Evaluating Plant Uptake Pathways of Chemical Contaminants in State Models for Risk Assessments of Contaminated Urban Gardening Sites

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Abstract: This document provides an overview of the current state models and parameters used in assessing the plant uptake pathways of chemical contaminants found in urban agriculture (UA) scenarios. UA includes growing food for human consumption, fiber, plant-based dyes, and other crops. Exposure assessments are utilized as an effective tool for estimating risk associated with exposure to harmful chemicals. Current implemented risk assessment methods include the U.S. EPA (2020) Preliminary Remediation Goals (PRG) calculator for radionuclide (RAD) contaminants at Superfund sites. A PRG calculator that encompasses all classes of chemical contaminants does not currently exist, resulting in unclear and inconsistent recommendations regarding best practices for urban growers. The specific aims of this report will highlight contaminants of emerging concern (CECs) found in urban soil media and their subsequent exposure risks, along with the existing plant uptake methods used to quantify the concentrations of such contaminants. A portion will be dedicated to outlining research gaps which require remediation to facilitate a more accurate characterization of potential food exposure to ensure enough data is provided to form a national screening level.

Keywords: Plant uptake; Soil contamination; