	21.1	46.0	21.0*	6.7	5.1
SOM2	-	28.4	51.6	12.2	-	7.8
SOM3	-	24.9	-	8.1	57.6	9.4
SOM4	-	72.3	-	15.1	-	9.3
SOM5	63.9	15.1	-	5.5	5.7	9.7

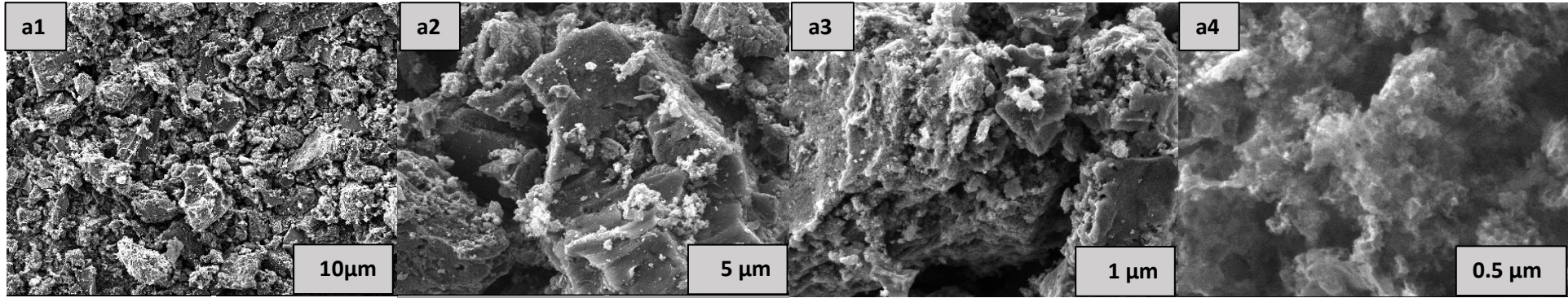
* – functional groups including C-O, C-N

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2-Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

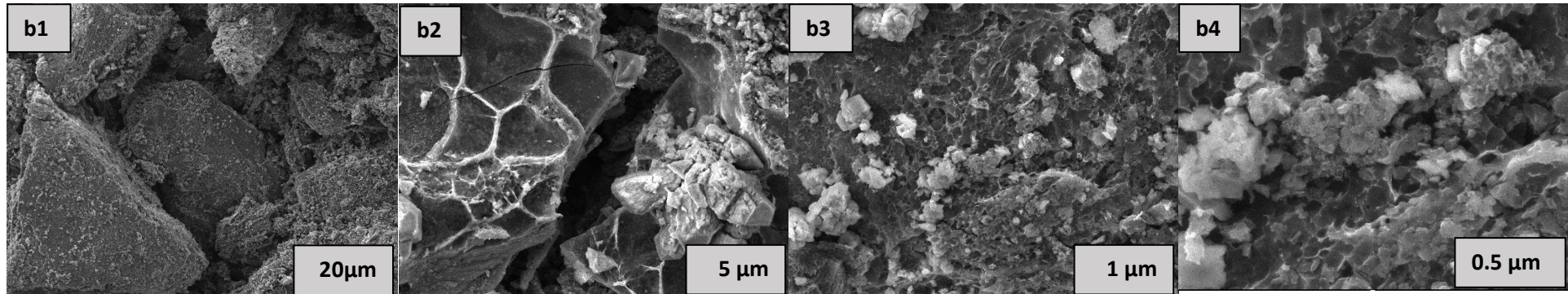
The morphology analysis of the investigated SMs are shown in Figure 26 with a magnification from 10 to 0.5 μm . In general, samples AC1, AC2, BC1 and BC2 (Figure 26a-d) have a pronounced porous structure that differs notable from the structure of SOM-type samples (Figure 26e-i). Samples AC1 (Figure 26a), AC2 (Figure 26b) and BC2 (Figure 26d) represented heterogenous structure characterized by flocculent inclusions and particles of a lamellar-stepped shape in a carbon matrix. A large, dispersed formations in AC2 and BC1 can be explained by the presence of a small quantity of mineral elements (table 19) such as silicon (Si), calcium (Ca), potassium (K) and chlorine (Cl). In contrast, BC1 (Figure 26c) has a more homogeneous rough surface with occasional plaque inclusions.

The SOM1 (peat) is notable different from other SOM samples by its plant structure and presence of various shaped cells (Figure 26e). SOM2 (humic acid) and SOM 3 (fulvic acid) have a very similar square and rectangular structures with white deposits in the form of salts of mineral elements (Figures 26f and g26). Morphology of SOM4 (Figure 26i) demonstrated by irregular in shape of petals with pointed edges. Most particles are irregular in shape and vary in size. SOM5 (raw brown coal Shoptykol) represents a solid structure similar to AC1 and AC2 but with very poor degree of porosity (Figure 26i)

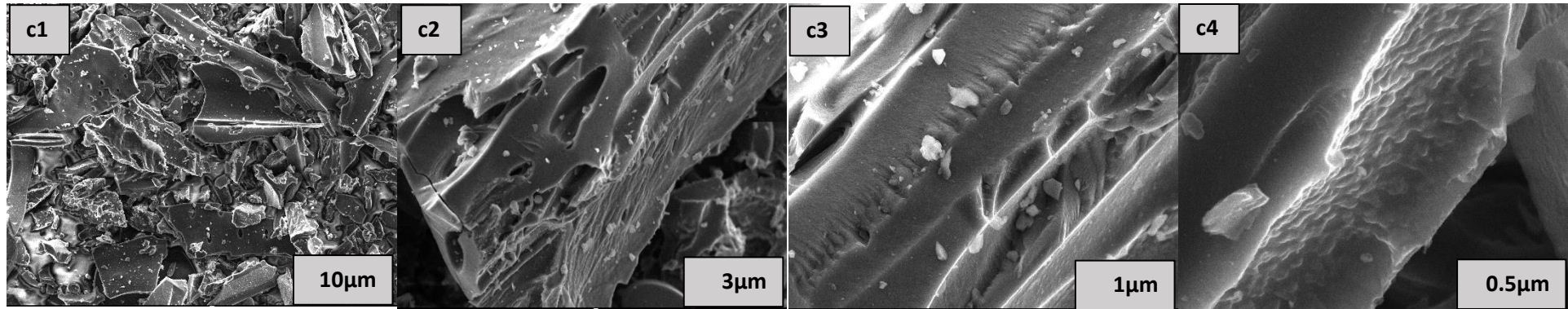
AC1 (DARCO)



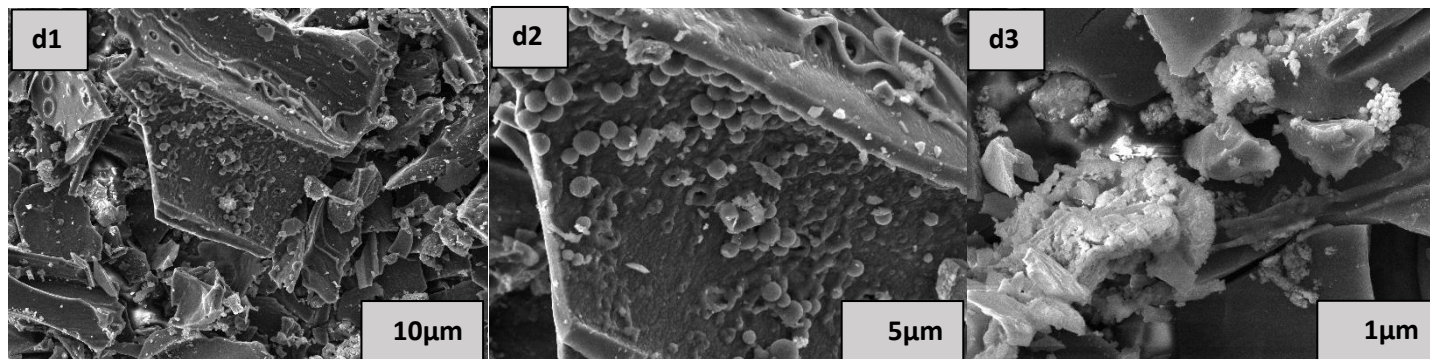
AC2 (Shubarkol)



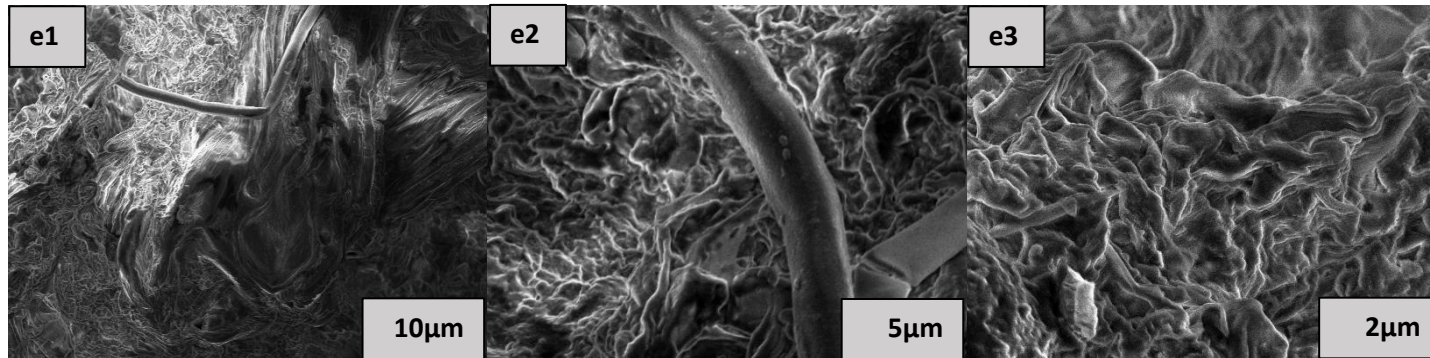
BC1 (Oak)



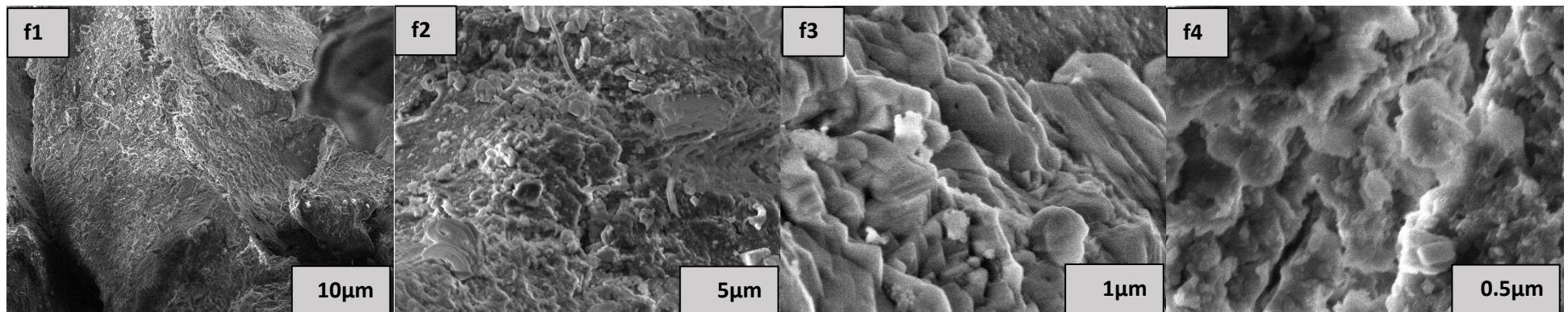
BC2 (Japanese Knotweed)



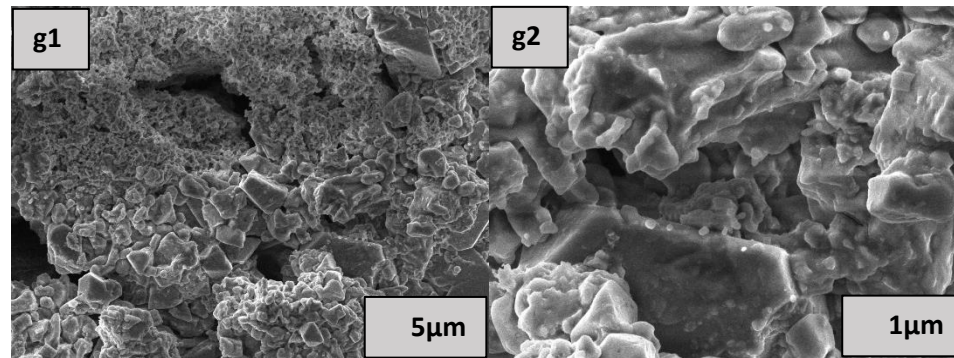
SOM1 (Sphagnum peat)



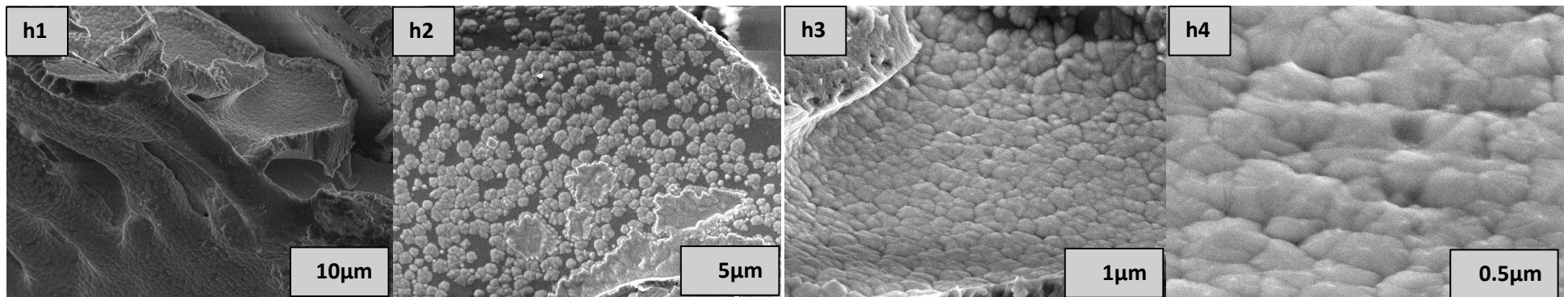
SOM2 (Humic acid)



SOM3 (Fulvic acid)



SOM4 (Potassium Humate)



SOM5 (Shoptokol)

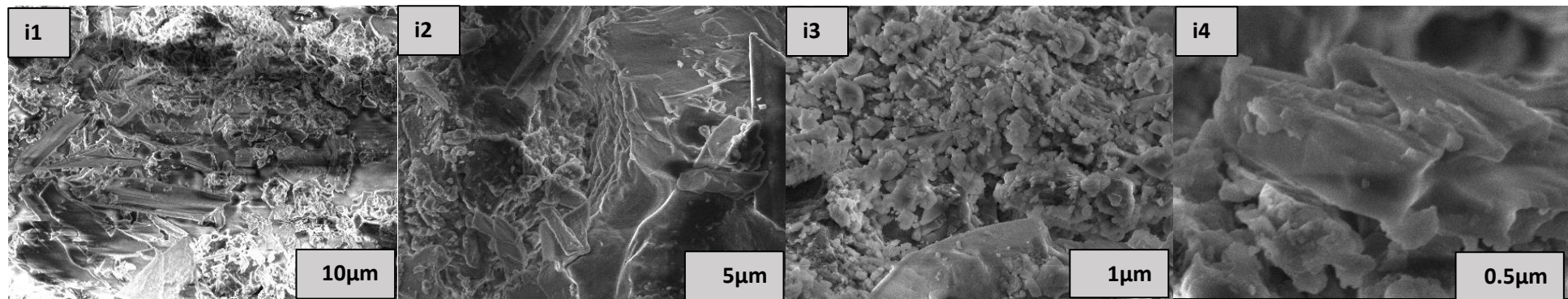


Figure 26 - Scanning electron microscopy (SEM) images of surface of studied SMs with magnification 10, 5, 1 and 0.5 μm (from left to right).

3.2 Effect of Contact Time

Adsorption of organochlorine pesticides (chlordecone, α -HCH, β -HCH, δ -HCH, 2,4'-DDD, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT) from aqueous solution (50 $\mu\text{g/L}$) onto 20 mg of studied ACs/BCs/SOMs were measured after different contact time (1 min, 10 min, 30 min, 60 min, 120 min and 240 min).

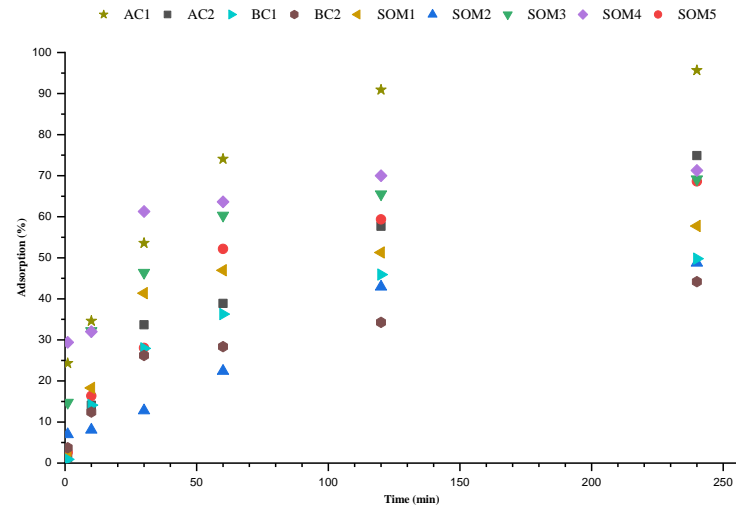
As expected, Figure 27 showed the adsorption efficiency of the sequestrants-OCPs are time-dependent i.e., the longer the contact time the higher the adsorption. According to the results (Figure 27) only activated carbons (AC1, AC2) achieved an equilibrium time after 2 hours for all OCPs. Interestingly, SOMs such as potassium humate, peat and fulvic acid showed the same equilibrium time but preferable for DDT and its metabolites as well as CLD. These results could be explained by higher hydrophobic nature of DDT and its metabolites (K_{ow} between 6.6 and 6.9) and CLD ($K_{ow}=4.5$) compared to HCH isomers (K_{ow} between 3.7 and 3.8). Indeed, according to elsewhere (Barone et al., 2018; Chianese et al., 2020), POPs with medium to high hydrophobic properties ($K_{ow} >4.5$) tend to remove from aqueous media more efficiently and bind to SOM. Achieving an equilibrium means that OCPs are fully saturated on the adsorbent matrix (or in case of AC/BCs on pore space) and thus the adsorption becomes stable after reaching a plateau. Indeed, Figure 27 showed that most studied ACs achieving a time-stable adsorption values remained higher than 50%. Referenced AC DARCO revealed the highest adsorption of studied OCPs ranging between 75 and 80% after 2 hours of contact.

However, there were also a SMs which did not achieve equilibrium such as BC1, BC2 and SOM2. Adsorption of OCPs for these SMs was continuing to increase during the four hours of the kinetic study (Figure 27). These data indicated that contact time of more than 4 hours would be needed to achieve an equilibrium for above-mentioned adsorbents.

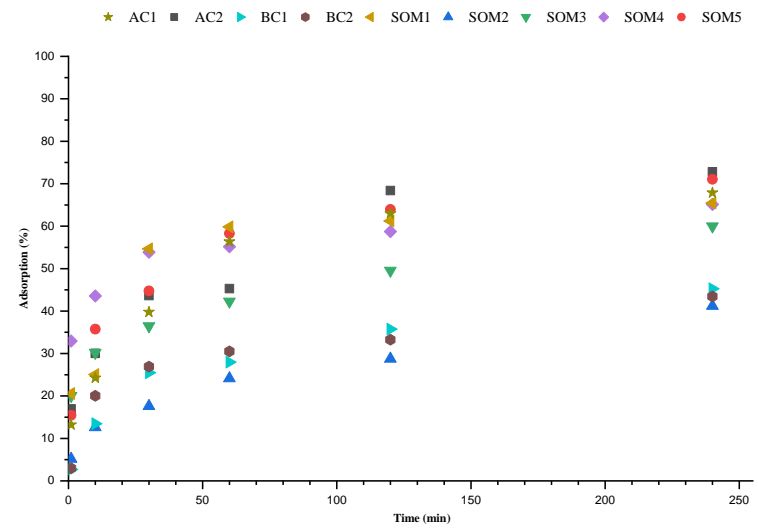
Equilibrium time of OCPs in this study was generally in agreement with literature data indicated in table 21. However, for completed saturation on the adsorbent (especially to organic matter) a longer time was needed as adsorption of the pesticides in our study was lower than elsewhere (El-Kady et al., 2013; Rana et al., 2017; Ratola et al., 2003; Sahmarani et al., 2021). In addition to this, low adsorption of OCPs (<50%) could also be explained by two points: i) competition process occurred between the different studied pesticides for active adsorption sites and ii) the adsorbent concentration of 0.13 g/L was 10 to 100 times lower than in similar studies (table 4). Perhaps, increasing adsorption dose to several times would increase adsorption degree and decrease the time to reach equilibrium for studied OCPs. Therefore 48 hours as the contact time was set in

subsequent adsorption isotherm studies to guarantee achieving of adsorption equilibrium. Effect of different adsorbent concentrations was also investigated to describe the adsorption efficiency for studied OCPs-adsorbents after 48 hours.

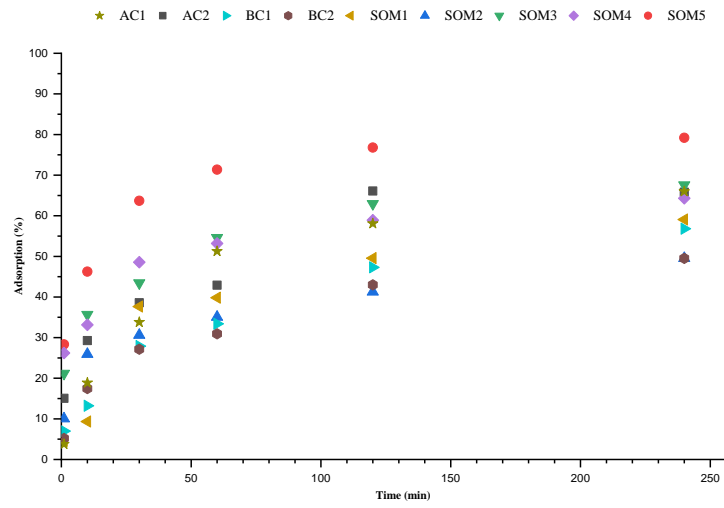
4,4-DDT



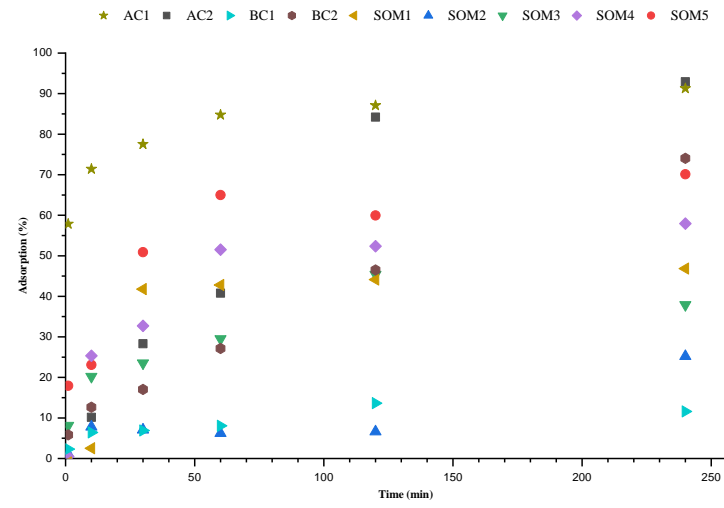
4,4-DDD



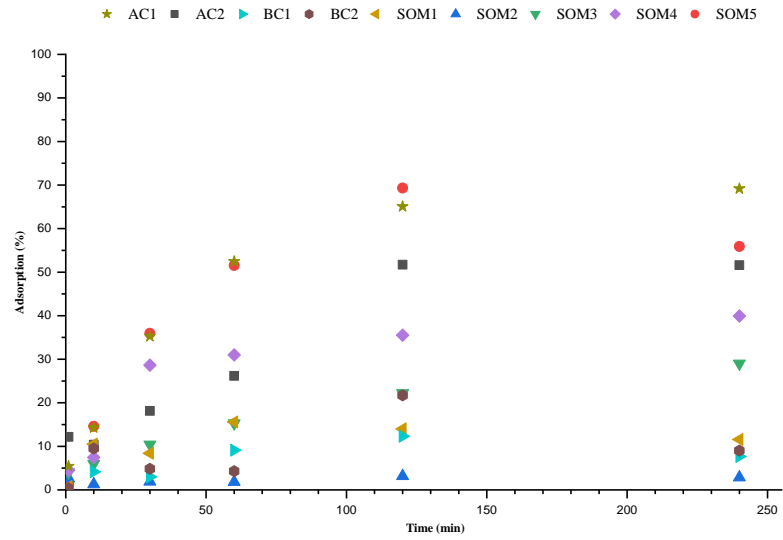
4,4-DDE



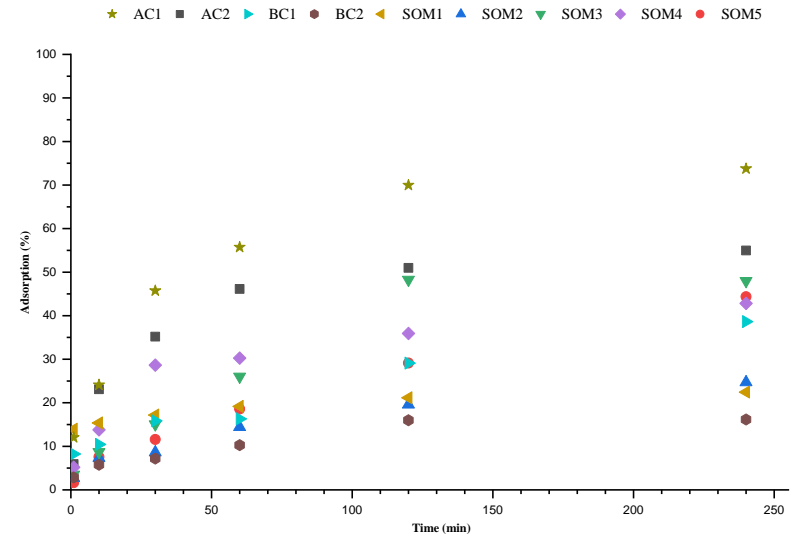
CLD



α -HCH



β -HCH



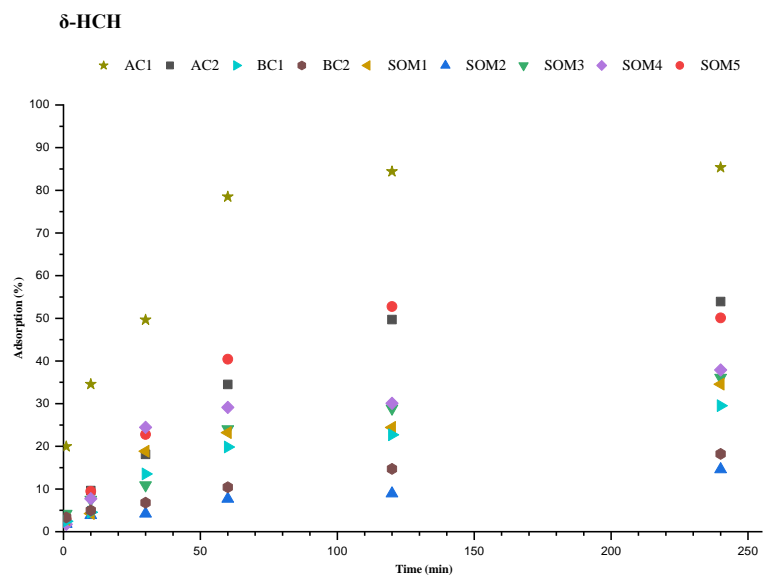


Fig. 27 – Effect of contact time on adsorption of chlordecone (CLD), α , β , δ -HCH isomers, 4,4-DDT, 4,4-DDE and 4,4-DDD on different SMs. OCPs and SMs concentrations were 50 $\mu\text{g/L}$ and 0.13 g/L, respectively. Results based on 2 replicates. Indications: AC1- DARCO, AC2- Shubarkol, BC1-Oak tree, BC2 - Japanese knotweed, SOM1 - Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5 - Shoptykol.

Table 21 – Comparison of adsorption kinetic parameters achieved in current study and in literature.

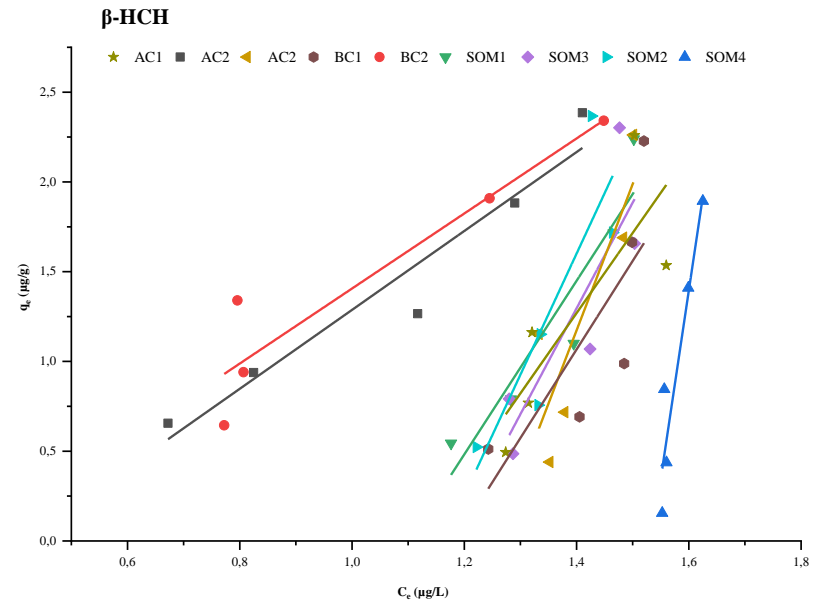
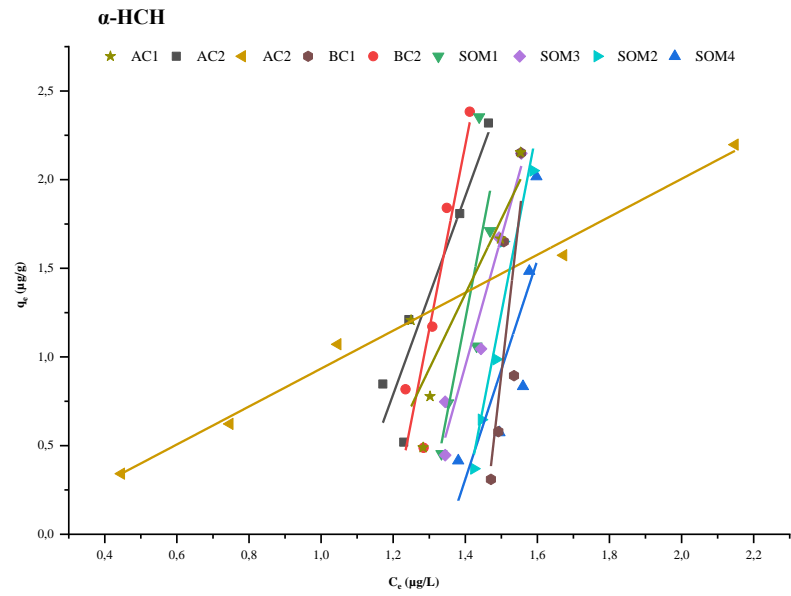
OCP name. concentration. µg/L	Adsorbent. concentration (g/L)	Total time and equilibrium time (h)	Adsorption (%)	Reference	
DDT and metabolites	50	AC DARCO AC Shubarkol Shoptykol 0.13 Potassium humate Peat Fulvic acid	2	77	Current study
			4	71	
			4	75	
			4	67	
			4	61	
			4	66	
DDT and metabolites	20	AC Palm date stone 5	2 >2	90-98	Sahmarani et al., 2021
4.4-DDT	20000	AC Nutshell 1	1.2 1	65	Ejidike et al., 2019
4.4-DDT	5000	AC Coconut shell 1	24 6	75	Aziz et al. 2021
4.4-DDT and 4.4- DDE	2500	Clay 10	24 8	70	Saha et al., 2013
HCH isomers	50	AC DARCO AC Shubarkol 0.13	4	76	Current study
			4	51	
γ-HCH	20	AC pine bark 5	9 >3	80	Ratola et al., 2003
γ-HCH	100 000	AC date stone 1	24 4	98.6	El-Kady et al., 2013
α-HCH. β-HCH	20	AC palm date stone 5 AC palm date stone	2 >1	93-98	Sahmarani et al., 2021
			2 >1	93-98	
Chlordecone	50	AC DARCO AC Shubarkol Shoptykol 0.13 Potassium humate Peat	2	91	Current study
			4	93	
			4	70	
			4	58	
			4	47	
Chlordecone	2200	AC DARCO (FeOs Nps) AC DARCO	24 >24	95	Rana et al., 2017
				62	
Chlordecone	2500	AC bagasse 0.06	200 50	-	Ranguin et al., 2017

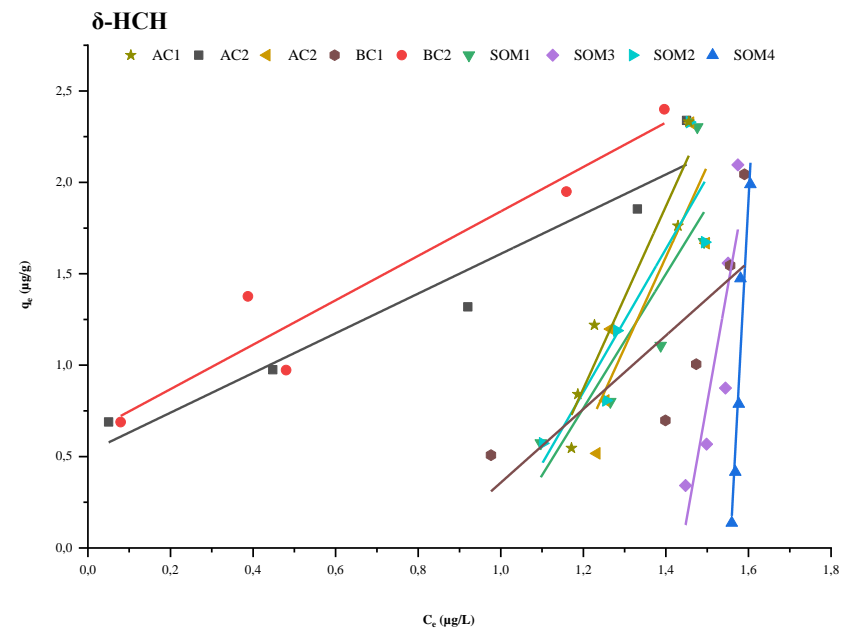
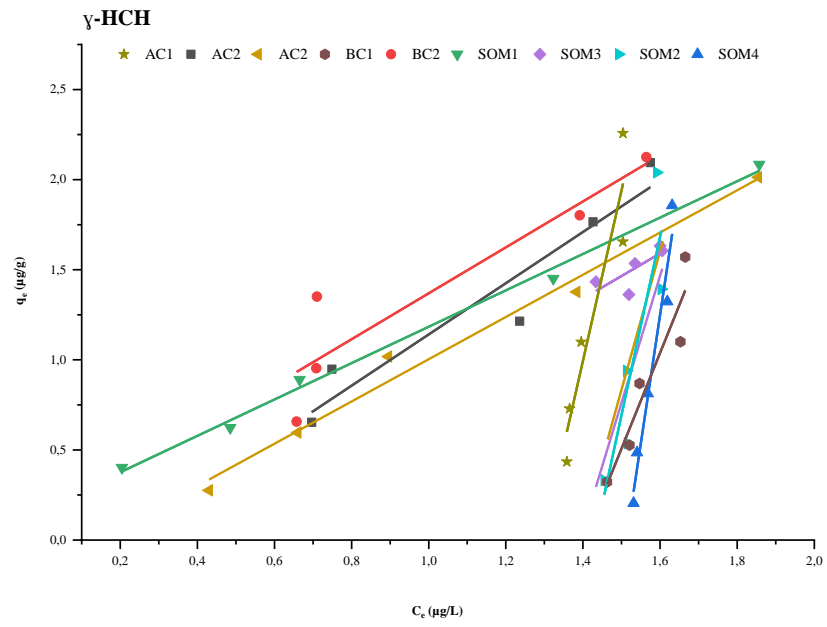
CA-T - Composite adsorbent with triolein. GAC-granular activated carbon

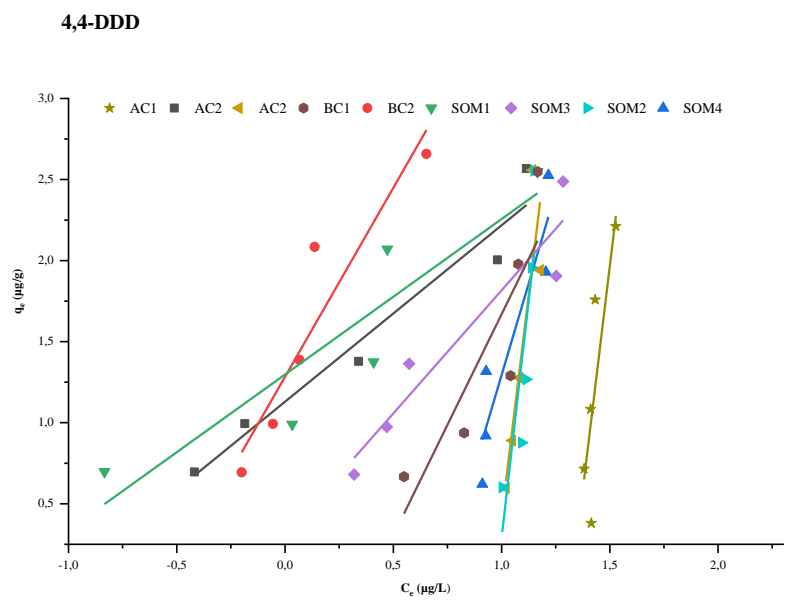
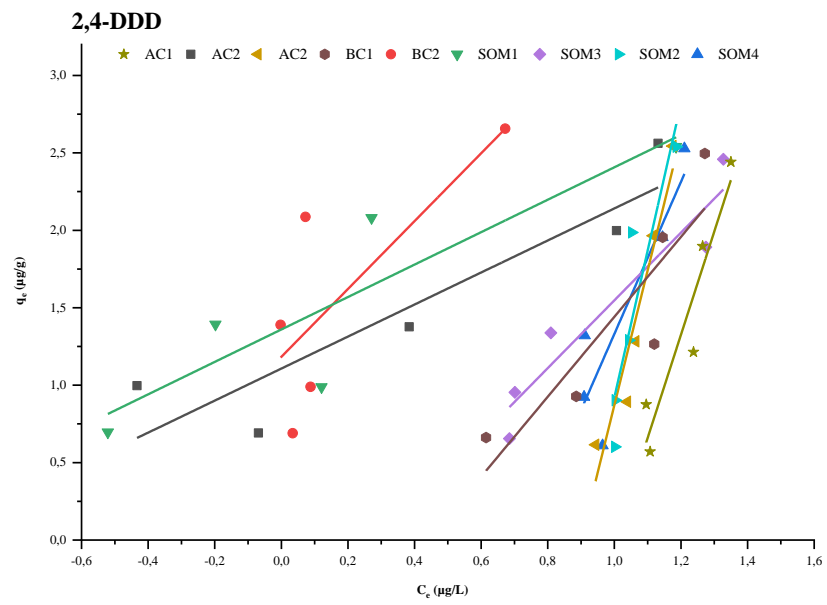
3.3 Adsorption isotherms

Adsorption isotherm is the relationship between studied compound (OCPs) in the liquid phase and the compound adsorbed on the surface of the adsorbent at equilibrium at constant temperature. Adsorption isotherms represented an experimental dataset based on the aqueous solution of the pesticide mixture with a concentration of 50 µg/L, which interacted with different adsorbent doses (0.1, 0.4, 2.0, 5.0, 10 g/L) during 48 hours.

Experimental data were applied to Freundlich isotherm model and shown as logarithmic plots which were based on concentration of OCPs (C_e) versus adsorbed amount of OCPs (q_e) at equilibrium (Figure 28).







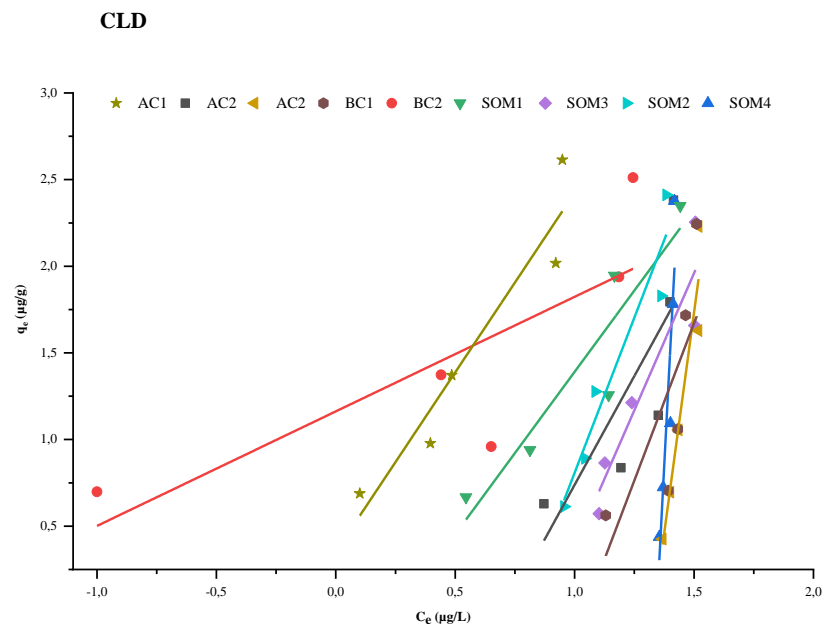
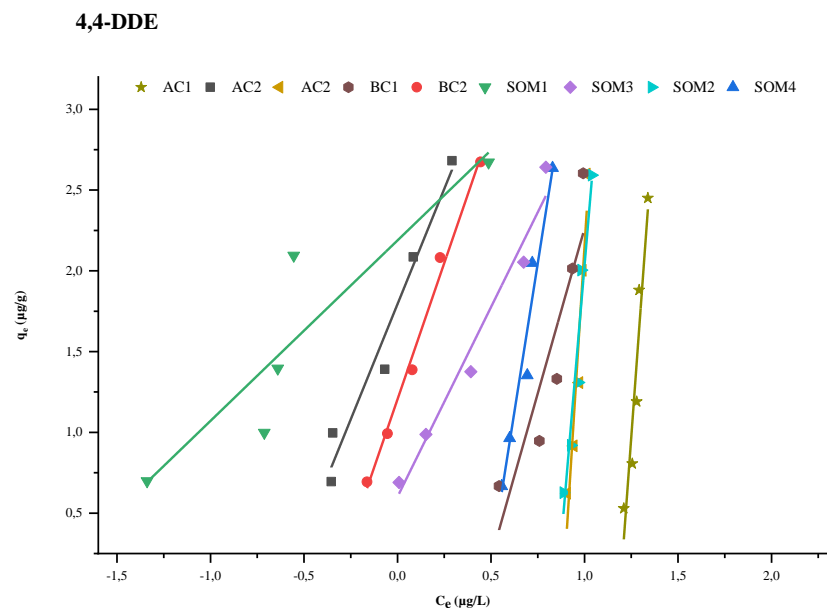


Figure 28 - Freundlich adsorption isotherms of OCPs onto studied ACs/BCs/SOMs. Working conditions: Contact time 48 h, temperature 25°C, agitation 150 rpm, initial OCP concentration 50 $\mu\text{g/L}$, SM concentrations: 0.1. 0.4. 2.0. 5.0. 10 g/L. Indications: AC1- DARCO, AC2-Shubarkol, AC3-Shoptykol, BC1-Oak tree, BC2 - Japanese knotweed, SOM1-Peat, SOM2 - Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate.

Analysis of variance (ANOVA) performed for initial parameters (C_e and q_e) and used to build Freundlich isotherms revealed 3 levels of relationships: very significant ($P \leq 0.01$), significant ($P \leq 0.05$ but > 0.01) and non-significant ($P > 0.05$) fitted to the Freundlich isotherm model and showed as correlation coefficients in table 22. The correlation coefficients (R^2) were derived from linear regression plots and were based on correlations between concentration of OCPs ($\mu\text{g/L}$) (X-axis) and adsorbed amounts of OCPs (μg) per gram of SM (Y-axis) at equilibrium (Figure 28). Resulted R^2 values ranked between 0.587 to 0.995 for all studied OCP-SMs (table 22).

Table 22 – Correlation coefficients (R^2) of studied OCPs-SMs indicating different fitting qualities to the Freundlich isotherm model.

α -HCH	β -HCH	γ -HCH	δ -HCH	2,4-DDD	4,4-DDD	4,4-DDE	CLD
SOM5 0.992	AC2 0.936	SOM1 0.995	AC2 0.929	SOM5 0.918	AC2 0.954	BC2 0.992	SOM2 0.923
SOM3 0.945	SOM4 0.894	SOM5 0.984	BC2 0.924	SOM3 0.909	SOM3 0.907	SOM3 0.97	AC1 0.918
SOM2 0.923	BC2 0.888	SOM4 0.957	SOM4 0.916	AC1 0.895	BC2 0.884	AC2 0.965	SOM5 0.916
AC2 0.872	SOM1 0.877	AC2 0.915	AC1 0.913	AC2 0.846	SOM4 0.855	SOM4 0.951	SOM3 0.886
BC2 0.824	SOM5 0.735	BC1 0.893	SOM2 0.793	SOM2 0.818	SOM1 0.84	SOM2 0.944	SOM1 0.866
AC1 0.758	SOM3 0.73	AC1 0.891	SOM3 0.781	BC1 0.792	SOM5 0.796	SOM5 0.911	SOM4 0.853
SOM4 0.657	SOM2 0.728	BC2 0.856	SOM5 0.759	SOM4 0.786	BC1 0.768	AC1 0.909	BC2 0.666
SOM1 0.649	AC1 0.686	SOM2 0.781	SOM1 0.745	SOM1 0.78	SOM2 0.724	SOM1 0.83	AC2 0.621
BC1 0.611	BC1 0.613	SOM3 0.595	BC1 0.624	BC2 0.587	AC1 0.681	BC1 0.83	BC1 0.586

Abbreviations: AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

Color indications: values in dark grey cells are very significant fitting ($P \leq 0.01$), light grey cells are significant fitting ($P \leq 0.05$ and > 0.01), and white grounded cells are not significant ($P > 0.05$).

The parameters of the Freundlich isotherm model such as adsorption capacity (K_F) and adsorption intensity (N) for different OCPs-adsorbents were presented in summary tables 23 and 25, respectively. A very high variation of K_F and N values between OCP profile and studied SMs were observed. Therefore, Pearson correlation test was performed for adsorption capacities (table 24) as well as adsorption intensities (table 26) between OCP couples.

Pearson correlation tests applied on adsorption capacity K_F values showed that DDT metabolites (2,4-DDD, 4,4-DDD and 4,4-DDE) have the most significant correlation ($P \leq 0.0001$) within all SMs (table 24). In addition, γ -HCH also showed a significant correlation ($P < 0.05$) to DDT and its

metabolites. This means that these OCPs demonstrated a very similar uptake behavior during interaction with SMs. Comparison of the remained pesticide pairs within all sets of SMs for K_F was not significant.

Regarding adsorption intensity data (N values), Pearson correlation indicated that DDT metabolites had the strongest correlation (≤ 0.0001) (table 26) for all SMs. In addition, both β -HCH and CLD also showed a significant correlation to all studied DDT metabolites with $P < 0.05$. These relations mean that these OCPs revealed similar distribution during adsorption to SMs and therefore competition process may occur between them for heterogeneous active sites on the SMs matrix (Ayawei et al., 2017).

Table 23 – The adsorption capacity K_F ($\mu\text{g/g}$ ($\mu\text{g/L}$)^{1/n}) of studied couples of OCPs-SMs determined by the Freundlich equation

SMs	α -HCH	β -HCH	γ -HCH	δ -HCH	2,4-DDD	4,4-DDD	4,4-DDE	CLD
AC1	0.000028	0.00001	5.80E-13	7.70E-06	2.10E-07	2.30E-15	1.30E-19	2.25
AC2	1.20E-06	0.12	0.52	3.33	12.8	13.48	62.24	0.02
BC1	1.10E-26	1.50E-06	4.50E-08	0.02	0.07	0.09	0.02	0.0002
BC2	4.40E-13	0.21	1.24	0.63	1.18	1.28	1.2	1.16
SOM1	2.70E-13	4.70E-06	1.49	0.00023	22.9	19.8	154.3	0.33
SOM2	3.20E-15	1.50E-08	7.00E-15	1.40E-04	2.70E-09	4.00E-12	2.60E-12	0.002
SOM3	6.30E-10	1.10E-07	0.39	4.70E-19	0.23	1.99	3.99	0.002
SOM4	4.70E-09	6.90E-33	2.40E-02	2.50E-67	0.0003	0.0007	0.0003	1.90E-36
SOM5	0.73	5.80E-11	2.00E-11	4.40E-06	1.50E-08	3.10E-11	3.80E-17	2.70E-14

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2-Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol

Table 24 - Pearson coefficients of determination (R^2) applied on adsorption capacity K_F values

OCPs	α -HCH	β -HCH	γ -HCH	δ -HCH	2,4-DDD	4,4-DDD	4,4-DDE	CLD
α -HCH	1							
β -HCH	0.033	1						
γ -HCH	0.069	0.285	1					
δ -HCH	0.023	0.330	0.030	1				
2,4-DDD	0.036	0.007	0.513*	0.139	1			
4,4-DDD	0.043	0.015	0.496*	0.208	0.985**	1		
4,4-DDE	0.031	0.000	0.512*	0.056	0.979**	0.941**	1	
CLD	0.040	0.051	0.013	0.016	0.015	0.023	0.014	1

Bold mean significant correlation between pesticide pairs.

** - P-value ≤ 0.0001 , *P-value < 0.05 .

Table 25 – The absorption intensity N (dimensionless) of studied couples OCPs-SMs determined by the Freundlich equation

SMs	α -HCH	β -HCH	γ -HCH	δ -HCH	2,4-DDD	4,4-DDD	4,4-DDE	CLD
AC1	0.24	0.22	0.11	0.2	0.15	0.09	0.06	0.48
AC2	0.18	0.46	0.7	0.92	0.97	0.92	0.35	0.4
BC1	0.06	0.2	0.19	0.5	0.39	0.37	0.24	0.28

BC2	0.1	0.48	0.78	1.22	2.19	2.33	3.37	0.66
SOM1	0.09	0.21	0.99	0.27	0.95	1	0.9	0.5
SOM2	0.1	0.15	0.1	0.26	0.11	0.09	0.07	0.28
SOM3	0.14	0.17	0.8	0.08	0.46	0.66	0.43	0.32
SOM4	0.16	0.05	0.07	0.02	0.2	0.22	0.14	0.04
SOM5	0.93	0.12	0.13	0.2	0.11	0.09	0.05	0.1

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2-Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

Table 26 - Pearson coefficients of determination applied on adsorption intensity values

OCPs	α -HCH	β -HCH	γ -HCH	δ -HCH	2.4-DDD	4.4-DDD	4.4-DDE	CLD
α-HCH	1							
β-HCH	0.072	1						
γ-HCH	0.114	0.324	1					
δ-HCH	0.051	0.8870***	0.181	1				
2.4-DDD	0.107	0.689**	0.500*	0.729**	1			
4.4-DDD	0.113	0.625*	0.544*	0.655**	0.9885***	1		
4.4-DDE	0.068	0.456*	0.305	0.561*	0.8937***	0.909***	1	
CLD	0.207	0.600*	0.415	0.429	0.575*	0.552*	0.493*	1

Bold mean a significant correlation between pesticide pairs.

***P-value ≤ 0.0001 , **P-value from 0.003 to 0.008, *P-value from 0.01 to 0.05

All SMs demonstrated a variable degree of non-linearity ($N \neq 1$) which corresponds to N-values (table 29). Non-linear sorption confirms the dominance of pesticide adsorption onto the studied SM rather than absorption. Results showed that N-values of all SMs (with exception BC2 for some of the studied OCPs) were generally less than 1 and represented a favorable isotherm. This could indicate on high SM loading at low OCP concentrations (Bedia et al., 2018). Contrary to this, adsorption intensities (N) of DDT and metabolites as well as δ -HCH for BC2 (oak) were between 1.22 and 3.37 indicating on unfavorable isotherms (Bedia et al., 2018; Worch E., 2012).

The isotherm adsorption of all studied OCP-SMs follows a C-type profile for linear curves according to Giles et al., 1960. The C-type is characterized by two main observations: i) target OCPs have a higher affinity for SMs than for solvent and therefore ii) studied OCPs have a better penetration power due to molecular geometry into SM matrix. In this case, the linearity of the data obtained can be interpreted as the constant presence of active sites on the surface of the SM. i.e. the more pesticide molecules are adsorbed, the more active sites are created.

3.4 Relationship between adsorption capabilities and characteristics of OCP-SMs

To better understand relationship of studied physico-chemical properties of SM and adsorption of OCPs, PCA with all variables (K_F , porosity via BET SSA, micro-, and macroporous volume, as well as mineral elements and functional groups) was performed (not shown). Squared cosines were derived from this PCA analysis to demonstrate correlation between the studied variables and factors (table 27). The analysis showed a modest impact of porosity on the obtained results (table 27). This could be partly explained by the nature of SOM-type samples, which are non-porous and represent more than half of the studied matrices. The SOM samples adsorption behavior could be explained only by mineral composition and functional groups presented on their surfaces. In addition, studied SMs have a very diverse elemental composition and surface functional groups (table 19 and table 20, respectively) containing a lot of zero values complicating the overall view. Therefore, AHC was done separately for mineral elements and functional groups of SMs and revealed 3 classes of SMs (Figure 29).

Table 27 - Squared cosines of the PCA variables (K_F , porosit, mineral elements and functional groups of SMs)

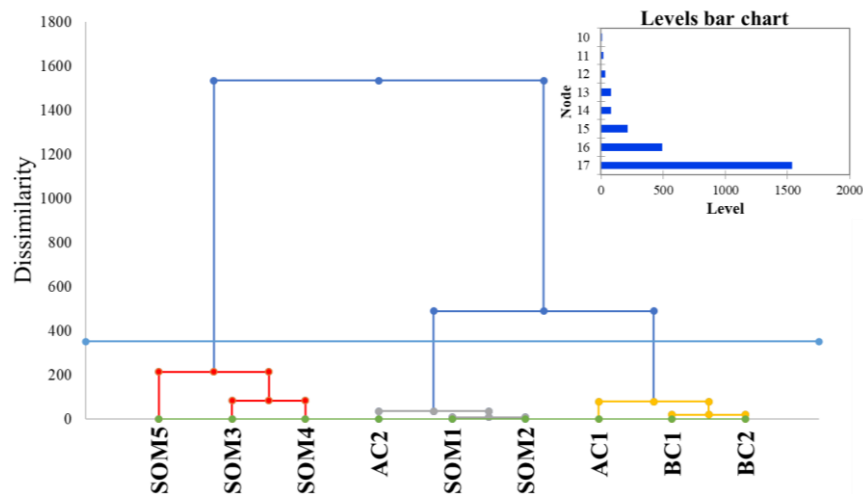
Variables	F1 (48.3%)	F2 (20.0%)	F3 (14.5%)	F4 (10.1%)	F5 (6.8%)
$K_F \alpha$ -HCH	0,095	0,154	0,162	0,571	0,018
$K_F \beta$ -HCH	0,110	0,706	0,083	0,048	0,049
$K_F \gamma$ -HCH	0,686	0,047	0,047	0,080	0,136
$K_F \delta$ -HCH	0,243	0,166	0,432	0,039	0,118
K_F 2,4-DDD	0,924	0,059	0,002	0,001	0,012
K_F 4,4-DDD	0,940	0,043	0,001	0,000	0,015
K_F 4,4-DDE	0,862	0,108	0,022	0,002	0,004
K_F CLD	0,005	0,320	0,409	0,069	0,197
SSA	0,020	0,295	0,000	0,015	0,654
%,C	0,013	0,223	0,344	0,068	0,040
%,O	0,004	0,256	0,435	0,086	0,028
%,K	0,185	0,160	0,132	0,252	0,003
%,Ca	0,002	0,369	0,006	0,026	0,413
%,Cl	0,064	0,044	0,010	0,006	0,083
%,Na	0,048	0,014	0,000	0,087	0,020
%,Fe	0,017	0,011	0,001	0,043	0,079
%,Cr	0,017	0,011	0,001	0,043	0,079
%,N	0,268	0,184	0,131	0,000	0,078
%,Al	0,050	0,010	0,187	0,126	0,005
%,Si	0,141	0,044	0,422	0,140	0,132
O:C	0,013	0,257	0,381	0,191	0,006
CSp2	0,089	0,210	0,044	0,583	0,074
C-C/C-H	0,026	0,018	0,001	0,199	0,013
C=C	0,165	0,037	0,070	0,241	0,004

C-O	0,326	0,161	0,116	0,036	0,155
C=O	0,005	0,039	0,002	0,013	0,081
O-C=O	0,079	0,230	0,116	0,014	0,334
Microporosity	0,002	0,277	0,023	0,007	0,675
Mesoporosity	0,239	0,205	0,440	0,020	0,096

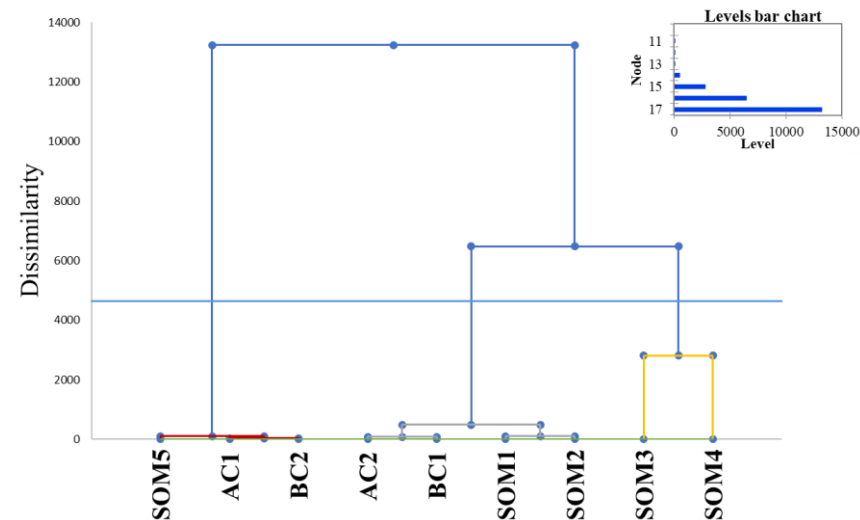
The results corresponding to the supplementary variables are displayed in the second part of the table. Values in bold correspond for each variable to the factor for which the squared cosine is the largest.

Classification of studied SMs by mineral elements was mainly dependent on carbon content: **1st class** (AC1, BC1 and BC2) or carbon content $90\pm 5.5\%$, **2^d class** (AC2, SOM1 and SOM2) or carbon content $76\pm 3.5\%$, **3^d class** (SOM3, SOM4, SOM5) or carbon content $59\pm 7.4\%$ (Figure 29). The SMs classification by functional groups revealed a very similar distribution with exception for BC1 and SOM5 (Figure 29). Thus, results of the cluster analysis were integrated into further PCA analysis to explain an adsorption processes between OCPs and SMs (Figure 30).

Hierarchical clustering of SM by its mineral elements



Hierarchical clustering of SM by its functional groups



Class	SMs	C	O	K	Ca	Cl	Na	Fe	Cr	N	Al	Si
1	AC1	90	9	0.3	0.4	0.1	0	0	0	0	0	0
	BC1	(5.5)	(4.4)	(0.5)	(0.6)	(0.2)						
	BC2											
2	AC2											
	SOM1	76	20	0	0.1	0.7	0.8	0	0	0.6	0.4	0.5
	SOM2	(3.5)	(2.2)		(0.2)	(0.9)	(1.4)			(1)	(0.7)	(0.9)
3	SOM3	59	25	8				0.6	0.3	0.5	0.5	0.2
	SOM4	(7.4)	(6.2)	(5.4)	0.2	4.3	0	(0.9)	(0.5)	(0.9)	(0.8)	(0.3)
	SOM5				(0.4)	(4.8)						

Class	SMs	C _{Sp2}	C-C/ C-H	C=C	C-O	C=O	O- C=O
1	AC1	69	17		6.7	1.9	4.9
	BC2	(5.1)	(2.9)	0	(2.1)	(3.3)	(4.8)
	SOM5						
2	AC2						
	BC1	0	22	58	12	1.7	4.9
	SOM1		(5.5)	(12)	(6.1)	(3.3)	(2.1)
	SOM2						
3	SOM3	0	49		12	29	9.4
	SOM4		(33.5)	0	(4.9)	(40.7)	(0.07)

Figure 29 - Hierarchical classification of SM by mean values of mineral elements (percent) and functional groups. Values in parentheses are standard deviations. AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

The PCA analysis showed 3 major distinctions of the investigated OCP-SM couples showing obvious molecular effect (Figure 30). Thus, each group of pesticides DDT metabolites (2,4-DDD, 4,4-DDD and 4,4-DDE), HCH-isomers, and CLD showed a different degree of affinity and adsorption to the studied SM and the two main axis (axis F1 and F2) of the PCA explained 68% of the total variation. The exception in this distribution was alpha-HCH, which, unlike other HCH isomers, showed the highest affinity for SOM-type SMs (Figure 29). Different hypothesis could explain this different adsorption behavior: 1) Even if alpha-HCH has similar hydrophilicity ($K_{ow}=3.7$) than the other HCH isomers (3.8), the position of the chlorine atoms and by consequence metabolic stability differs. Moreover, its mole fraction in water is much lower (Henry's constant $K_H >6,8 \times 10^{-6}$) than in other HCH isomers $K_H \leq 3,5 \times 10^{-6}$), 2) SOM-type SMs have a very polar surface containing oxygen containing functional groups (Table 20) and therefore are very soluble in water (compare to AC/BCs).

Adsorption behavior of studied DDT metabolites explaining 48 % of variations (F1 axis) showed the highest adsorption potential for SOM1 (raw peat) and AC2 which is characterized by the highest mesoporosity.

The second PCA-axis (F2, 20%) indicated that HCH isomers (except α -HCH) and CLD showed the preferential adsorption to AC1, AC2 and BC2 but with different adsorption degree. Adsorption capacities of these OCPs-SMs couples is not alike which could be also due to the molecular properties of HCHs and CLD. Indeed, ketone groups of CLD may easily interact with other functional groups (i.e., hydrogen) of SMs due to the presence of an oxygen atom in the structure even despite on the larger molecular weight (491 amu) and moderate hydrophobicity (K_{ow} 4.5) compared to HCHs (291 amu and K_{ow} 3.7-4.1) and DDTs (318-320 amu and K_{ow} 6.0-6.5). Adsorption of HCHs to these highly porous SMs could be associated with lowest molecular weight and as consequence indicate on a higher speed of adsorption during the competition with other molecules.

In general, PCA supported the previous observations, and confirmed that the adsorption of OCPs on studied SMs was driven by various physico-chemical properties. Therefore, it is difficult to select one key property to explain the efficiency of OCPs adsorption and affinity between OCPs and SMs is the result of a combination of several factors, within lipophilicity, presence of functional groups and carbon content seem to be key parameters. It seems likely that parameters describing the surface charges, the degree of competition between different compounds in soil for adsorption on SMs (OCPs but also other soil compounds) and strong variations in porosity of SMs would also make vary the effective adsorption of OCPs by different SMs.

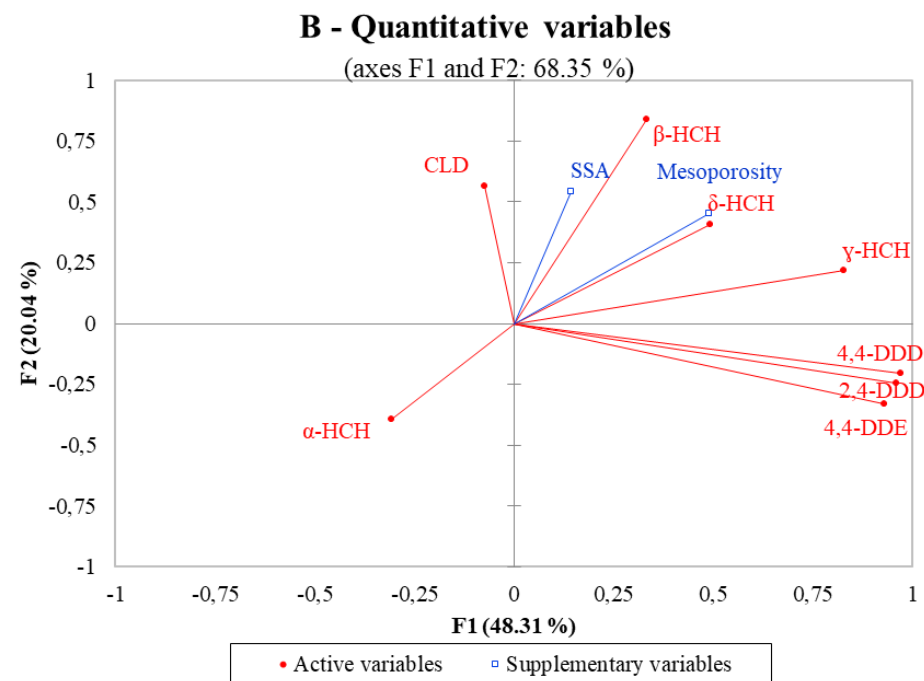
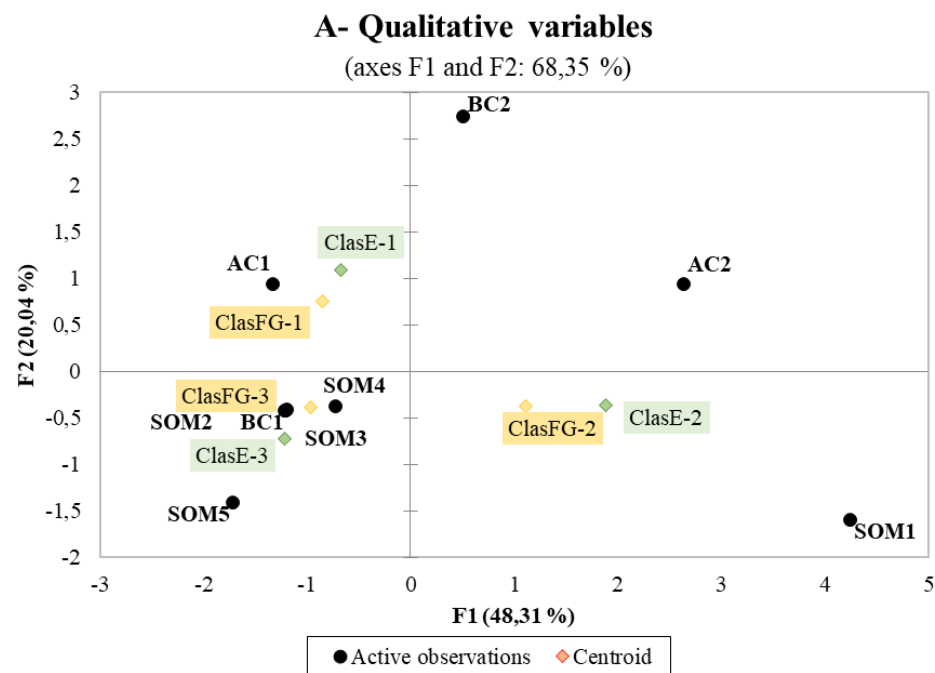


Figure 30 - Dispersion of A-qualitative and B-quantitative variables describing sequestration materials (A) and adsorption capacities of OCPs-SMs couples (B).

A-the qualitative descriptors used to qualify the SMs depending on the class of functional group (yellow, ClasFG) and class of elemental composition (green, ClasE). The different SMs (AC/BC/SOM) were arranged as illustrative data presented in bold black. Indication of SMs: AC1 - DARCO, AC2 - Shubarkol, SOM5 - Shoptkykol, BC1 - Oak tree, BC2 - Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate.

B-the quantitative descriptors of the materials are composed of adsorption capacities (K_F) indicated as OCPs (red color) and porosity properties (blue color).

4. Conclusions

Adsorption kinetic and adsorption isotherm studies have been shown to be an effective tool to investigate adsorption behavior of OCPs to different contrasted SMs. The classification of SMs in ACs, BCs and SOMs allows a better understanding of adsorption mechanisms. Indeed, a very high proportion of carbon in biochars and DARCO allowed them a high adsorption degree, especially on hydrophobic OCPs even if other physico-chemical characteristics as the presence of functional groups make vary the degree of adsorption. The most effective SM which could effectively adsorb all studied compounds were mainly AC1, AC2, BC1, BC2, SOM1 and SOM2. This study demonstrated that SMs parameters, which favorable affected on adsorption of OCPs were porosity, i.e SSA and mesoporosity (porous SMs), mineral elements (especially carbon) and functional groups (SOM type samples). Other factors as competition between different OCPs present in soil or between OCPs and soil compounds should be included to improve the prediction of adsorption. Finally, the proportion of amended SM on soil and by consequence the amount of available adsorption surface should be pathways to reduce the OCP availability in contaminated soils.

The data presented allow to conclude that above mentioned SMs could be effectively used in sequestration strategy studies as amendment which could immobilize OCPs in contaminated soil and water.

PART III: Reducing availability of DDT and its metabolites using a soil amendment strategy: impact of the granulometry of carbonaceous materials and the amendment rates

1. Introduction

Organochlorine pesticides (OCPs) were extensively used worldwide during the 20th century as effective means to preserve crop cultures from insects deterioration (Pimentel, 2009), as well as a part of sanitary policies to limit the spread of disease carriers for both humans (Biggs et al., 1945; Bishopp, 1945) and animals (McDaniel, 1945). If their use highly improved these both priority aspects (food production and diseases controls), downsides of this methodology were revealed well after when environmental and toxicological considerations began to arise in late 60's (Lawrence J. Blus, 2002). 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) and its metabolites are paragons of this flow of history. Found to have insecticides and acaricide properties in late 30's, DDT was the most used pesticide after the World War II (400 000 tons used annually between 1945-60) (Turusov et al., 2002). Toxicological pointed out in 60's tremendous neurological, endocrinal and oncological effects for human health and a high ecotoxicity (Turusov et al., 2002). Due to its particular persistency in soil (caused by their high partitioning onto organic matter) such contaminants could last decades, soil acting as a reservoir of this pollution. In spite of this high affinity to soil, such molecules transfer highly to biota and are bioaccumulated then (Turusov et al., 2002).

In Kazakhstan, such pesticides were used until 1990 even if formal ban for current agricultural use occurred in 70's (Djungalina et al., 2020). Remaining banned pesticides were collected and stored in several storage facilities throughout the country until further process (Djungalina et al., 2020). Due to degrading conditions, confinement of these facilities begun to fail and spread of DDTs arise the past decades (Djungalina et al., 2020). The villages of Kyzylrat and Beskainar are two examples of this past use of DDTs and possible leakage from these storage facilities (Djungalina et al., 2020). A major problem of such contamination is the heterogeneity of its extent and concentrations found onsite, even at a relatively small scale (Shen et al., 2021). Nevertheless, even on moderately contaminated sites, agronomic production services offer by the soil is put at threat as this contamination may transfer to food product (Amutova et al., 2021; Piutti et al., 2022). Thus, without extensive concentration data, risk management of such contamination results in avoidance of agronomic production on these contaminated areas, limiting often a needed local resource.

Other ways to limit transfer of DDTs may be to remediate potential contaminated areas in order to rehabilitate the soil production services. Despite tangible proofs of natural degradation and also possible means to chemically or biologically degrade such molecules, remediation appears expensive, present high variability yields and may require a rather long duration (Purnomo et al., 2011). In this perspective, the production ecosystemic property of the soil may be preserved by acting only on the transfer of such molecules to agronomic resources (vegetables, farm animals). In this frame, sequestration strategies consisting of a soil amendment by carbon-rich materials such as BCs or ACs showed interesting efficiency and represent a promising way (Delannoy et al., 2018; Ranguin et al., 2021). Due to their porous structure providing adsorption of organic contaminants on their large surface, these materials are known to adsorb efficiently organic contaminants (Ahmad et al., 2014). Such application was proven effective to limit transfer to different agronomic biota such as plants, farm animals, and for different organic pollutants presenting high lipophilicity such as PCBs, Dioxins and Furans as well as CLD (el Wanny et al., 2022).

Previous studies demonstrated recently the impact of biomass origin on the characteristics of BCs and ACs and therefore on their sequestration efficiency (Li H. et al., 2017; Ranguin et al., 2020). However, concerning lipophilic organic pollutants, a clear difference of efficiency has been reported in literature between BCs and ACs. Indeed, if both porous materials can be produced from different raw materials such as plants, or animal by products, the activation process appears to be a key parameter for the adsorption of soil-bound POPs. Such processing is known to enhance the porous surface as it limits residues on the surface of the pyrolyzed material (Ranguin et al., 2020). However, due to the specific processes needed, such materials are known to be expensive and may involve chemicals raising environmental concerns. Recently, Ranguin et al., 2021 have shown that brown algae of *Sargassum spp* can be used as a precursor material for BCs. This pilot study demonstrated that BCs derived from *Sargassum spp* and pyrolyzed (3h at 700°C) present a high degree of porosity (specific surface area of 872 m².g⁻¹) and a high efficiency to adsorb another lipophilic POP : chlordecone (CLD). Application on soil led to more than 80% of reduction of CLD environmental availability in Nitisols (Ranguin et al., 2020). Further investigations appear needed in order to determine if this efficiency could be also interesting for other widespread contaminants like DDT, which residues have been found in soils at numerous places around the world.

In the present study, two objectives were followed successively: (1) refine a Sargasso biochar-based sequestration strategy of DDT and its metabolites present in the soil by investigating the

amendment rate and the granulometry. (2) Compare the refined strategy to AC-based sequestration strategies.

2. Material and Methods

2.1 Preparation of the sequestering material of Sargasso Biochar

Three different carbonaceous materials were prepared from *Sargassum spp*: Details of the production process of the original Sargasso Biochar (referred as Sarg) have been extensively described in Ranguin et al., 2021. Two other biochars were prepared from this raw material by grinding it for 2 minutes using an analytical grinder (IKA Tube-Mill 100, Staufen, Germany) and subsequently sieved using a 150 µm apparatus. Two fractions of particle-size were distinguished: fraction sieved until a 150µm sieve (referred as Sarg <) and the residue of the sieving process presenting the largest particles (referred as Sarg >).

2.2 Characterization of the sequestering matrices particle size

In addition to the three distinct samples of biochars (Sarg, Sarg < and Sarg >), two commercial ACs were added. The granulometry was characterized in order to assess the effect of the particle size on the obtained relative environmental availability (Data analysis) using a laser diffraction analyzer (Mastersizer 3000, Malvern Panalytical, France). Briefly, two lasers with distinct wavelengths were used during this analysis, one He-NE red light at 632.8 nm and a blue LED light at 470 nm. A subsample of 20 mg of each granulometric fraction of each BC and AC (as described above) was let to be suspended in 10 mL ultrapure water. The subsample was introduced in the dispersion unit of the Mastersizer 3000 a maximum stirring speed of 3500 rpm and 100% sonication power were applied for the duration of each measurement event (~2 min). Analyses were performed 15 times. From the dispersion unit, the sample was circulated in the measurement cell where diffraction was measured. Very low variability (CV <10%) was obtained. Distribution of the size of AC and BC samples was obtained from the device acquisition software as the mean of the 15 analyses (Mastersizer 3000, version 3.81, Malvern Panalytical, France).

2.3 Characterization of the porous surface of the sequestering materials

Specific surface areas of ACs were derived from previous published data (Ranguin et al., 2020). Specific surface areas (SSA) and porosity of studied BCs were determined at the LIEC laboratory (LIEC, Vandœuvre-les-Nancy, France) as previously described (Delannoy et al., 2018). Physical characteristics of studied carbonaceous materials presented in table 31.

Table 31 - Physical characterization of the different carbonaceous materials

Sequestration materials	Precursor	Pyrolysis	Activation	Textural parameters		
				BET Surface area (m ² .g ⁻¹)	V _{Micropores} (D-R) (cm ³ .g ⁻¹)	V _{Mesopores} (BJH) (cm ³ .g ⁻¹)
Sarg	<i>Sargassum spp.</i>	700°C for 3h	None	872	0.44	0.55
ORBO™	Coconut	N/A	Chemical (Phosphoric Acid)	1121	0.46	N/A
DARCO	Lignite	N/A	Physical (water)	794	-	-

N/A: information no provided by the manufacturer

2.4 Soil sampling and amendment of soil

Soil samples were collected in two villages in the Almaty region (Kazakhstan): Kyzylkairat (GPS N 43°17'58"; E 77°11'39") and Beskainar (GPS N 43°19'27; E 77°06'20") near local storehouses for obsolete and banned pesticides. These soils will be referred respectively as K and B. Soil samples were air dried until mass stabilization and was then sieved over a sieve of 250 µm. Then, soils were amended by one of the five sequestering material at rates of 0.25%, 0.5%, 1% or 2% (w/w). These samples were hand-mixed for 10 minutes. Then, water was added to reach up to 15% of humidity and were let aged for 3 months at ambient temperature (20±2°C). Each amendment was realized in quadruplicate (n=4). For each soil, 8 subsamples were let non-amended as controls (C) (n=8).

2.5 Assessment of DDT and DDT metabolites environmental availability

Environmental availability assays were performed on each artificial and natural soil sample. The used protocol was adapted from the XP ISO/TS 16 751 Part B as previously described elsewhere (Ranguin et al., 2020). Briefly, 600 ± 25 mg of Tenax[®] (60–80 mesh, Sigma-Aldrich, Saint-Louis), 28 mL of ultrapure water were added to soil samples and ¹³C labelled DDT o,p (Cambridge Isotope Laboratories, Tewksbury, MA, USA). After a 20 h agitation period, Tenax[®] was recovered and then extracted 3 times with acetone (LV-GC, Biosolve, Lyon) using an ultrasonic bath. All extracts were pooled and concentrated prior GC-MS/MS analysis.

2.6 GC-MS/MS analysis

DDT and its metabolites analyses were performed on a gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 9000 GC-MS/MS ThermoFisher Scientific, Massachusetts,

USA), equipped with a TG-5SiIMS (30 m, 0.25 mm, 0.25 µm) silica capillary column (ThermoFisher Scientific). Splitless injection was performed on a PTV injector at 75°C with a gradual heating to 300°C at the rate of 2.5°C/s and 3 min at 300°C. The cleaning of the injector was at 330°C since 20 min. A constant flow of 1.2mL helium/min was used as carrier gas and argon was used as collision gaz. The analysis was performed as follows: 1.5 min at 40°C, gradual heating to 90°C at the rate of 25°C/min, 1.5 min at 90°C, gradual heating to 180°C at the rate of 25°C/min, gradual heating to 280°C at the rate of 5°C/min. The transfer line temperature and the ion source temperature were set at 250°C and 300°C respectively. Three transitions were selected, one for quantitation (Q) and two for qualification for each compound. Transitions and collision energy for each compound are summarized in Table 2. Control blanks were introduced between each sample to assess the absence of interferences peaks. Calibration solutions were analyzed at the beginning and at the end of each sequences.

Table 32 - MS/MS detection parameters

Compound	Retention time (min)	Transition	Colision Energy (eV)	Quantification or Qualification
DDE p, p	27.01	246> 176.1	28	Quantification
		317.8> 246	20	Qualification
		317.8> 248	18	Qualification
DDT o,p	29.66	235> 165.1	22	Quantification
		235> 199.5	10	Qualification
		236.8 > 165	22	Qualification
¹³ C DDT op	29.66	247> 177.1	22	Quantification
		177.1> 176.1	22	Qualification
		249> 177.1	20	Qualification
DDD p, p	29.73	235 >165.1	20	Quantification
		235> 199	14	Qualification
		236.8 >165	20	Qualification
DDT p,p	30.45	<u>235> 199.5</u>	22	Quantification
		235> 199.5	10	Qualification
		236.8 >165	22	Qualification

2.7 Data analysis

2.7.1 Relative environmental availability calculation analysis

Four replicates were performed for each amendment strategy. By consequence, four experimental sets were performed comprising each tested soil. Two non-amended soil were added in each test. Calculations were performed using data within each set. Relative environmental availability

factors were calculated as ratio between the found available concentration from a tested group and the mean environmental availability concentrations from the non-amended soil of the same set. This relative environmental availability is expressed in % and represents the remaining available portion obtained after an amendment strategy.

2.7.2 Reduction factor

For each tested strategy of sequestration, 90th percentile (p90) confidence interval was calculated. Then, Reduction factors were calculated as the difference between the relative environmental availability and 100%.

2.7.3 Data curation

In relation with the lowest concentrations found in B soil, some data originating from B soil appeared irrelevant (difference >35% to the mean relative environmental availability found in the tested group). These data were removed from the dataset.

2.7.4 Statistical analysis

ANOVAs were used and each congener relative environmental availability was set as the quantitative data. Then, a one-way Dunnett post-hoc test was applied. When significantly different groups have been revealed with this Dunnett test, the significance of the different groups was assessed by a t-test followed by a Tukey-Kramer post-hoc test. Analyzed data, tested factors for the two-factor ANOVAs, comparative controls used for Dunnett tests are explained for each objective in following subsections.

Statistical analyses were performed using R software (4.0.1, Vienna) setting differences were considered significant at $P < 0.05$.

2.7.5 Refining the Sargasso biochar sequestration strategy

For the first objective, relative environmental availability data from the groups Sargasso biochar amended and non-amended soil for each congener and soil were used for the two-factor ANOVA. The two assessed factors were the amendment rate (4 levels) and granulometry (3 levels). For the Dunnett-test, non-amended soil group was set as comparative control.

2.7.6 Assessment of the efficiency of the selected Sargasso-based strategy against AC-based strategies

For the second objective, relative environmental availability data from the selected Sargasso BC amended and AC-amended soil groups were used for the four-factor ANOVA. The four assessed factors were the carbonaceous matrix effect (3 levels), the soil effect (2 levels), the congener effect (4 levels) and the amendment rate (4 levels). The selected Sargasso BC amended soil was set as comparative control for the Dunnett-test.

3. Results

3.1 Improving a *Sargasso* biochar-based sequestration strategy

In order to improve the sequestration efficiency of the amendment of a *Sargasso* biochar on DDT and DDT metabolites contaminated soils, two effects were assessed: the rate of amendment and the particle size of the *Sargasso* biochar (Figure 31).

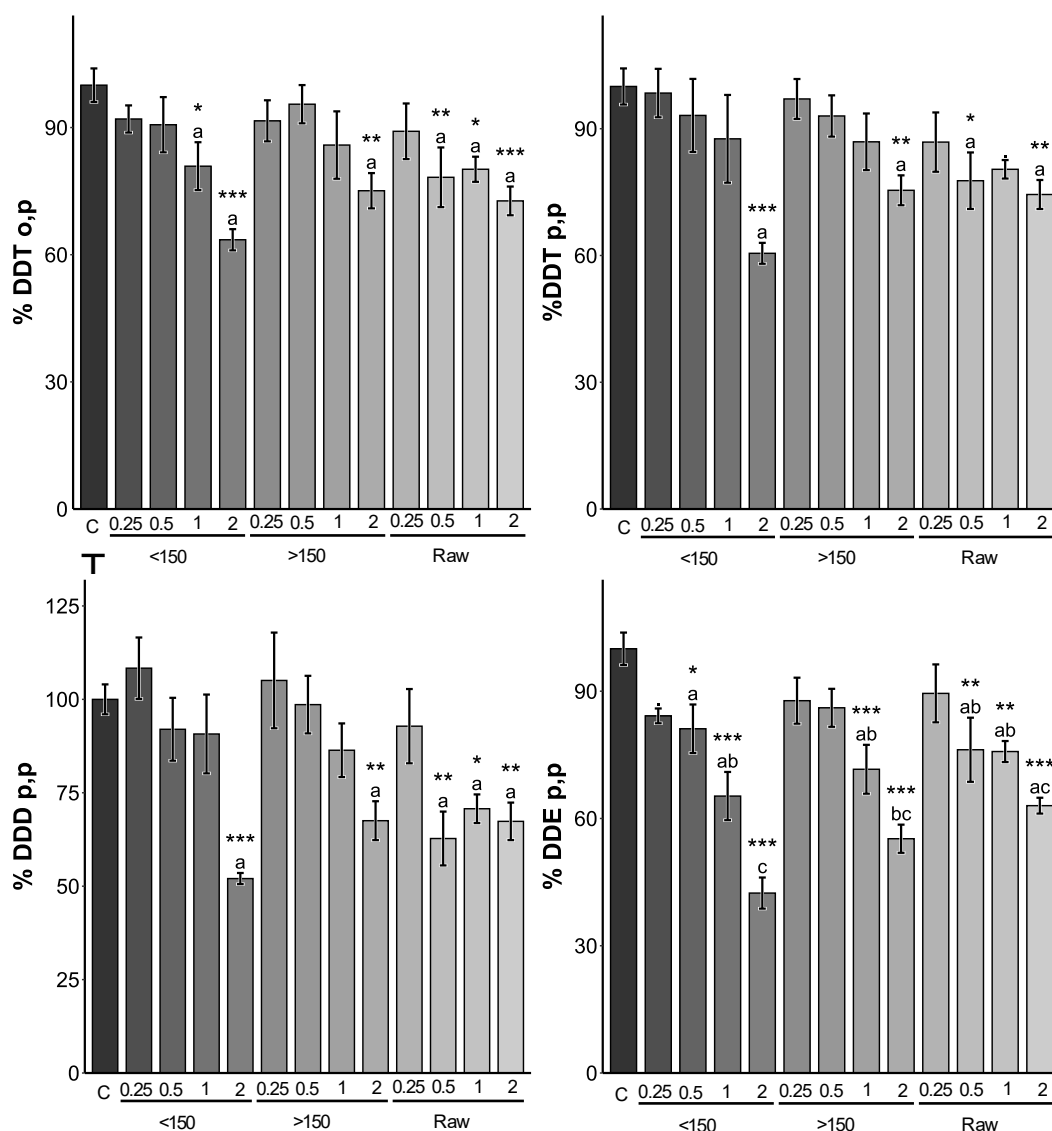


Figure 31 - Relative environmental availability of DDTs and DDT metabolites in Kyzylkairat soil following amendment of *Sargasso* Biochars at different rates and particle sizes. “<150” group represents grinded and sieved until <150 μ m amended groups; “>150”, the fraction above 150 μ m and “raw” the non-grinded, raw biochar material. Value from 0.25 to 2 refer to applied amendment rate. Values correspond to the mean \pm Standard Error (SE) (n = 4). Group mean values with superscript asterisks are statistically different from non-amended soil (C) (0.05: * > 0.01: ** > 0.001: ***) using a variance analysis and a Dunnett post-hoc test. Groups mean concentrations with different superscript letters (a, b, c) are statistically different (p < 0.05) from each other using a complementary variance analysis followed by a Tukey post-hoc test on previously found significant groups using Dunnett’s.

3.1.1 Amendment rate effect

Only the 2% rate appeared as significantly different from the non-amended soil (Figure 31). From this rate $62.6 \pm 9.1\%$, $53.4 \pm 6.7\%$, $70.4 \pm 5.9\%$ and $70.1 \pm 6.0\%$ (mean \pm SE) relative environmental availability were obtained for respectively DDD p,p; DDE p, p; DDT o,p; DDT p,p in K soil. Concerning the biochar, the amendment rate appears to be the most significant effect of the relative environmental availability found with a clear significant effect of this rate: the more the biochar is applied, the less the different congeners were environmentally available ($P < 0.001$).

As expected, an increase in the BC amendment rate in both soils leads to a significant decrease of the DDT and its metabolites relative availability (Table 3). These results are in line with previous data which demonstrated the impact of the amendment rate on the ability of the DDTs to be sequestered by activated carbons (Tomaszewski et al., 2007). Thus, the rise of the BC amount in soils logically increases contact surfaces with contaminated soil and result in a higher trapping of DDT and its metabolites molecules.

3.1.2 Granulometry effect

Up to $54.4 \pm 6.5\%$ (mean of congeners \pm SE) of relative environmental availability was obtained from the grinded and sieved Sargasso BC ($< 150 \mu\text{m}$) whereas the highest granulometric fraction showed $68.7 \pm 15.5\%$ similarly to the raw material ($69.2 \pm 9.7\%$) when amended at 2% rates. Thus, up to 1.4 times lower level of relative environmental availability may be observed from soil amended by the finest fractions of the BC compare to soil amended by the largest. In addition, a notable reduced variability was shown when the finest portion was used. Such observations however were not statistically significant ($P > 0.05$) for B soil as much more variable results were observed.

Thus, granulometry appears of a particular importance to explain the obtained results: the finer the particles of BC are, the better the sequestration is. However, this tendency reached signification threshold only at the highest application rate (2%), indicating that such material is not (statistically) efficient at lower amendment rates (0.25%, 0.5% and 1%).

It appears from this preliminary experiment that at least 2% of amendment rate should be used to ensure the efficiency of the strategy when using Sargasso BC especially in the context of DDT contaminated soils. As reduced particle size appears to enhance also a significant reduction,

grinding and sieving until $<150\mu\text{m}$ appear also as interesting steps to implement.

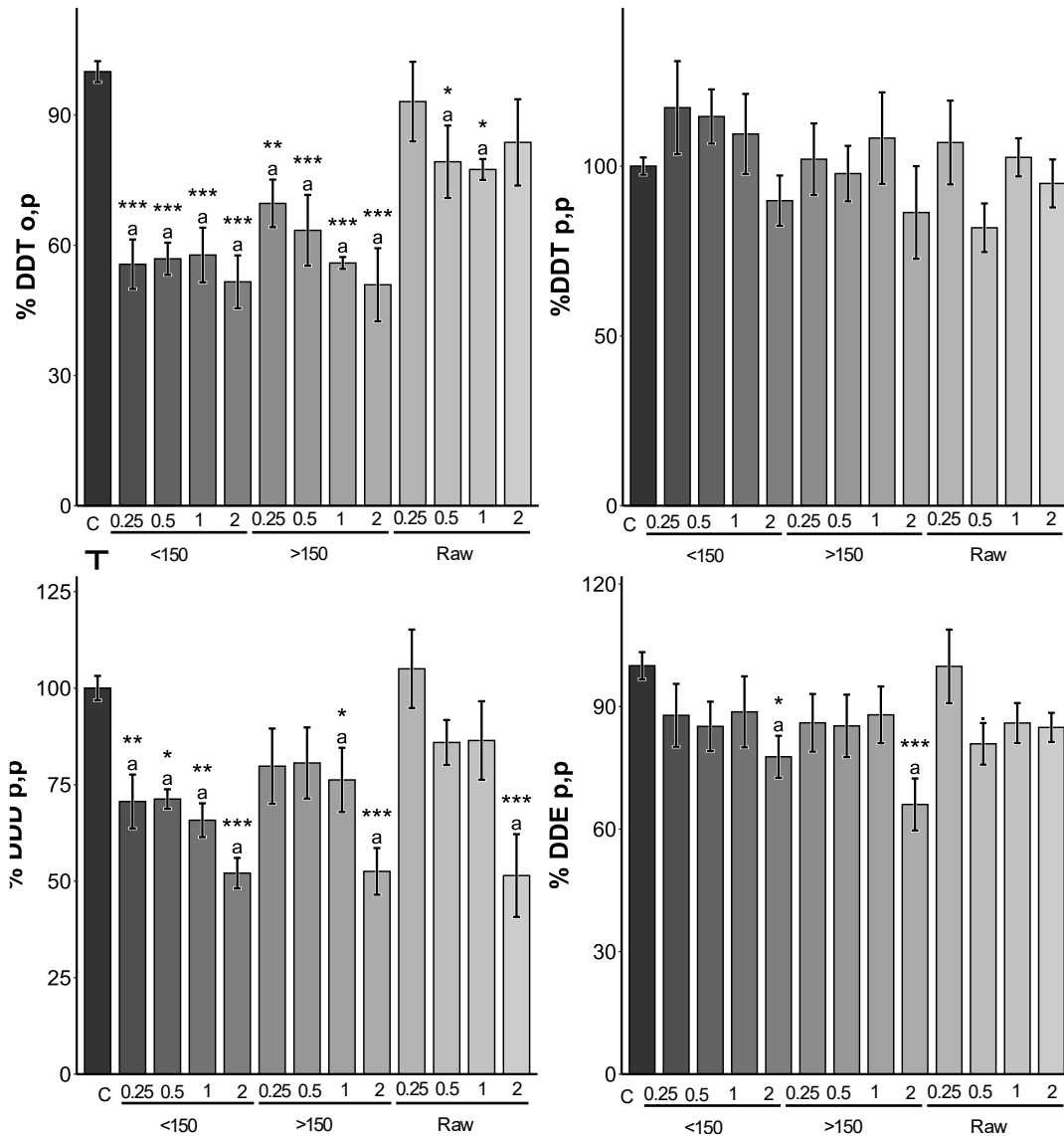


Figure 32 - Relative environmental availability of DDTs and DDT metabolites in Beskainar soil following amendment of Sargasso Biochars at different rates and particle sizes.

“<150” group represents grinded and sieved until $<150\mu\text{m}$ amended groups; “>150”, the fraction above $150\mu\text{m}$ and “raw” the non-grinded, raw biochar material. Values from 0.25 to 2 refer to applied amendment rate. Values correspond to the mean \pm Standard Error (SE) ($n = 4$). Group mean values with superscript asterisks are statistically different from non-amended soil (C) (0.05: * > 0.01 ; ** > 0.001 ; ***) using a variance analysis and a Dunnett post-hoc test. A complementary variance analysis followed by a Tukey post-hoc test on previously found significant groups using Dunnett’s show no statistical differences, presenting the same letter.

Then, the improving phase of this sequestration strategy showed a grinding and a sieving until $<150\mu\text{m}$ lead to a significant decrease in the relative environmental availability of DDT and its metabolites in both K and B soils. This result may be due to a better contact between the contaminated soil particles and the BC when the carbonaceous particles are smaller (Stephan et al., 2022). It is also possible that BC’s specific surface area may increase when grinded and sieved

as a negative correlation was found between particle size and surface specific area (Ranguin et al., 2020). Such considerations are in line with recent investigations demonstrating for another POPs that sequestration efficiency of carbonaceous materials is positively correlated to their specific surface area (Ranguin et al., 2021). Indeed, such surface is known to provide physical sorption explaining the adsorption of POPs and, then, their sequestration. A greater surface meaning also a greater extent of sites for potential adsorption of these POPs explaining this positive correlation. Such considerations were reported thoroughly concerning sequestration of organic pollutants in sediments. Matrices composed of particle diameters between 180 and 300 μm in diameter (i.e. fine granular activated carbons) were shown to have the greatest capacity to sequester hydrophobic organic contaminants such as PCBs or PAHs (Y.-M. Cho et al., 2009; Cornelissen et al., 2006; Sun and Ghosh, 2008; Zimmerman et al., 2005, 2004). In their work evaluating the effects of activated carbon amendment towards the immobilization of these substances (from contaminated sediments collected from Hunters Point Naval Shipyard, San Francisco Bay, CA, USA). Zimmerman et al., 2005 clearly demonstrated the importance of carbon particle size (0.025 to 1.7 mm) and dose (0.34 to 3.4% (m:m)) in reducing environmental availability (assessed by passive sampling via semi-permeable membrane devices of the SPMD type traditionally used for the assessment of the aqueous fraction of organic pollutants) and potential bioaccumulation of pollutants in benthic organisms (*Neanthes arenaceodentata* and *Leptocheirus plumulosus*).

3.2 Comparing *Sargasso* BC to AC-based sequestration strategies

The second set of experiments aimed to compare the most efficient methodology using *Sargasso* BC and more expensive carbonaceous material: high-quality activated carbons (ORBO, DARCO) introduced at different rates. All effects were shown statistically significant through ANOVA test but the presence of interactions between effects need to perform a further description of each effect.

3.2.1 Carbonaceous matrix effect

AC-based sequestration strategy was proven to be the most efficient (Figure 33 and Figure 34). Overall, relative environmental availability from DARCO amended soils significantly reduced compared to those of ORBO amended soil when considering the same congener, the same soil and the same amendment rate (by a 1.2 factor mean). Indeed, for example, comparing results of 2% amendment rate of DARCO and ORBO, values of environmental availability were ranged from 7

to 26 and from 30 to 69, respectively. Such result is not in line with the specific surface found previously, as ORBO presents the highest surface area (Table 31). Indeed, specific surface was found to be negatively correlated to environmental availability and relative bioavailability (Delannoy et al., 2018) when comparing different media with a large range of specific surfaces (between 52 and 1130 $\text{m}^2.\text{g}^{-1}$). In the present study, carbonaceous materials present higher specific surface (between 872 and 1121 $\text{m}^2.\text{g}^{-1}$). As these materials are highly porous, other characteristics such as pore size distribution or chemical surface group may explain the noticeable differences (el Wanny et al., 2022). This is in line with previous observations showing a specific surface threshold around 700 $\text{m}^2.\text{g}^{-1}$ to attain an efficient sequestration for another organic compound, CLD (Ranguin et al., 2020).

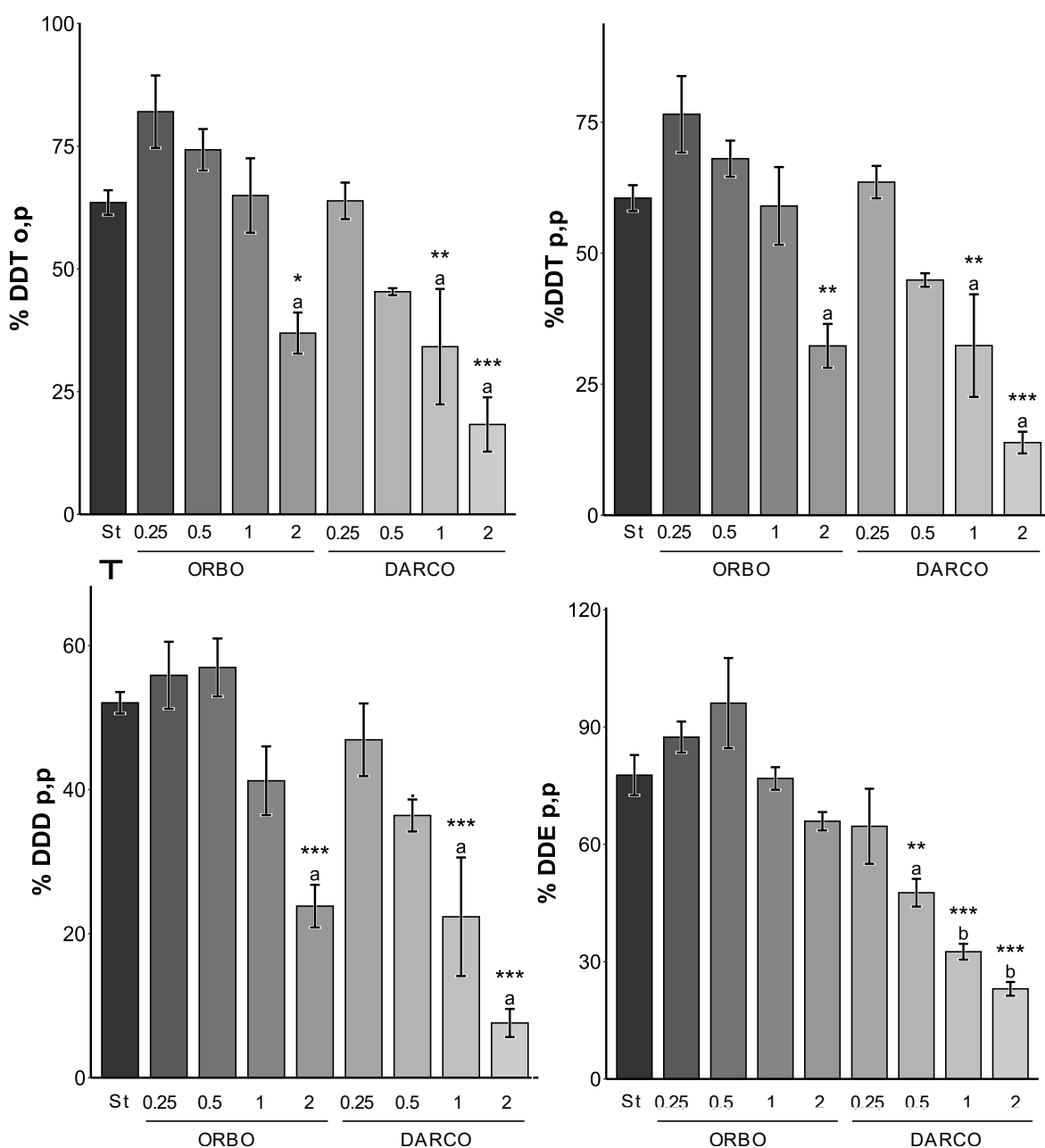


Figure 33: Relative environmental availability of DDTs and DDT metabolites in Kyzylkairat soil: comparison between selected biochar strategy and AC-based strategy.

“ORBO” group represents amended soil with ORBO “DARCO”, amended soil with DARCO, “St” represents the selected strategy : amendment of soil by 2% of <150 µm Sargasso Biochar. Values correspond to the mean ± Standard Error (SE) (n = 4). Group mean values with superscript asterisks are statistically different from selected strategy (St) (0.05: * > 0.01; ** > 0.001; ***) using a variance analysis and a Dunnett post-hoc test. Groups mean concentrations with different superscript letters (a, b) are statistically different (p < 0.05) from each other using a complementary variance analysis followed by a Tukey post-hoc test on previously found significant groups using Dunnett’s.

One possible explanation of such difference is the granulometry dispersion of this material as ORBO presents higher particle size, which may reduce the accessibility to its surface when mixed in the soil. Such a difference may also be explained by (i) a higher mesoporous volume of this media (Table 31) (ii) and possibly more adequate chemical group surfaces (Experimental part II). However, when compared to Sargasso biochar at the same amendment rate, biochar appears to be a far less efficient material even if its surface area is similar to this of DARCO ($P < 0.001$).

3.2.2 Soil effect

Another difference in relative environmental availability responses were found when both soils were compared. Indeed, the environmental availability of DDT and DDT metabolites appeared to be more reduced in soil K than in soil B when the same type and rate of amendment were applied (Figure 31 and Figure 32, respectively). This difference may be due to the differences in the concentrations found in both soils. The soil K presented the highest available concentration for each compounds ($3\,960 \pm 220 \mu\text{g.kg}^{-1}$ of DDE p,p; $74.4 \pm 4.4 \mu\text{g.kg}^{-1}$ of DDD p,p; $1290 \pm 70 \mu\text{g.kg}^{-1}$ of DDT o,p and $3750 \pm 210 \mu\text{g.kg}^{-1}$ of DDT p, p), up to two order more than environmental availability of non-amended B soil ($18.4 \pm 0.7 \mu\text{g.kg}^{-1}$ of DDE p,p; $91.5 \pm 3.3 \mu\text{g.kg}^{-1}$ of DDD p,p; $1.7 \pm 0.1 \mu\text{g.kg}^{-1}$ of DDT o,p and $4.7 \pm 0.2 \mu\text{g.kg}^{-1}$ of DDT p, p). This high difference of concentrations between soils, amendment strategy appeared to be less efficient when used on less contaminated soil. For example, when considering a 2% amendment rate, all obtained relative environmental availabilities were higher in B than in K soil but one value, for every material studied and congener (Figure 32). It is possible that other parameters may also contribute to differences between these both soils as (i) differences of soil composition (especially the content of organic matter), (ii) possible differences of contamination process and age of the contamination between the two sites.

3.2.3 Congener of DDT and DDT metabolites

Finally, congeners appeared also to have a different sensitiveness to the studied sequestration strategies. In K soil, DDD p,p appeared to be the most sensitive congener to sequestration strategies used, followed by DDE p,p whereas the parent compound DDT (congener o,p but also p,p) was the most recalcitrant congener. Considering soil K and the highest amendment rate, DDD p,p and DDE p,p presented a relative environmental availability of 0.64-0.70 times that of DDT o,p (average obtained for the 3 materials). Only a slight difference was noticed for DDTp,p which presented a value 0.90 times that of DDT o,p.

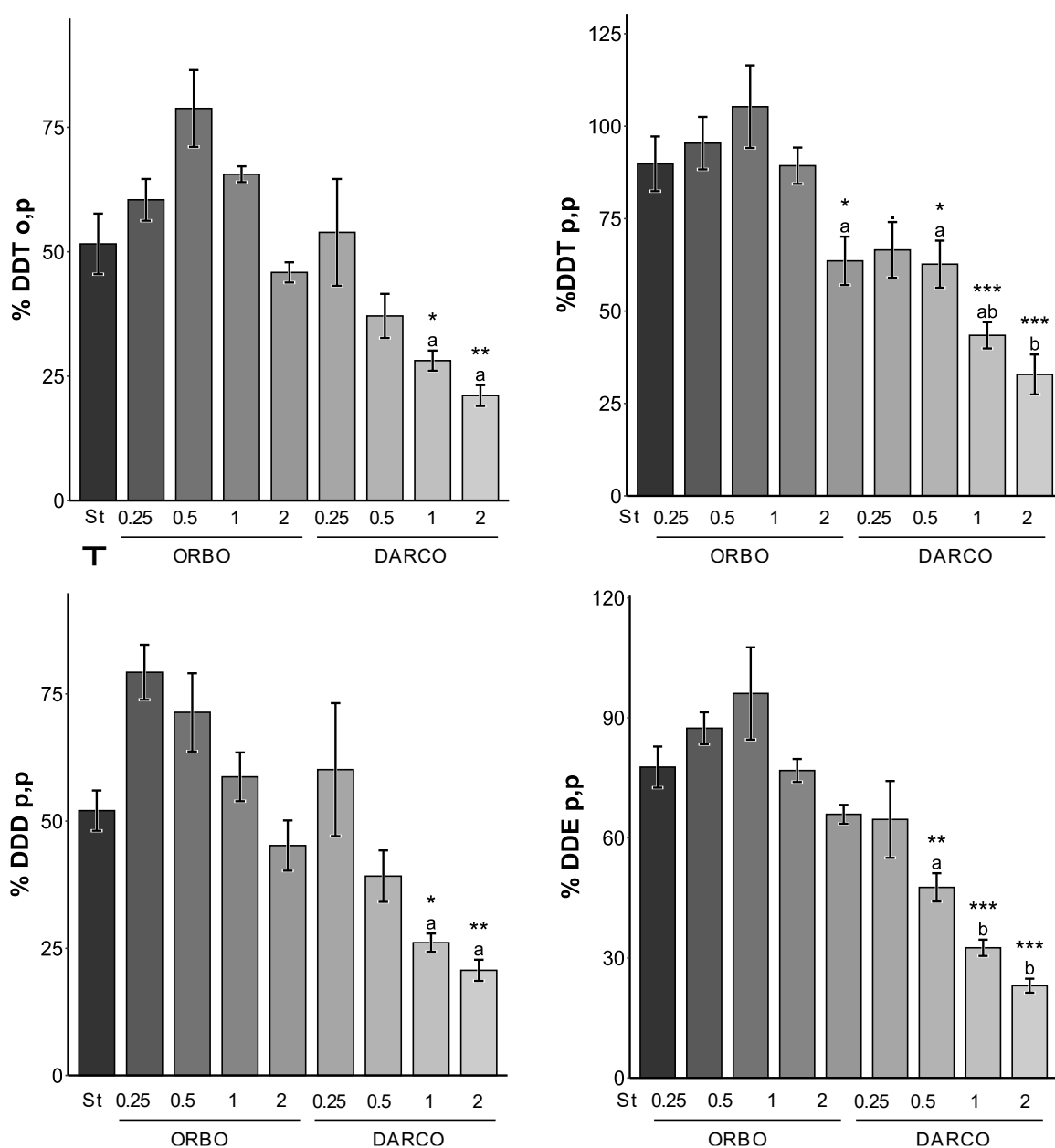


Figure 34: Relative environmental availability of DDTs and DDT metabolites in Beskainar soil: comparison between selected biochar strategy and AC-based strategy.

“ORBO” group represents amended soil with ORBO “DARCO”, amended soil with DARCO, “St” represents the selected strategy: amendment of soil by 2% of <150 μm Sargasso Biochar. Values

correspond to the mean \pm Standard Error (SE) ($n = 4$). Group mean values with superscript asterisks are statistically different from selected strategy (St) (0.05: * > 0.01: ** > 0.001: ***) using a variance analysis and a Dunnett post-hoc test. Groups mean concentrations with different superscript letters (a, b) are statistically different ($p < 0.05$) from each other using a complementary variance analysis followed by a Tukey post-hoc test on previously found significant groups using Dunnett's.

In the clearly less contaminated soil B, the same order was found with the notable exception of DDT o,p for which the sequestration appeared far greater than in soil K. Such similarities between (i) parent DDTs for one hand and the metabolites DDD and (ii) DDE for other hand were expected as they dispose of very similar chemical characteristics.

Some evidence of the effect of congener on the overall efficiency of the sequestration could be found in the literature. Indeed, Freundlich model parameter $\text{Log } K_{F, AC}$ values (reflecting the affinity of pollutants for solid activated carbon phases) for PCBs (7.2; interquartile range (IQR) 7.0 - 7.5) and for PAHs (8.5; IQR 8.3 - 8.8) illustrate a higher efficiency of sequestration for PAHs than for PCBs in a same sequestration context (Kupryianchyk et al., 2012). Such difference may be explained theoretically by the potential of PAHs to initiate more interaction notably π - π binding and molecular surface interactions associated with the flatness of these compounds compared to PCBs (Jonker and Koelmans, 2002; Jonker and Smedes, 2000). Several works have further testified to the greater sorption of non-ortho substituted coplanar PCBs compared to their ortho substituted non-coplanar congeners for similar $\text{Log } K_{ow}$ values (Bucheli and Gustafsson, 2003; Jonker and Koelmans, 2002). (Bucheli and Gustafsson, 2003; Jonker and Koelmans, 2002). To illustrate, a recent study showed similar trends concerning the conformation of the molecules (and moreover flatness) and their ability to be sequestered (El Wannay et al., 2022). Such conformation difference may explain the observed differences between DDT parent compounds and metabolites.

3.2.4 Rate of amendment effect

Another obvious effect on the environmental availability of the soil bound OCPs is the amendment rate for AC-based sequestration strategy. A tendency of linear reduction of relative environmental availability of each congener was observed against the amendment rate of AC. For DDT p,p and ORBO amendment in K soil, the linear reduction pattern indicate that an increase of the application rate by a factor 2 would enhance an additional reduction of 8 to 13%. For the same congener and the same soil but a DARCO amendment, the linear reduction seems to indicate an additional 11-16% reduction when the application rate increased by a factor 2, what is higher than in the previous case of ORBO amendment.

In comparison to BC, only the amendment rate of 0.5% (4 times less) of DARCO give similar or slightly better sequestration than the highest amendment rate of BC, 1% for ORBO. That shows 2 times less efficiency of ORBO amendment in comparison to DARCO amendment.

Currently, few studies have investigated such amendment rate effect on contaminated soils whereas such parameter was extensively studied for contaminated sediment. Several studies have indicated that activated carbon dosages in the range of 3-4% (m:m) are generally sufficient to reduce the concentration of hydrophobic organic contaminants in the sediment phase by 90-99% after approximately 18 months of treatment (Cho et al., 2009; Patmont et al., 2015; Werner et al., 2005). Recently, a first attempt concerning sequestration of CLD in soil demonstrate the importance of amendment rate to immobilize such pollutant, notably for Sargasso biochar which can be efficient up to 82% when amended at 2%.

3.3 Expected reduction of transfer using sequestration strategies

A 90th confidence intervals were calculated from all the tested modalities presented above in order to predict the effect of such a strategy in terms of the transfer reduction. Obtained results demonstrated possible high reduction of transfer of DDT and its metabolites with a minimal reduction of 80% for a 2% amendment with DARCO in soil K (P-90; DDT p,p) but also a minimal reduction of 57% in soil B (P-90, DDT p,p). Alternatively, a 2% application rate of Sargassum biochar grinded and sieved until 150 μm showed a minimal reduction of 31% (p90 DDT o,p) in soil K. However, such a strategy was found non-efficient for the less contaminated soil B as no really reduction (i.e. 0%) was calculated as p90 for DDTp,p.

Overall, the results of the two experiments provided insight into the sequestration of DDT and its metabolites in two different historically contaminated soils. They demonstrated the potential of certain carbonaceous matrices from Sargassum spp to limit the environmental availability of DDT and its metabolites. However, the experiments only considered the sequestration potential offered by BC and AC while eluding the potentially negative effects on soil health. Indeed, such carbonaceous materials can immobilize nutrients, making them unavailable to plants and thus affecting crop growth. (Kim et al., 2015) reported that amendment rates of 0.5 and 1% can be beneficial as biomass increases compared to unamended soil, while rates of 2, 5, and 10% have a negative impact on this parameter.. Another issue of such amendments is their potential to bring other contaminants when amending soil as for ex trace elements. Indeed, Sargassum spp is known to contain variable amounts of Arsenic. Thus, it appears important to take into consideration all

the impacts of BC or AC amendments on soil functionalities and ecology when choosing the amendment type and rate.

Table 33 - Environmental 90th confidence interval and reduction factor of Kyzylkairat soil

90th confidence intervals were derived from relative environmental availability data and reduction factors upon P-90. Value beneath 0 were replaced by “-”.

SM	Amendment rate		90 th Confidence Interval				Reduction factor							
			DDDp,p		DDEp,p		DDTo,p		DDTp,p		DDDp,p	DDEp,p	DDTo,p	DDTp,p
Sargasso biochar	<150	0.25%	108%	[89 - 128]	84%	[80 - 88]	92%	[84 - 100]	98%	[85 - 112]	13%	-	31%	-
		0.5%	92%	[72 - 112]	81%	[68 - 95]	91%	[75 - 106]	93%	[73 - 113]	23%	1%	34%	-
		1%	91%	[66 - 116]	65%	[52 - 79]	81%	[68 - 94]	88%	[63 - 112]	24%	-	27%	-
		2%	52%	[49 - 56]	42%	[34 - 51]	64%	[58 - 69]	61%	[55 - 66]	39%	10%	31%	-
	>150	0.25%	105%	[75 - 135]	88%	[75 - 101]	92%	[80 - 103]	97%	[86 - 108]	-	-	17%	-
		0.5%	99%	[80 - 117]	86%	[76 - 97]	96%	[85 - 106]	93%	[82 - 105]	-	-	17%	-
		1%	86%	[69 - 103]	72%	[58 - 85]	86%	[67 - 105]	87%	[71 - 103]	4%	-	41%	-
		2%	68%	[55 - 80]	55%	[47 - 63]	75%	[65 - 85]	75%	[67 - 84]	33%	19%	29%	-
	All	0.25%	93%	[69 - 116]	89%	[73 - 106]	89%	[74 - 105]	87%	[70 - 103]	-	-	-	-
		0.5%	63%	[46 - 80]	76%	[58 - 94]	78%	[62 - 95]	78%	[62 - 93]	0%	7%	1%	1%
		1%	71%	[62 - 80]	76%	[70 - 82]	80%	[73 - 87]	80%	[75 - 86]	-	3%	17%	-
		2%	67%	[56 - 79]	63%	[59 - 67]	73%	[65 - 81]	74%	[66 - 83]	17%	7%	-	-
ORBO	0.25%	56%	[45 - 67]	66%	[49 - 84]	82%	[65 - 99]	77%	[59 - 94]	8%	3%	30%	-	
	0.5%	57%	[47 - 66]	51%	[41 - 62]	74%	[64 - 84]	68%	[60 - 76]	6%	-	3%	-	
	1%	41%	[30 - 52]	36%	[19 - 53]	65%	[47 - 83]	59%	[42 - 76]	27%	15%	24%	-	
	2%	24%	[17 - 31]	19%	[13 - 25]	37%	[27 - 47]	32%	[22 - 42]	43%	29%	49%	21%	
DARCO	0.25%	47%	[35 - 59]	56%	[46 - 66]	64%	[55 - 73]	64%	[56 - 71]	9%	13%	21%	16%	
	0.5%	36%	[31 - 42]	38%	[36 - 39]	45%	[44 - 47]	45%	[42 - 48]	49%	44%	52%	22%	
	1%	22%	[3.0 - 42]	23%	[10 - 35]	34%	[6.5 - 62]	32%	[9.3 - 55]	70%	63%	67%	48%	
	2%	7.6%	[3.6 - 12]	15%	[5.2 - 24]	18%	[5.3 - 31]	14%	[9.6 - 18]	73%	72%	73%	51%	

Table 34 - Environmental 90th confidence interval and reduction factor of Beskainar soil

90th confidence intervals were derived from relative environmental availability data and reduction factors upon P-90. Value beneath 0 were replaced by “-”.

SM	Amendment rate		90th Confidence Interval								Reduction factor			
			DDD _{p,p}		DDE _{p,p}		DDT _{o,p}		DDT _{p,p}		DDD _{p,p}	DDE _{p,p}	DDT _{o,p}	DDT _{p,p}
Sargasso biochar	<150	0.25%	71%	[54 - 87]	88%	[70 - 106]	56%	[42 - 69]	117%	[85 - 149]	13%	-	31%	-
		0.5%	71%	[65 - 77]	85%	[71 - 99]	57%	[48 - 66]	115%	[91 - 138]	23%	1%	34%	-
		1%	66%	[55 - 76]	89%	[68 - 109]	58%	[43 - 73]	109%	[82 - 137]	24%	-	27%	-
		2%	52%	[43 - 61]	78%	[66 - 90]	52%	[34 - 69]	90%	[72 - 107]	39%	10%	31%	-
	>150	0.25%	80%	[57 - 103]	86%	[69 - 103]	70%	[57 - 83]	102%	[77 - 127]	-	-	17%	-
		0.5%	81%	[59 - 102]	85%	[67 - 103]	63%	[44 - 83]	98%	[79 - 117]	-	-	17%	-
		1%	76%	[57 - 96]	88%	[72 - 104]	56%	[53 - 59]	108%	[77 - 140]	4%	-	41%	-
		2%	53%	[38 - 67]	66%	[51 - 81]	51%	[31 - 71]	86%	[54 - 118]	33%	19%	29%	-
	All	0.25%	105%	[81 - 129]	100%	[79 - 121]	93%	[72 - 115]	107%	[78 - 136]	-	-	-	-
		0.5%	86%	[72 - 100]	81%	[69 - 93]	79%	[60 - 99]	82%	[65 - 99]	0%	7%	1%	1%
		1%	86%	[63 - 110]	86%	[74 - 97]	77%	[72 - 83]	103%	[89 - 116]	-	3%	17%	-
		2%	51%	[20 - 83]	85%	[76 - 93]	84%	[21 - 146]	95%	[78 - 112]	17%	7%	-	-
ORBO	0.25%	79%	[67 - 92]	87%	[78 - 97]	60%	[51 - 70]	95%	[79 - 112]	8%	3%	30%	-	
	0.5%	71%	[49 - 94]	96%	[69 - 123]	79%	[61 - 97]	105%	[79 - 132]	6%	-	3%	-	
	1%	59%	[45 - 73]	77%	[68 - 85]	66%	[56 - 76]	89%	[75 - 104]	27%	15%	24%	-	
	2%	45%	[34 - 57]	66%	[60 - 71]	46%	[41 - 51]	64%	[48 - 79]	43%	29%	49%	21%	
DARCO	0.25%	60%	[29 - 91]	65%	[42 - 87]	54%	[29 - 79]	67%	[49 - 84]	9%	13%	21%	16%	
	0.5%	39%	[27 - 51]	48%	[39 - 56]	37%	[27 - 48]	63%	[48 - 78]	49%	44%	52%	22%	
	1%	26%	[22 - 30]	33%	[28 - 37]	28%	[23 - 33]	43%	[35 - 52]	70%	63%	67%	48%	
	2%	21%	[15 - 27]	23%	[18 - 28]	21%	[15 - 27]	33%	[17 - 49]	73%	72%	73%	51%	

4. Conclusion

Sequestration strategy involving highly carbonaceous materials appeared to significantly reduce the relative environmental of DDT and DDT metabolites making it an interesting option of rehabilitation of contaminated soil. This strategy appeared effective particularly for BC after a grinding and a sieving process aiming at reducing the particle size and when at least 2% rate of amendment is used. In that particular case, reduction levels above 40% have been observed for DDT and DDT metabolites. AC-based sequestration strategy appeared more effective as higher reduction levels (up to 90%) were obtained for 2% amended soils. For both strategies, increasing the rate of amendment lead to an increase of efficiency. A noticeable congener effect was also observed and sequestration efficiency appeared to follow the order: DDE p,p = DDD p,p > DDT p,p = DDT o,p. Due to the particular cost-efficiency of biochar, such a strategy should be further investigated to (i) improve the sequestration potential before application and (ii) evaluate the innocuity of such amendment.

PART 4: Reducing the transfer of OCP from contaminated soil to farm animals using the sequestration strategy

The current chapter represents the experimental data derived from the article «Evaluation of two contrasted activated carbon-based sequestration strategies to reduce soil-bound chlordecone bioavailability in piglets» published in *Environmental Science and Pollution Research* journal as part of the experimental work of this PhD thesis (Delannoy et al., 2020b). The experiment was performed to study CLD transfer from contaminated soil to piglets. In addition, to reduce CLD transfer, sequestration strategies based on two different ACs were proposed as environmentally promising and socially acceptable solutions aiming to highly reduce the CLD bioavailability of contaminated soils.

1. Introduction

Chlordecone (CLD) biocidal activity against a wide spectrum of insects formerly led to its extensive use in the tropics, and particularly in Martinique and Guadeloupe (French West Indies) in order to fight against the banana black weevil (*Cosmopolites sordidus*) (Cabidoche et al, 2009).

As an illustration, almost one-sixth (~ 300 t) of the CLD total world production was spread in French West Indies banana fields from 1972 to 1993, when it was formally banned in 1990 (Babusiaux et al, 1990). Since this pollutant is strongly retained and persistent in soils, superficial layers of large areas of agricultural land still remain highly contaminated, with registered values exceeding 1 mg of CLD kg⁻¹ of soil dry matter (DM) (Cabidoche et al, 2009; Le Déaut and Procaccia 2009; Levillain et al, 2012). This soil contamination will persist for several centuries (Cabidoche et al, 2009) due to the CLD recalcitrance to biodegradation under environmental conditions (Cabidoche et al, 2009). Thus, CLD was added as a Persistent Organic Pollutant (POP) to the Stockholm Convention in 2009 due to its high persistence and serious risks to human health and the environment (Cabidoche et al, 2009). Indeed, recent Guadeloupean epidemiological studies suggested that CLD impairs both cognitive and motor developments during early life stages (Dallaire et al, 2012; Boucher et al, 2013), and acts as an endocrine-disruptor (Cordier et al, 2015; Multigner et al, 2016).

This long-term CLD soil pollution results in transfer and bio-accumulation of CLD in the food chain (Guldner et al, 2010; Cabidoche and Lesueur-Jannoyer 2012; Boucher et al, 2013). Regarding outdoor-reared animals and derived food products, a number of studies showed that involuntary soil ingestion represents a major route for meat contamination (Jondreville et al, 2013;

Bouveret et al, 2013; Jurjanz et al, 2014). Those recent investigations dedicated to assess the relative bioavailability of contaminants as “the comparative bioavailabilities of different forms of a chemical or for different exposure media containing the chemical (e.g., bioavailability of a chemical from soil relative to its bioavailability from water) and is expressed as a fractional relative absorption factor” (NEPI 2000). These articles clearly demonstrated that soil-bound CLD is fully bioavailable for pig- lets, lambs, and laying hens. This is of great concern in terms of potential impact on human health protection of French West Indian population (Multigner et al, 2010).

Within this context, there is an urgent and growing need to propose an environmentally and socially acceptable solution aiming to highly reduce the CLD bioavailability of contaminated soils. The approach which was investigated in this study consisted in the use of activated carbons given either via soil or via feed the CLD transfer to animals. These media are indeed efficient to sequester organic pollutants due to their important porous structure as expressed by surface specific areas (SSA) (Hilber and Bucheli 2010). Concerning CLD, some articles already show the effectiveness of using ACs to sequester CLD (Durimel et al, 2013; Gaspard et al, 2014; Woignier et al, 2015; Yehya et al, 2017). Thus, the present study was conducted to assess the potential of two contrasted ACs (DARCO® and ORBO™ respectively originating from peat bog and coconut shells) to efficiently retain CLD during digestive processes of piglets when provided either via feed incorporation or via soil amendment.

2. Materials and methods

2.2 Animals, ethics, and housing

The overall experimental design is depicted in Figure 35.

The experimental protocol was approved by the Ethical Committee of Lorraine and authorized by Ministry of Agriculture for Animal Research (MAAR) (Permit Number: 00270.02), This study was carried out in strict accordance with the recommendations in the Guide for the Care and Use of Laboratory Animals of the French Ministry of Agriculture for Animal Research (MAAR) and European Council Directive (European directive 2010/63/EU). Twenty 35-day-old castrated male piglets (*Sus scrofa domesticus*, EARL des deux chênes, Saint-Maurice-aux-Forges, France) were involved in this experiment. A 7-day acclimation period was realized prior to the start of the exposure period. Each experimental group (n = 4) was kept in an individual cage covered with duckboard and individual feeders in the animal facility of Plateforme Biodisponibilité-Bioactivité (Université de Lorraine, Vandœuvre-les-Nancy France), Temperature was kept at 24–25 °C. In

order to closely control CLD exposure of animals, all animals were individually weighed three times a week.

Feed was provided daily (SUPER VE, Lorial, Coopérative Agricole Lorraine, France) at 4,5% of body weight (BW). Water was provided ad libitum by nipple waterers throughout the entire study.

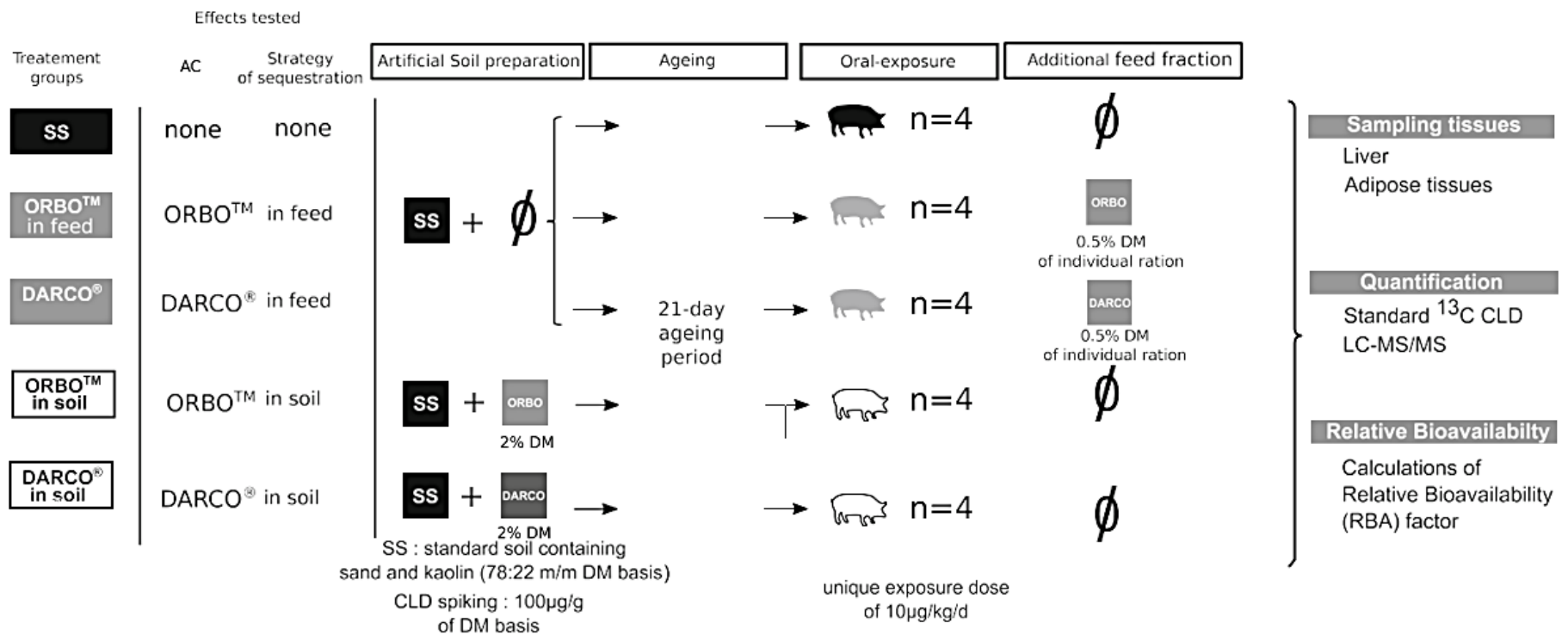


Figure 35 - Experimental design of the present study with piglets

2.3 Dosing material and method of exposure to CLD

2.2.1 Contaminated soils

Three artificial soils were prepared as described in Table 35 according to the OECD guideline 207 (OECD 1984). First, the artificial standard soil (referred to as SS) contained sand and kaolin only (Sigma-Aldrich, St Louis, USA). This exposure matrix was adapted from the OECD guideline as the composition was modified by not introducing Sphagnum peat to avoid sorption competition of CLD. The second soil (referred to as DARCO) and the third one (referred to as ORBO) were based on SS, and they were amended respectively by a 2% mass (dry basis) of DARCO[®] (Sigma-Aldrich, St Louis, USA) and ORBO[™] (Sigma-Aldrich, St Louis, USA) activated carbons. All the three soils were spiked with 100 µg of CLD (Kepone, Supelco, Sigma-Aldrich, Saint-Louis) per gram of dry matter (DM). CLD was spread over soil as a methanol:water solution (20:80; vol:vol; methanol:water). After spiking, solvent traces were evaporated under an extractor hood overnight. Then, artificial soils were moistened with milliQ water to reach 17,5% mass of humidity (wet mass basis). All soils were stored at 20 °C in amber glass vials during 3 weeks of maturation prior to the first day of CLD- ingestion (day 1).

Table 35 - Composition of the different artificial soils and treatment of the experiment

	Sand	Kaolin	Activated carbon	Activated carbon	Chlordecone	Time of maturation,
	See Sand (Carl Roth GmbH, Karlsruhe, Germany)	(Sigma-Aldrich, St Louis, USA)	DARCO [®] (Sigma-Aldrich, St Louis, USA)	ORBO [™] 32 (Sigma-Aldrich, St Louis, USA)	Concentration (µg.g ⁻¹ of DM) (Sigma-Aldrich, Supelco)	In days
Standard soil (SS)	77,8%	22,2%	–	–	100	21
Soil with DARCO [®]	76,2%	21,8%	2%	–	100	21
Soil with ORBO [™] (AC)	76,2%	21,8%	–	2%	100	21

Percentages are DM basis of artificial soil

2.2.2 AC feed supplementation preparation

Two of the three piglet groups exposed to CLD via SS were additionally fed with dough balls containing one of the two ACs: ORBO[™] or DARCO[®]. A mass of AC corresponding to 0,5% of the ration of piglets was introduced in additional dough balls. This mass was chosen according to daily ingested quantities of such materials when feeding animal with commercial AC-enriched feed when applied to prevent gastro- intestinal disorders of animals (Chu et al, 2013a, b). Those

AC-enriched dough balls were given to piglets at the same time as CLD contaminated ones (which did not contain any initial AC amendment).

2.2.3 Activated carbons characterization

Specific surface areas (SSA) of both commercialized ACs, ORBO™, and DARCO® were measured at the LIEC laboratory (LIEC, Vandœuvre-lès-Nancy, France). The measurements were performed on the basis of nitrogen adsorption-desorption volumetry at liquid N₂ temperature of 77 K (− 196 °C), Nitrogen adsorption-desorption isotherms were recorded on a Belsorp-mini II set-up (BEL Japan, Inc). The device is equipped with pressure sensors in the range 0–133 kPa.

After outgassing the samples at 30 °C during 12 h under a residual vacuum of 0,01 Pa, nitrogen adsorption-desorption isotherms (i.e., volume of nitrogen adsorbed at 77 K vs, relative pressure P/P_0 , where P is the equilibrium pressure of the adsorbing gas at that temperature and P_0 is the vapor saturation pressure) were performed using a step-by-step method in the interval of relative pressures, P/P_0 , extending from 10^{-5} to 0,98. All experiments were carried out with ultra-pure nitrogen (> 99,9995%). The Brunauer–Emmet–Teller (BET) method was used to estimate the SSA, using a 16,3 Å cross-sectional area of nitrogen molecules (Brunauer et al, 1938). The De Boer method (or t-plot, De Boer et al, 1965) was carried out to determine microporous volume and external surface area. Micropore filling happens at low and very low relative pressure values, and then includes the domain of the monolayer adsorption on external surface. To be able to distinguish adsorption onto external surface from adsorption into the micropores (pore size < 20 Å), the experimental isotherm is compared with a reference curve obtained for a non-porous solid, with chemical features and energetic constant as close as possible to the studied matrix.

2.4 Piglet sample collection and chemical analysis of biological matrices

After 10 days of exposure, piglets were anaesthetized by electronarcosis followed by immediate exsanguination, Pericaudal adipose tissue and liver were collected, stored at − 20 °C, and freeze-dried, Then, liver samples were analyzed for dry matter (DM) by desiccation (103 °C, 48 h).

The CLD Quantification was performed on both of these biological matrices using liquid chromatography-tandem mass spectrometry (LC-MS/MS) by following the analytical method “ANSES PBM Pest LSA-INS-0164 v5” which was initially developed by the French Agency for Food, Environmental and Occupational Health and Safety (ANSES, national reference laboratory, Maisons-Alfort Laboratory for food safety). This methodology is the current regulatory analytical reference used in France (French Ministry of Agriculture 2015) to control CLD in

foodstuffs in line with the maximum residue levels established in European regulation (Commission of the European Communities 2008). This methodology was described in Yehya et al, (2017) and was performed by the Departmental Analytical Laboratory of Morbihan (LDA 56, Saint-Ave, France). The limit of quantification (LOQ) was 2,0 µg CLD kg⁻¹ in these matrices.

Briefly, prior to the extraction step, a ¹³C (¹³C⁸C₂Cl₁₀O, Azur-isotope, Marseille, France, 98% of purity) internal standard of CLD was added to subsamples. Briefly, biological matrices were extracted sequentially. (i) For adipose tissue, 0,5 g of sample were added to 3 ml of a mix of acetonitrile and dichloromethane 75:25 (v:v). After centrifugation (1200×g, 20 min at - 20 °C), the supernatant was extracted. This extraction was performed 2 times. Then, the solvent was evaporated at 40 °C under a nitrogen flux until dry. A mix of 15 ml of hexane/acetone 85:15 (v:v) was then added. (ii) For liver, a sample of 2 g was used. Ten milliliters of hexane:acetone 85:15 (v:v) was added to the sample, which was then grinded using Ultraturrax® (10 000 rpm, 1 min, S25N-10G). After mixing (Vortex® apparatus) and centrifugation (750×g, 3 min), the supernatant was collected.

An alkalization step followed by an acidification step were performed to obtain CLD hydrate and to reform CLD, as described elsewhere (Bordet et al, 2007). Analytical grade sodium hydroxide solution (addition of 5 mL of 0,5 M NaOH aqueous solution to supernatant). After a mixing procedure (Vortex® apparatus) and centrifugation (750×g, 3 min), the supernatant was collected. This step was repeated two times.

The resulting aqueous phase was washed with 5 mL hexane to eliminate fat. The supernatant was collected after centrifugation (750×g, 3 min). CLD was reformed through acidification of the solution by means of sulfuric acid (5 mL of 60% solution). A second extraction phase was carried out with hexane:acetone (5 mL of 85:15 v/v), followed by mixing (Vortex® apparatus) and centrifugation (750×g, 3 min). This extraction step was repeated 3 times. The organic phase was then rinsed with 2 mL of water, before being subsequently evaporated until dry and 1 mL of methanol was then added.

Separation of CLD was achieved using a Phenomenex Aqua C18 column (150 × 2,0 mm 3 µm) and a precolumn Phenomenex Aqua C18 (4 × 3,0 mm). Two phases were used to perform the separation step: water with 0,1% formic acid (A) and methanol with 0,1% formic acid (B). Five microliters of sample was injected per run and the flow was set to 200 µl/ min. After separation, a rinse sequence using acetonitrile was performed. Quantitation by isotope-dilution was performed on API 5500. Parent ions (PI) and child ones (CI) were used to respectively quantify (507/427 Da;

PI/CI) and quantify (509/ 429 Da; PI/CI) ^{12}C CLD and quantify (517/436 Da; PI/CI) ^{13}C CLD.

2.5 Data analyses

2.5.1 Quality control

In order to optimize the precision of measurements, Belsorp-mini II device is regularly controlled against TiO_2 reference material (Community Bureau of reference, $\text{SSA} = 8.23 \pm 0.21 \text{ m}^2 \text{ g}^{-1}$). Experimental error is estimated to $0,50 \text{ m}^2 \text{ g}^{-1}$,

CLD quantification in animal tissues was carried out in strict accordance with the COFRAC (French Quality Accreditation Committee) quality accreditation of LDA 56. Values below LOQ ($2.0 \mu\text{g kg}^{-1}$ of dry matter) were replaced by LOQ value in the data set.

2.5.2 Tissues concentrations of CLD

In order to assess the impact of ACs on CLD bioavailability, an analysis of variances was performed. The experimental unit was the piglet. Concentrations of CLD in adipose tissue and liver were compared between the five treatment groups SS versus ORBO or DARCO brought either via amended soil or supplemented feed using the ANOVA procedure and the Tukey–Kramer post hoc test of R version 3,2,3 (R Foundation for Statistical Computing, Vienna, Austria). Differences were considered significant at $P < 0,05$.

2.5.3 Relative bioavailability (RBA) factor calculation

The relative bioavailability (RBA) was used as “the comparative bioavailabilities of different forms of a chemical or for different exposure media containing the chemical (e.g., bio- availability of a chemical from soil relative to its bioavailability from water) and is expressed as a fractional relative absorption factor” (NEPI 2000). Statistical analyses were carried out using R (version 3.2.3, R Foundation for Statistical Computing) on CLD concentration using the package agricolae (de Mendiburu 2019). Each piglet was considered as an experimental unit. A 95th confidence interval of concentrations was calculated as described elsewhere (Shafer and Zhang 2013, p, 318).

The RBA was calculated by dividing “CLD concentrations in one tissue (liver or adipose tissue) after one treatment (DARCO[®] or ORBO[™]) either in soil or in feed” by “CLD concentrations obtained in the same tissue after SS treatment (100% reference),” adapted from a method previously described (Wittsiepe et al, 2007; Delannoy et al, 2014a; Yehya et al, 2017). Linearity between the CLD-dose of exposure and CLD concentrations in the organ was a prerequisite of this method (Littell et al, 1997). This linearity was demonstrated previously for CLD in piglets

(Bouveret et al, 2013).

The corresponding equation (1) to calculate RBA of CLD after one AC treatment in the liver is provided below (Yehya et al, 2017).

$$RBA_{AC\ treatment\ liver} = \frac{C^{\circ}_{AC\ treatment\ liver}}{C^{\circ}_{SS\ treatment\ liver}} \quad (1)$$

$RBA_{AC\ treatment\ liver}$: Relative bioavailability of CLD after one AC–treatment in the liver

$C^{\circ}_{AC\ treatment\ liver}$: CLD concentration in liver after one AC treatment

$C^{\circ}_{SS\ treatment\ liver}$: CLD concentration in liver after one SS treatment

As each part of the division comprises uncertainties, a 95th confidence interval of the RBA factor was calculated via the propagation of uncertainty rule (Ku 1966), The corresponding equation (2) is provided above:

$$\frac{\Delta_{RBA}}{RBA} = \frac{\Delta_{C^{\circ}_{AC\ treatment}}}{C^{\circ}_{AC\ treatment}} + \frac{\Delta_{C^{\circ}_{SS\ treatment}}}{C^{\circ}_{SS\ treatment}} \quad (2)$$

Δ_{RBA} : Relative uncertainty of relative bioavailability after one AC–treatment

RBA: Relative bioavailability

$\Delta_{C^{\circ}_{AC\ treatment}}$: Relative uncertainty of concentration found in one tissue after one AC–treatment

$C^{\circ}_{AC\ treatment}$: CLD concentration after one AC treatment

$\Delta_{C^{\circ}_{SS\ treatment}}$: Relative uncertainty of CLD concentration found in one tissue after SS treatment

$C^{\circ}_{SS\ treatment}$: CLD concentration found in one tissue after SS treatment

2.5.4 Calculation of the transfer reduction factor

A factor of CLD transfer reduction by AC was determined as the ratio between concentrations obtained after SS treatment and concentrations obtained using ORBO™ and DARCO® bought either via soil amendment or in feed, in the same biological matrix. In order to be conservative, this factor was minimized using the lowest and highest values of the 95th confidence interval of concentrations of CLD. Details of the calculations are provided below using concentrations of CLD in liver (eq.3):

$$R_{AC\ treatment\ liver} = \frac{Min_{95} C^{\circ}_{AC\ treatment\ liver}}{Max_{95} C^{\circ}_{SS\ treatment\ liver}} \quad (3)$$

$R_{AC\ treatment\ liver}$: factor of CLD retention by AC DARCO® using concentrations of CLD in liver

$Min_{95} C^{\circ}_{AC\ Treatment\ liver}$: lowest value of 95th confidence interval of CLD concentration in liver

with DARCO[®] treatment

Max₉₅ C^o_{SS} treatment liver: highest value of 95th confidence interval of CLD concentration in liver with SS treatment.

5. Results

The impact of these two microporous ACs to limit CLD contamination of piglets' organs through two contrasted strategies (to provide AC via incorporation in feed or via soil amendment) was assessed. Then, the identification of the two ACs surface microstructure through inert gas adsorption such as N₂ was a prerequisite to determine their SSA (Sing 1982).

5.1 Determination of CLD concentration in biological matrices and CLD relative bioavailability (RBA) calculation

CLD concentrations in biological matrices showed important differences between the treatment groups as presented in figure 36.

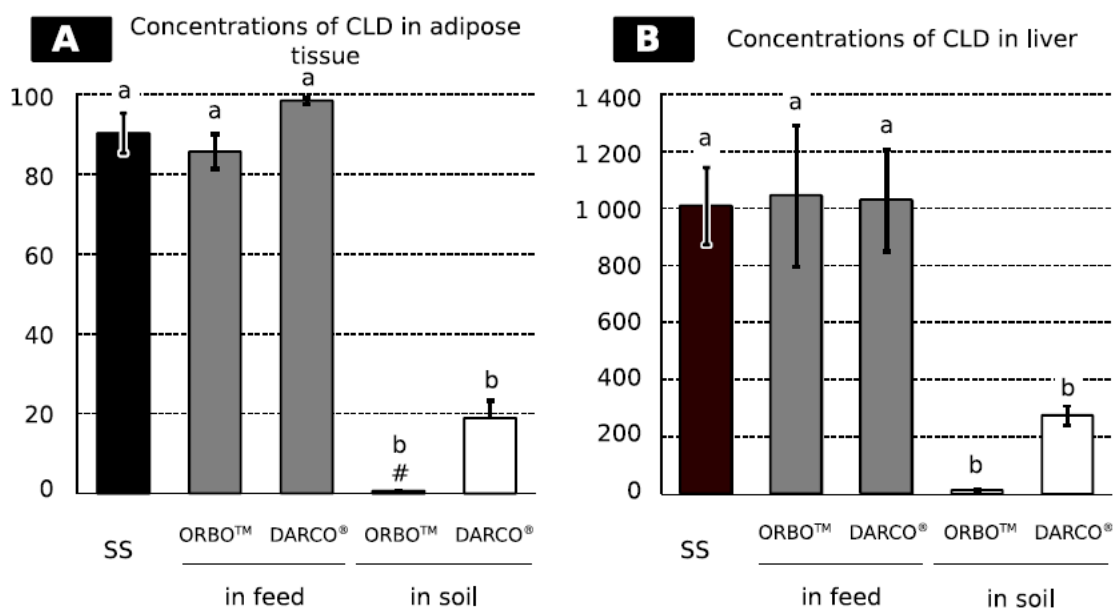


Figure 36 - Concentrations of CLD in biological matrices (ng of CLD per gram of DM). Values correspond to the mean \pm SD (n = 4). Mean values with different superscript letters (a, b) are statistically different (P < 0.05). Statistical analysis was performed using the two-way ANOVA procedure of R software and Tukey post hoc test. Two effects were used in the model: AC (none, ORBO, and DARCO) and strategy of sequestration (none, in feed, in soil). Both effects were significant (P < 0.0001) and (RMSE = 6.97 for adipose tissue) and RMSE = 530 (n = 4), Interaction effect was not significant (P > 0.10). RMSE, root means square error, # values are below limit of quantification.

As expected, one of the highest CLD concentrations was obtained in the SS group (control) for both matrices: 90 ± 5 ng g⁻¹ of DM (adipose tissue; mean \pm SD) and 1010 ± 103 ng g⁻¹ of DM (liver; mean \pm SD). Interestingly, similar levels as SS group were found in both groups where ACs

were introduced into the feed, regardless the type of AC used (for ORBO™: 86 ± 4.4 and 1040 ± 250 ng g⁻¹ of DM for adipose tissue and liver respectively; for DARCO®: 98 ± 0.8 and 1030 ± 180 ng g⁻¹ of DM for adipose tissue and liver respectively (Figure 36). In contrast, significantly lower CLD concentrations were obtained in organs when animals were exposed to DARCO® soil: 18.9 ± 4.3 ng g⁻¹ of DM (adipose tissue; mean ± SD); 276 ± 35 ng g⁻¹ of DM (liver; mean ± SD), and the lowest CLD concentrations were found when piglets were exposed to ORBO™ aged soil resulting in non-quantifiable levels in adipose tissue (< 2 ng/g DM) and 13.7 ± 1 ng g⁻¹ DM in liver (mean ± SD) (Figure 36). Further investigation using a post hoc Tukey test demonstrated that treatment groups from strategy of sequestration by amendment of soil were distinct from the other ones (P < 0.001). The ANOVA analyses revealed a significant strategy effect (Figure 36) for all biological matrices (P < 0.0001). The activated carbon effect was significant in adipose tissue demonstrating a significant difference between DARCO® and ORBO™; (P = 0.006). This significance was not achieved in liver (P = 0.11).

Secondly, the RBA factors were calculated in order to estimate the CLD bioavailable fraction depending on the following treatments: ORBO™ or DARCO®, incorporated either in piglet feed or directly in a contaminated soil. Statistical analyses were performed to obtain 95th confidence interval as presented in Table 36. Concerning “Feed-ACs” groups, RBA was not different from 100% (Table 36) as concentrations found in organs for these both treatments did not statistically differ from SS group (Figure 36 a, b). For “soil-ACs” groups compared with SS, the DARCO® treatment showed RBAs of 21.0% and 27.4% (respectively from adipose tissue and liver), whereas the ORBO™ treatment revealed RBAs of 0,7% (maximum value from adipose tissue) and 1,4% (liver) (Table 36). Overall, similar RBA factors were obtained for adipose tissue and liver within each treatment group (Table 36). At last, in order to assess the CLD sequestration efficiency by ACs during the digestive processes, a sequestration factor was calculated representing a conservative proportion of the CLD retained by the ACs during digestive processes (Table 36). DARCO® exhibited a reduction of 64% (adipose tissue) and 63% (liver tissue) (Table 36). ORBO™ displayed a greater reduction of 85% (adipose tissue; based on LOQ) and 86% (liver) (Table 36).

Table 36 - Relative bioavailability factors

	Adipose tissue	Liver
1. Relative bioavailability factors of CLD in biological matrices (% and 95th confidence interval)		
ORBO™ in feed	100% [#]	100% [#]
DARCO® in feed	100% [#]	100% [#]
ORBO™ in soil	0.7% [□] (NA)	1.4% (1.0–1.8%)
DARCO® in soil	21.0% (13.5–28.34%)	27.4% (14.7–40.1%)

2. Reduction factor (%)

ORBO™ in feed	0%#	0%#
DARCO® in feed	0%#	0%#
ORBO™ in soil	85%	86%
DARCO® in soil	64%	63%

Values in parenthesis indicate 95% confidence interval ($3.18 \times SE$). SE were calculated via propagation of errors formula ($n = 5$). Reduction factor are calculated as described in material and method section

5.2 Characterization of activated carbons

The isotherms obtained from N₂ adsorption-desorption on ORBO™ and DARCO® are shown on Figure 37.

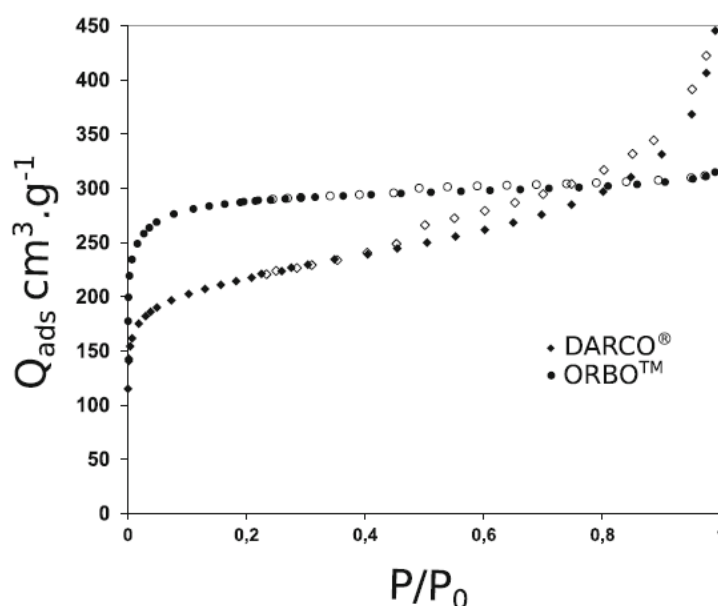


Figure 37 - Adsorption isotherms of nitrogen gas on ORBO™ and DARCO® activated carbons at 77 K, Adsorption of N₂ was performed at 77 K on a Belsorp-mini II device (BELJAPAN, Inc Chemicals, JAPAN). Both isotherms exhibit a type IV profile according to the IUPAC classification, Q_{ads}, quantity of N₂ adsorbed on activated carbon (cm³ g⁻¹)

As depicted in figure 37, the isotherm obtained from gaseous sorption on ORBO™ was characterized by a rapid increase at low relative pressure values (in the domain of $P/P_0 < 0.1$), indicating an instantaneously monolayer coverage of micropores (Sing 1982). By contrast, the latter observations suggest that the isotherm reaches a plateau with only little adsorption occurring after micropore filling, Therefore, according to the IUPAC classification, the isotherm from ORBO™ exhibited a typical type I profile (Sing 1982). This is characteristic of microporous adsorbents with a monomodal pore size distribution which is dominated by an average pore diameter below 2 nm (Sing 1982). The isotherm obtained from DARCO® also exhibited type I characteristics (fig.3), indicating a micropore-dominant microstructure (Sing 1982). However, the larger quantity of adsorbed N₂ at higher relative pressure values (i.e., in the domain of $P/P_0 > 0.8$, Figure 37) suggests a transition from a monolayer to a multilayer gaseous adsorption phenomenon (and probably N₂ capillary condensation into wide pores (Branton and Bradley 2010)).

Hence, the total SBET and pore volume of ORBO™ reach 1130 m² g⁻¹ and 260 cm³ g⁻¹ respectively (Table 37). These values were about 1,4 times higher than those of DARCO®, which presented a total SBET of 790 m² g⁻¹ and a pore volume of 180 cm³ g⁻¹ (Table 37). As DARCO® and ORBO™ presented typical characteristics of microporous media as defined in IUPAC classification (Sing 1982), the t-plot method was secondly used to distinguish the relative part of the total surface due to micropores in these both matrices (de Boer et al, 1966). ORBO™ presented a higher surface of microporosity (970 m² g⁻¹, 85% of the total surface) than DARCO® (490 m² g⁻¹, 58% of the total surface) (Table 37). These differences in surface porosity could be explained by a greater N₂ adsorption onto the external surface of the DARCO® AC in comparison with ORBO™.

Table 37 - Adsorption characteristics of the ACs

	BET surface area	Total pore volume	Total surface	Microporosity surface	Non-microporous surface
	m ² g ⁻¹	cm ³ g ⁻¹	m ² g ⁻¹	m ² g ⁻¹	m ² g ⁻¹
DARCO®(AC)	793.8 ± 14.5	181.6	829.9	486.8	382.1
ORBO™ (AC)	1126.3 ± 11.9	257.7	1136.3	971.8	242.4

6. Discussion

1.1 Ineffectiveness of the AC feed supplementation strategy

As expected, the highest concentrations of CLD in tissues were found in the SS group. This result is in accordance with previous data obtained with the same soil and for different organic pollutants (Delannoy et al, 2014a, b) and CLD (Yehya et al, 2017). Compared with SS, the feed supplementation strategy (Feed-ACs) was not effective to reduce CLD transfer from soil to piglets. Two main assumptions could explain this absence of sequestration:

–The administration of ACs via feed was performed right after the CLD exposure of piglets to favor the contact between ACs and CLD. As no reduction of CLD transfer to piglet was observed, the contact time between the CLD and ACs in the intestinal lumen was probably too short to allow the CLD adsorption on ACs.

–As recently shown by Wang et al, (2016) with Polychlorinated Biphenyls in bi-solute and chemical mixture systems, competition may occur for sorption sites on porous carbonaceous matrix, as well as pore filling mechanisms by non-target organic compounds. As feed components and digestive enzymes are abundant in the gastro- intestinal chyme, such competition process could limit the CLD adsorption effectiveness of ACs in the digestive tract.

These both parameters, contact time, and competition, may have synergistically alleviated

adsorption (Knettig et al, 1986) of CLD in digestive compartments.

1.2 Efficiency of the AC soil amendment strategy to limit

When using the soil amendment strategy, CLD remained mainly adsorbed on ACs during the digestive processes. It has to be recalled that the duration of contact between ACs and CLD in soil was of 21 days (i.e., a much longer time than the digestive process in piglets which is not longer than 24 h). Adsorption of CLD onto ACs appears to be of particular efficiency even if differences between both ACs could be showed. Indeed, the characteristics of ACs used are of particular importance. In the present study, physical characteristics of ACs clearly show that both ACs exhibit a microporosity which could be characterized by the narrowness of their pores (< 2 nm). This particular narrow pore range matches the size of CLD (i.e., 0,652 nm) (Durimel et al, 2013). It should be expected a highly effective entrapment of this hydrophobic organic contaminant, potentially resulting in greater CLD sequestration with ORBO™ compared with the use of micro- to mesoporous DARCO®. This element is in line with RBA results, as the most important CLD RBA limitation was obtained with the highly microporous coconut shell-derived ORBO™ AC (Figure 36 a, b), whereas a less efficient retention was obtained from DARCO® AC. This latter AC comprises a substantial part of meso- to macro- are less effective in limiting contact with the chyme.

Mechanistically, this sequestration of CLD by ACs resulted from adsorption of this POP onto ACs surface. This adsorption relies on physico-chemical weak bindings between chemical functions of CLD and the surface of AC. Such mechanism is also depicted when a POP is adsorbed onto different soil organic matters (Woignier et al, 2012; Ahmad et al, 2014; Delannoy et al, 2014b). It has been theorized that physico- chemical interactions between sorbent media and the pollutant could likely be disrupted along the digestive tract course due to the peculiar variation of conditions in the distinct gastro- intestinal compartments (such as pH, chemical and enzyme activities, and micellar formation). This ultimately leads to a release of POPs and their solubilization of organic contaminants in the chime (Delannoy et al, 2014b). Due to the particular binding of POPs on ACs and its structure, such a release should be very limited.

When AC was incorporated in feed, there was no reduction of CLD transfer to piglets. In contrast, when AC were amended to soil major reductions in CLD concentrations were found in piglet adipose tissue or in livers. Thus, relative bioavailability reduction factors varied from 63 to 86% in liver and 64 to 85% in adipose tissue for DARCO® and ORBO™, respectively,

The coconut shell AC efficiency (i.e. ORBO™) to immobilize CLD was of particular interest since

coconut shell is a low-cost and renewable AC source especially abundant in the French West Indies (Arsène et al, 2013), by contrast with conventional raw material of degraded plant matter like peat (i.e. DARCO® precursor). Then, the implementation of a CLD sequestration strategy based on local biomasses may be a real remediation alternative.

It has to be noticed that the interesting results obtained in artificial soils may not be representative to the soils found in French West Indies (volcanic and tropical). Indeed, the contamination in antillean soils is ancient: 30 years. So, the residual chlordecone retained in tropical soils may not be easily available for adsorption onto ACS surface like in our experience, The pore features (specific surface area and pore size) of the volcanic clay could limit the chlordecone adsorption to the ACs surface. Therefore, this experiment should also be performed in in situ conditions.

2. Conclusions

Overall, this study gives interesting insight in the area of the CDL sequestration by ACs. In the study, it can be noticed that a significant decrease of CLD concentrations in liver and adipose tissue was observed when the soil was amended by ACs. This decrease was particularly important for the coconut shell activated carbon where relative bioavailability was found lower than 1,8% for both tissues. In contrast, no reduction of relative bioavailability was noticed when ACs were introduced directly in the feed.

CHAPTER 3: GENERAL DISCUSSION

PART 1: Transfer patterns in food safety risk assessment approaches

Nowadays, it is admitted that 90% of chronic human exposure to POPs occurs through food products (Çok et al., 2009; Hoogenboom et al., 2015; Polder et al., 2010; Rodríguez-Hernández et al., 2015). Food of animal origin is a predominant source of human exposure to POPs (Malisch and Kotz, 2014) especially such families as PCDD/Fs, PCBs and OCPs due to their high bioaccumulation in fatty tissues and high persistency as was described in the literature synthesis (Chapter 1). The contamination of such food is directly related to daily ingestions of farm animals including different feed ingredients and even contaminated soil, especially in free-ranged animals (laying hens, dairy cattle). Control of POP presence in feed for animals and food of animal origin is usually included in governmental monitoring, and legislation defines maximum tolerable concentrations of the concerned compounds in these matters. Indeed, numerous countries defined maximum residues levels (MRL), which established a maximum tolerable concentration of POPs, which has shown to be safe for human health. However, such MRLs do not cover the POPs presence in soil, which could have much higher concentrations compared to feed due to its strong affinity and retention of these contaminants (Chapter 1, part I). Indeed, results of this study and many others also indicated a high bioavailability of soil borne POPs for livestock animals such as dairy cows, goats, pigs and poultry and lead to bioaccumulation in tissues and to excretion with milk or eggs (Amutova et al., 2021b; Collas et al., 2019; Delannoy et al., 2020c; Feidt et al., 2013; Jondreville et al., 2013; Jurjanz et al., 2017, 2014).

On the one hand, MRL is a threshold over which contaminated products are completely excluded from the market, and further identification and elimination of the source on the farm are performed.

On the other hand, determining the concentrations of POPs in a contaminated area would make it possible to overestimate the risk of contamination due to many factors which could create high variabilities such as the analytical method of detection, source and type of contamination, animal species, grazing conditions, and animal productivity. The meta-analysis carried out in the framework of this thesis (Chapter 2, part I) reviewed transfer of different POPs to different food of animal origin and showed that transfer data of PCDD/Fs and PCBs are very solid and included different species, rearing systems and exposure conditions compared to OCPs. OCPs transfer data are limited by a few studies with hens (Aulakh et al., 2006; Tao et al., 2009b) and yak (Pan et al., 2014b) achieved in field (non-controlled) conditions and as consequence create a high variability. Thus, OCP transfer to farm animals requires a cautious attention in risk assessment and a higher

human protection measures. Therefore, an integrative approach in assessing exposure situations with POPs pollution on farms are necessary.

The degree of risk can be assessed by a backward calculation from MRLs (considered as safe threshold) via animal rearing systems and permissible exposure via feed (regulation threshold) to the maximum permissible concentration in soil. MRL together with transfer coefficients such as TR and BCF could be used to minimize the uncertainties related with risk assessment studies. This approach depends on the preciseness of available transfer data and could allow to estimate the concentrations of pollutants as precise as possible (or to establish security factors which would multiply the risk). Knowledge of exact quantity of pollutant which would transfer from total ingested matrix to the final food product allow to classify farm production systems depending on their sensitiveness (security factor) if there would be a contamination situation. By consequence, the overestimation due to increased security factors when parameters are imprecise would be restrained, allowing to limit economic and social consequences in a situation of a pollution incident but while ensuring a perfect protection of the consumers. Therefore, the precise establishment but also the efficient reduction of bioavailability of pollutants can be considered as the main way to manage a situation in a contaminated area.

Thus, we simulated the transfer risk for different POPs in different farm animals. This modelization has been built in respect to European MRLs (Commission Regulation (EC) No 149/2008, 2008) for feed, milk, eggs and different edible animal tissues as presented in tables 38-40. The most toxic POPs such as TCDD/Fs, DDT and lindane were chosen as examples. This simulation was built based on the estimated transfer coefficients (TRs) for milk and eggs as well as BCFs for body tissues taken from (Amutova et al., 2021; Hoogenboom et al., 2015). Then, the maximal amount of daily ingested polluted matrix was calculated especially soil, which allows to respect the MRL in the foodstuff.

These modelizations distinguish two breeding systems: low and high productivity for two animals with daily excretion: dairy cows and laying hens. Moreover, different zootechnical parameters were fixed such as classical daily feed intake (Dong et al. 2017, Grant et al. 2001, Fries et al. 1999) and daily soil intake (Jondreville C. et al., 2010b; Jurjanz S. et al., 2012) of dairy cows and hens for reliable estimation. This approach (table 38 and table 39) allowed to:

- 1) Express quantitatively the intake amount of POP per kg fresh milk or per 1 whole egg. This value is calculated through the proportion of MRLs in a given food product and correspondent TRs derived from our meta-analysis (Amutova et al., 2021)

- 2) Quantitatively estimate the maximum permissible daily ingested amount of POP entered via total ration for two breeding system
- 3) Quantitatively estimate permissible daily ingestion of POPs via soil and maximum permissible concentration in soil based on soil intake of dairy cows and laying hens.
- 4) Calculate a security factor indicating the multiple between the POP concentration in soil before overpassing MRLs in food products (i.e. the higher the value of security factor the safer the product).

Table 40 presented data of the same approach but related to animals such as broilers, pigs, lamb and cattle producing tissues edible for human consumption as meat or offals. As in previous approach, we integrated classical daily feed and soil intake for these animals which were derived from a correspondent literature (Fries G., 1999; Jurjanz, 2011; Kemm E., 1988; Rodríguez et al., 2008; Rose et al., 2012) to calculate permissible concentration of POPs in soil (table 3).

Results of these simulations showed that soil ingestion is a very important factor, which has to be taken into account during risk assessment of POP exposure on livestock farms. Indeed, extrapolation of established EU MRLs of TCDD/F, DDT and lindane for feed and food and estimated TRs (table 38) or BCFs (table 40) showed several observations:

1) In the field conditions of POP exposure, low productive dairy cows and laying hens may be more susceptible to uptake through the soil than high-yielding animals (Table 39), even if the feed would respect MRLs. Negative values of permissible concentration of POP in soil as well as security factors indicated on the vulnerability of low-producing livestock, and, accordingly, the danger of consuming milk or eggs (Table 39). This could be explained by higher bioaccumulation of pollutants in their body due to slow depuration processes as consequence of low excretion (Jurjanz et al., 2018). One of the most toxic cancerogenic dioxin congener TCDD showed the lowest safety factors for both animal rearing systems with values -16 and -3 for low and high lactating cows as well as -4 for hens with production of 2 eggs per week. OCPs such as DDT (-1 and 2) and lindane (-3 and 1) showed also very low safety factors for low productive and high productive hens, respectively.

2) Risk assessment of meat producing animals (broilers, pigs, lamb, cows) showed that the most sensitive edible tissues and organs are liver, muscle and fat (table 40). Despite on a positive value of permissible concentration of POP in soil, these groups of animals is also under the high risk of POP contamination and therefore could produce contaminated edible tissues. In case of soil ingestion, the safety factors could vary between -20 to 29.

3) Soil should be considered as the main POPs carrier in the case of contamination situation on the farm. Indeed, water media is a weak vector of POPs and contaminated vegetation could be

easily removed from such areas. The management of contaminated soil could be the main problem: soil may accumulate a lot of POPs for long time which are hardly possible to remove from the areas.

Soil ingestion should be considered as a limiting factor when animals raised within intensive breeding system. If this parameter would be controlled in such conditions therefore it allow to minimize the risk of overpassing MRLs.

However, control of soil ingestion in breeding system of free-range animals is not practically reasonable. Detection of POPs levels in foodstuffs (both animal and vegetable origin) exceeding the threshold values leads to the immediate termination of animal husbandry in the contaminated area.

In case of moderately overpassed MRLs, a strategy to reduce the bioavailability and by consequence transfer of POPs from soil to animals could be applied. Therefore, it may be useful to implement an application of sequestration materials such as ACs or BCs. Consequently, this approach would allow to derive safe levels in the soil to sustain various livestock systems in exposed areas.

Even a relatively low concentration of POPs in soil may lead to contaminations close to MRLs in food of animal origin (Tables 39 and 40). Therefore, the efficiency of sequestration based on AC/BCs applications on contaminated soils to reduce POP bioavailability to livestock animals should be investigated in the context of pollution management.

Table 38 – Zootechnical parameters of adult animals with depuration excretion (dairy cows and hens) to perform risk assessment associated with transfer of POPs from feed to food of animal origin

Food product	POP	EU MRLs, fat of food product ³	EU MRLs, fresh matter of food product ⁴	EU MRLs for feed ⁵	TR (%) ⁶	Intake amount of POP ⁷	Low productive animals ¹			High productive animals ²		
							Maximum permissible daily ingested amount of POP respecting MRL ⁸	Daily feed intake, kg/day ⁹	Daily amount of ingested POP via feed ¹⁰	Maximum permissible daily ingested amount of POP respecting MRL ⁸	Daily feed intake, kg/day ⁹	Daily amount of ingested POP via feed ¹⁰
Cow milk	TCDD/F	3 ng/kg	0.12 ng/kg	0.75 ng/kg	34	0.35 ng/kg	1.76 ng/day	10	7.5 ng/day	17.6 ng/day	25	18.8 ng/day
	TCDD/F	3 ng/kg	0.016 ng/kg	0.75 ng/kg	40	0.04 ng/egg	0.06 ng/day	0.1	0.075 pg/day	0.19 ng/day	0.1	0.075 pg/day
Hen eggs	DDT	50 µg/kg	0.27 µg/egg	50 µg/kg	14	1.90 µg/egg	2.9 µg/day	0.1	5.0 µg/day	8.9 µg/day	0.1	5.0 µg/day
	Lindane	10 µg/kg	0.054 µg/egg	10 µg/kg	22	0.25 µg/egg	0.37 µg/day	0.1	1.0 µg/day	1.1 µg/day	0.1	1.0 µg/day

1 – Low productivity animals: 5L/day for dairy cows and 1.5 g yolk fat/day (or 2eggs/week) for hens.

2 – High productivity animals: 50 L/day for dairy cows and 4.5 g yolk fat/day (or 6 eggs/week) for hens.

3 – European Union Maximum residual levels (MRLs), expressed in ng WHO TEQ/kg fat for TCDD/F and in µg/kg fat for OCPs.

4 – MRLs fresh matter was achieved through multiplying MRLs on 0.04 kg fat (per 1 kg cow milk) or on 0.0054 kg fat per 1 egg. Values of fat milk and fat yolk were derived from Jensen et al., 1991 and Amutova et al., 2021, respectively.

5 – MRLs of dairy cow feed was based on feed of plant origin and derived from directive 2006/13/EC (for PCDD/Fs) and MRLs of hen feed was based on cereals and derived from regulation (EC) 149/2008 (for DDT) and from regulation (EU) 2017/978 (for lindane).

6 – TR (%) - transfer rate corresponds to transfer of POP from ingested matter to food product) and derived from Amutova et al. 2021.

7 – Intake amount of POP was estimated by proportion of MRL in fresh matter and TR (%).

8 – Maximum permissible daily ingested amount of POP (total ration) was calculated by multiplying the ingested amount of POP (achieved through TR) on animal productivity (L/day or yolk fat/day) for cattle and hens.

9 – Daily feed intake (kg/day) was established according to Dong et al. 2017 (laying hens), Grant et al. 2001 and Fries et al. 1999 (dairy cattle).

10 –Daily amount of ingested POP via feed was calculated by multiplying daily feed intake (kg/day) on concentration of POP in feed.

Table 39 – Risk assessment of livestock exposed by POPs through soil ingestion using EU MRLs (maximum residual levels) and TRs (transfer rates)

Productivity	Type of animals	POP	Permissible daily ingested amount of POP via soil respecting MRL ¹	Daily soil intake (kg/day) ²	Permissible concentration of POP in dry soil ³	Detected concentration of POP in dry soil ⁴	Security factor ⁵	Risk to overpass MRL
Low productivity	dairy cows	TCDD/F	-5.7 ng/day	1	-5.7 ng/kg	0.36 ng/kg	-16	unavoidable
		TCDD/F	-0.014 ng/day	0.01	-1.4 ng/kg	0.36 ng/kg	-4	high
	laying hens	DDT	-3.1 µg/day	0.01	-0.3 µg/kg	250.0 µg/kg	-1	high
Lindane		-0.75 µg/day	0.01	-0.07 µg/kg	24.0 µg/kg	-3	high	
High productivity	dairy cows	TCDD/F	-1.1 ng/day	1	-1.1 ng/kg	0.36 ng/kg	-3	high
		TCDD/F	0.11 ng/day	0.01	11.1 ng/kg	0.36 ng/kg	31	possible
	laying hens	DDT	3.87 µg/day	0.01	0.4 µg/kg	250.0 µg/kg	2	high
Lindane		0.13 µg/day	0.01	0.013 µg/kg	24.0 µg/kg	1	high	

1 - Permissible daily ingested amount of POP via soil was calculated by difference between maximum permissible daily ingested amount of POP and daily amount of ingested POP via feed.

2 - Soil intake (kg/day) was established according to Healy,1968 (dairy cows) and Jondreville et al., 2010 (laying hens)

3 - Permissible concentration of POP in soil is achieved from the ratio of permissible daily ingested amount of POP via soil to classical soil intake (kg/day)

4 - Detected concentrations in soil for PCDD/F and PeCDD were derived from Schuler et al., 1997 and Piskorska-Pliszczynska et al. 2014, respectively and converted to WHO TEQ ng/kg, for DDT and lindane were taken from Sailaukhanuly et al. 2016

5 - Security factor calculated by the ratio of permissible concentration of POP in soil to detected concentration of POP in soil (derived from the literature). Security factor express a number by which POP concentration in soil is multiplied in order to increase safety for consumed food products (eggs or milk).

Table 40 - Risk assessment of livestock exposed by POPs through soil ingestion using EU MRLs and BCFs (bioconcentration factors)

Animal	Edible tissues	POP	EU MRLs in animal tissue, fat basis	EU MRLs in animal tissue, fresh matter	BCF ¹	Max. permissible concentration of POP in exposure matter ²	Daily feed intake (kg/d) ³	Daily soil intake (kg/d) ⁴	MRLs in feed	Permissible concentration of POP in soil ⁵	Security factor ⁶	Risk of overpassing MRL
Broilers	muscle	DDT	1 µg/kg	0,03 µg/kg	17	0,18 µg/kg	0,07	0,005	0,05 µg/kg	1,9 µg/kg	11	High
		Lindane	0,01 µg/kg	0,0003 µg/kg	2	0,015 µg/kg	0,07	0,005	0,01 µg/kg	0,09 µg/kg	6	High
	liver	DDT	1 µg/kg	0,06 µg/kg	18	0,33 µg/kg	0,07	0,005	0,05 µg/kg	4,3 µg/kg	13	High
		Lindane	0,01 µg/kg	0,0006 µg/kg	2	0,03 µg/kg	0,07	0,005	0,01 µg/kg	0,3 µg/kg	10	High
		TCDD	6 ng/kg	0,36 ng/kg	43	0,84 ng/kg	0,07	0,005	0,75 µg/kg	2,1 ng/kg	2	High
		TCDD	2 ng/kg	0,06 ng/kg	20	0,3 ng/kg	0,07	0,005	0,75 µg/kg	-6 ng/kg	-20	unavoidable
Pigs	fat	TCDD	1 ng/kg	0,15 ng/kg	2	7,5 ng/kg	2,5	0,08	0,75 µg/kg	218 ng/kg	29	possible
Lamb	fat	TCDD	1 ng/kg	0,15 ng/kg	2	7,5 ng/kg	0,8	0,08	0,75 µg/kg	75 ng/kg	10	High
Cows	liver	TCDD	6 ng/kg	0,36 ng/kg	11	3,3 ng/kg	20	2	0,75 µg/kg	28,5 ng/kg	9	High

1- BCF – bioconcentration factor (unitless) derived from Amutova et al. 2021.

2- Maximum permissible concentration of POP in exposure matter which was estimated by proportion of MRL in fresh tissue and BCF.

3- Daily feed intake for chicken, pigs, lamb, and cows derived from Fries G., 1999; Grant & Albright, 2001; Jurjahz, 2011; Kemm E., 1988; Rodríguez et al., 2008.

4- Daily soil intake for chicken, pigs, lamb, cows derived from Healy, 1968; Jurjahz, 2011; McGrath et al., 1982; Rose M. et al., 2012.

5- Permissible concentration of POP in soil was calculated according to the following equation:

$$\frac{\text{Max.permiss.conc.POP in exposure matter} \times (\text{Daily feed intake} + \text{Daily soil intake}) - (\text{Daily feed intake} \times \text{MRL feed})}{\text{Daily soil intake}}$$

6- Security factor calculated by the ratio of permissible concentration of POP in soil to maximum concentration of POP in exposure matter. Security factor express a number by which POP concentration in soil is multiplied in order to increase safety for consumed food products (edible tissues)

PART 2: Sequestration strategy based on AC/BCs to reduce exposure to contaminated soil

1. Efficiency of sequestration strategy

Agricultural soil is a vital limiting resource on earth (Landscape solutions, 2022). In addition, soil is a source to produce food of animal and vegetable origin. Pollution of soils with POPs and other contaminants is one of the factors leading to its unsuitability for food production leading to a reduced availability of soils and represents one of the global problems (Rodríguez-Eugenio N et al., 2018; Weber et al., 2019). Therefore, restorage of food production ecosystem services is required especially in contaminated areas.

Livestock farms with moderate contamination level of soil could be restored and remained sustained when the exposure to contaminants can be efficiently reduced. The application of sequestration strategies based on AC or BCs can offer solutions in some cases. Indeed, it can be cautiously assumed that the AC/BC amendment can be effective in the case of moderate soil contamination according to values of permissible concentrations of soil estimated by risk assessment simulation (Tables 38 to 40). As example, the calculated permissible concentrations of DDT in soil ingested by high productive hens and broilers were ranged between 0.4 to 4.3 µg/kg dry soil and therefore, by using the proportion of derived reduction factors in soil (results of Chapter 2, Part IV), we could predict pollutant concentration ranges in soil for an effective application of sequestration strategy based on AC/BCs (Table 41). By 2% amendment rate of AC/BC added to the contaminated soil, it is possible to reduce the environmental availability of POPs in soil up to 90% immobilizing it in soil and thus reduce its further transfer to food producing animals without endangering food safety.

Table 41 – Effectiveness of sequestration strategy in application of soil exposed to DDT and its metabolites

SMs	SM dose (DM, %)	Reduction factor (%) in soil*					Concentration ranges in soil DM (µg/kg) for an effective application of sequestration strategy
		p,p-DDT	o,p-DDT	p,p-DDE	p,p-DDD	Mean DDTs	
AC DARCO	2	86±2	82±6	85±4	92±2	86±4	0.4 – 0.7 ¹ 1.9 – 8.0 ²
AC ORBO	2	68±4	63±4	81±3	76±3	72±8	0.4 – 0.6 ¹ 1.9 – 3.2 ²
BC Sargassum	2	39±2	36±3	58±4	48±1	45±10	0.4 – 0.5 ¹ 1.9 – 2.7 ²

DM- dry matter

* – Reduction factor (%) of environmental availability of DDT and metabolites estimated for naturally contaminated soil from Kyzylkairat village which are represented a hot spot in Almaty, Kazakhstan.

¹ - Concentration range in soil estimated for high productive hen farms

² - Concentration range in soil estimated for broiler farms

Sequestration potential of ACs like DARCO and ORBO has been investigated by *in vivo* study (piglets study, Chapter 2, Part IV) with chlordecone where these SMs showed the strongest affinity and retention of hydrophobic OCPs what has been shown above. Investigation was performed to explore CLD adsorption on the ACs during digestive processes of piglets when provided by two different application pathways: *via* feed incorporation or *via* soil amendment. Results of this study showed that the most effective way to perform sequestration to limit POPs contamination in animals (and their body tissues) is performing an AC/BC amendment to the soil rather than to incorporate it in the animal feed. The bioavailability reduction coefficient of CLD reached up to 86% in the liver and fat of exposed piglets when AC were added to contaminated soil. The inefficiency of AC amendment to animal feed was explained by competition process occurred between CLD, digestive enzymes and various substances of feed for active sites on the surface of the adsorbent during digestion. Results of effectiveness of AC amendment to soil was explained by the duration of contact between ACs and CLD in soil (21 days) which was much longer time than the digestive process in piglets (less than 24 h). Therefore, it was concluded that sequestration process is time dependent. This is in line with results obtained with sequestration of OCPs (including DDT and metabolites and HCHs isomers) on other ACs/BCs (Chapter 2, Part II) in water. Indeed, aqueous media is simpler matrix compared to soil which is required much more contact time between target pollutants and SMs.

In addition, SMs locally produced in France and Kazakhstan were studied using their adsorption behavior (*via* kinetics and absorption isotherm) and physicochemical properties when interacting with OCPs (Chapter 2, Part II). Among the SMs, tested for a use in POP-contaminated soils, were BCs originated from oak tree (*Quercus ilex*), Japanese knotweed (*Reynoutria japonica*) but also ACs as DARCO and Shubarkol, originated from brown coal (fig.1). These carbon rich and porous SMs have been shown especially effectively for sequestration of different hydrophobic OCPs (HCHs, DDTs and CLD). Nevertheless, a notable difference between the adsorption degree of ACs and BCs have been observed, which was varied respectively between 51 and 93% and between 13 to 60% (Figure 38).

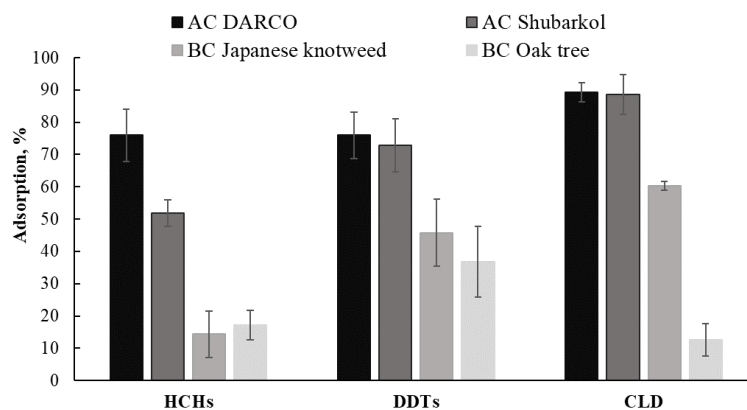


Figure 38 – Sequestration potential of 4 contrasted porous SMs to adsorb OCPs in aqueous media after 2 hours of contact time

2. Main properties responsible for efficient sequestration of OCPs

This work highlighted several properties driving the adsorption of OCPs to SMs and allow to predict the sequestration efficiency: 1) physical and chemical properties of SMs 2) amendment rate and granulometry of SMs, 3) contact time between OCPs and SMs and 4) characteristics of soil organic components.

The main *physical and chemical properties of SM* favoring interactions and effective adsorption of POPs (especially in the context of hydrophobic OCPs) on SMs are high carbon content (>72%), SM surface area (between 144 to 794 m²/g), mesoporosity, and the presence of various functional groups (Chapter 2, Part II). The high content of carbon in the composition of the SMs allow to attach a target organic molecule more strongly due to the formation of a high affinity between them (Guo et al., 2020; Hilber and Bucheli, 2010). A large specific surface and the formation of porosity in its outer areas create more active sites for the adsorption of target molecules (Rakowska et al., 2012).

The efficiency of the POPs sequestration process on AC/BCs depends on the optimization of the chosen conditions of the methodology. For example, the *SM amendment rate* and *SM texture* (i.e., in terms of granulometry) which both impacted on adsorption efficiency and intensity, as well as *the contact time* after which the effect of reducing the availability of contaminants in the target matrix would be potentially noticeable (Chapter 2, Part II). Model study of the adsorption kinetics showed that after the addition of porous SMs (20 mg) to an aqueous solution with an 8-component mixture of OCPs (50 µg/L), the adsorption process reached equilibrium already after 2 hours

demonstrating the maximum efficiency of adsorption between OCPs-SM (Chapter 2, Part II). Therefore, the concentration of SM in aqueous solution simulating soil amendment rate *in situ* has a positive effect on the OCP adsorption and accelerates this process (Chai et al., 2012; Guo et al., 2020; Hilber and Bucheli, 2010).

In terms of OCP sequestration in soil, SM amendment rate could be varied from 0.1 to 10% DM (Denyes et al., 2013; Hilber and Bucheli, 2010). We integrated 2 % DM AC/BCs amendment in both our studies i) soil environmental availability study (*in vitro*) with a contact time up to 3 months (Chapter 2, Part IV) and ii) in the piglet study. Indeed, the animals were exposed via soil aged during 3 weeks with AC/BCs (Chapter 2, Part III). Results of these works with 2% soil amendment rate allow to reach a very positive effect of bioavailability reduction (table 41) compared to utilization of smaller SM rates (from 0.25 to <2 %) (Chapter 2, Part IV).

Granulometry of SM amendment could be also improvement parameter of sequestration. Indeed, results of soil environmental availability of OCPs showed that SM with particle size <150 μm demonstrated higher availability reduction coefficients (45 \pm % vs 32%) than the particles >150 μm (Chapter 2, Part IV). Fine particles of SM compared to large ones could mix more homogeneously with the soil, thus possibly providing better physical contact for the interaction of soil contaminants onto the SM surface. Moreover, fine granulometry would multiply the SM surface to adsorb.

Composition of soil is also an important parameter impacted on sequestration based on AC/BCs which was partly covered by the current work and should be deeply explored in the future. We explored adsorption potential of 5 different basic substances of soil organic matter (Figure 39) to sequester OCPs in aqueous media (Chapter 2, Part II). Results showed that all studied SOM samples (Figure 39) could adsorb OCPs from 16 to 65% suggesting that the presence of these substances in the soil may lead to a natural reduction in the environmental availability of POPs. This could be explained by the high affinity of these pollutants, and by a very rich elemental composition (especially carbon atoms) and also by the presence of various functional groups promoting adsorption.

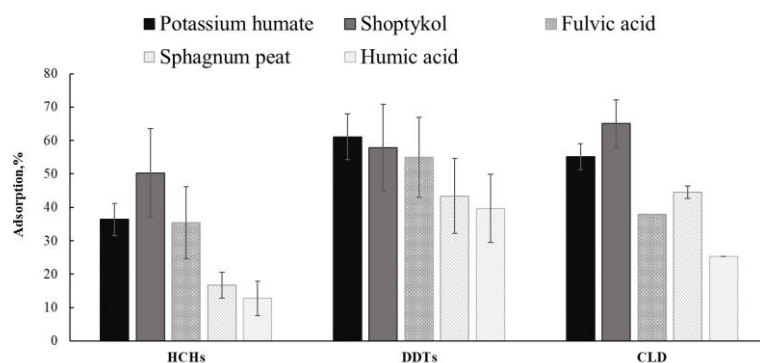


Figure 39 - OCPs adsorption by 5 different basic substances of SOM in aqueous media, after 2 hours

Finally, based on above mentioned observations, a general scheme of sequestration strategy based on AC/BCs are shown in Figure 40

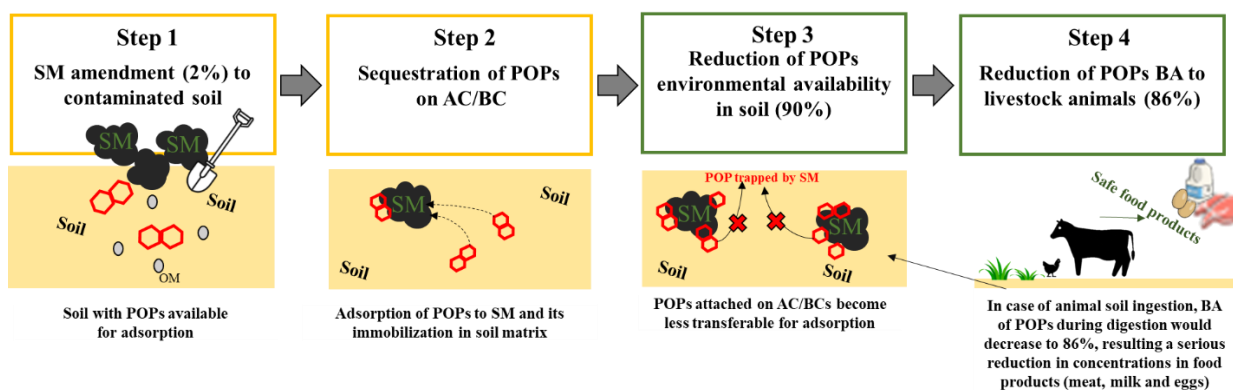


Figure 40 – Scheme of main processes occurred during application of sequestration strategy based on AC/BCs on contaminated soil and its impacts on food safety. Indications: SM- sequestration material, OM – organic matter of soil

3. Economic expediency and limitations of sequestration strategy based on AC/BCs

Application of sequestration strategy could be cost-effective especially when using locally available cheap raw materials which are represented by a wide variety depending on the area. Among studied SMs under the current work were commercial ACs: DARCO (lignite) and ORBO (coconut shell), Shubarkol originated from Kazakhstani brown coal, but also plant origin BCs: oak tree, Japanese knotweed and Sargassum.

To estimate the economic expediency, an AC DARCO, AC Shubarkol and BC oak tree were used as examples which are demonstrated a very similar sequestration effectiveness. Costs of BC Oak (0.3 USD) and AC Shubarkol (0.6 USD) is in 873 and 438 times, respectively, lower than cost of AC DARCO (262 USD), which also makes its use easier affordable, especially in the semi-scale

application of sequestration strategy in polluted lands (Table 42). However, one of the limitations of the strategy may be the availability of the mass of AC/BC necessary for the semi-industrial application of the sequestration strategy. Therefore, for example, sequestration of 1 ha of soil requires about 40 tons of activated carbon, which can be technically difficult to create a high-productive factories able to produce large amount of SMs.

However, sequestration strategy could be still effectively integrated on a small scale and in the moderately-contaminated context, i.e., for example in a private gardens where auto-production and auto-consumption of contaminated food is not controlled by authorities and as consequence poses a high risk for consumers.

Table 42 – Economical justification of effective application of a sequestration strategy for OCP-contaminated soil

SMs	Price per 1 kg of SM (USD)	Net price for sequestration of 50 kg soil, USD	Net price for sequestration of 1 ha soil, USD ⁴	Mass of AC necessary for sequestration of 1 ha soil, tons
AC DARCO	262 ¹	262	10.5 mln.	40
High quality AC	32 ²	32	1.3 mln	
AC Shubarkol	0.6 ³	0.6	24 000	
BC Oak	0.3 ²	0.3	12 000	

DM- dry matter

SF – security factor

¹ – Prices are taken from Sigma Aldrich website

²- Prices are taken from personal communication of Sarra Gaspar (COVACHIM Laboratory, University of Antilles)

³- Prices are taken from from Kazankapova M. et al., 2020

⁴ – One ha of land was considered as 2 mln. kg of soil. Amendment dose is 40 000 kg (2% DM).

4. Perspectives of sequestration strategies

Several directions for possible further research related to the application of the sequestration strategies were identified. Promising areas requiring experimental validation could be long-term influence of high-carbon matrices on soil quality and the impact of soil components on the efficiency of sequestration of target pollutants.

Long-term presence of SM amendment in soil. Large SM amendment rate to achieve intensive adsorption of target compounds in soil might not be reasonable due to the lack of existing knowledge of long-term effects of condensed aromatic carbon presence in the soil (Guo et al., 2020), and also considerations of its long residence time (90-1600 years) and effects on soil quality (Singh and Singh, 2017). Therefore, the rate of soil amendment should be chosen without disturbing

the balance of the soil and its fertility. Indeed, the effect of SMs may also affect the bioavailability of nutrients in soil, which would by consequence change the potential plant growth and the potential use of this soil. Such side effects have to be investigated before a large application of SMs even if it seems to be a promising technique. Moreover, the efficiency of the POP adsorption on the SMs to reduce their transfer to food chain has to be confirmed on a long-time scale as different natural processes (leaching, washing out, deterioration of soil fractions) may alter the adsorption potential.

Non-target compounds presented in soil. Soil contains many non-target compounds such as organic and inorganic contaminants, soil organic matter such as humin (with different degrees of complexation), humic and fulvic acids in different proportions (Ahmad et al., 2001b; Anderson and Schoneau, 2007b; Cousins' et al., 1999). These substances could both slow down or limit the process of soil sequestration based on AC/BC as it could provoke a competition between target pollutants (POPs) and the above-mentioned components for the AC/BC amendment introduced to soil. Therefore, it is needed to investigate the potential effects of the type and composition of the SOM on the sequestration strategy.

GENERAL CONCLUSION

The context of this work was mainly focused on strategies which could ensure the safety of food produced by livestock animals in POP contaminated areas. The work within this PhD dissertation was based on two directions related to food safety: 1) estimation of the transfer of POPs to animals via contaminated feed and soil and 2) proposing the strategies which could effectively use for reducing this transfer.

First, a comprehensive analysis of published data on the transfer of various families of POPs to food of animal origin (Chapter 2, part I) provided a better understanding of the behavior of these contaminants and their expected levels in edible products. Meta-analysis showed that specific methodologies such as TR and BCF allow to quantify and ranking the risk focusing on food safety. They allow to predict maximum POP levels when the exposure context (ingest dose of POPs) is accurately known and play by consequence a major role in risk assessments dealing with food contaminations. It was concluded that the most toxic POPs (tetra- to hexachlorinated dioxins and furans, highly chlorinated PCBs, especially congener 126, as well as DDT) are generally highly transferred to food producing animals (dairy cows, goats and laying hens) especially when they are raised on contaminated soils. The bioconcentration of these pollutants could threaten the animal rearing system and possess a high health risk for consumers.

Therefore, in second part of the work, a series of experiments were conducted in order to investigate application of sequestration strategies based on ACs and BCs as possible solutions for reduction of the OCPs (DDT and metabolites, HCH isomers and CLD) transfer from soil to food products in contaminated areas and especially in areas used for rearing livestock animals. This work revealed that several carbonaceous matrices such as ACs and BCs are able to adsorb different OCPs and therefore could be effectively used in sequestration strategies as soil amendment. Tested SMs for OCPs adsorption were: ACs DARCO, ORBO, Shubarkol and BCs Oak tree, Japanese knotweed and Sargassum. The verification of some of these SMs to sequester OCPs were performed via adsorption kinetics and adsorption isotherms batch tests in aqueous media as well as via *in vitro* environmental availability tests in soil and *in vivo* trials with piglets.

Overall results revealed that 1) physical and chemical properties of SMs, 2) amendment rate and granulometry of SMs, 3) contact time between contaminants and SMs and 4) fractions of soil organic matter appeared as factors explaining efficiency of sequestration strategy. The total porosity, i.e SSA and pore size distribution (micro- and mesoporosity), mineral elements (especially carbon) and functional groups of SMs were seems to be key properties responsible for the effective sequestration of OCPs in tested environmental media (water and soil). It was

concluded that 2 % (dry matter) of SM amendment with particle size less than 150 μm are optimal methodological parameters for the field application of sequestration strategies.

Simulation of impact scenarios (Chapter 3, part I) of OCPs on various livestock production systems (meat and products of low and high productive animals) showed that the sequestration strategy can be especially effective under conditions of moderate soil contamination, which could significantly reduce the transfer of pollutants into products (up to 90%) and, as a result, protect consumers.

On the economic side, it appeared that application of AC is by far more expensive than a BC amendment what raises the question of the economic feasibility. In addition, the sequestration strategy can be costly when applied on a large scale over several hectares of land due to the need for a large amount of SM requiring a large production capacity. However, this strategy can be economically viable and beneficial for smaller areas such as private gardens or small farms, especially on moderately contaminated soils.

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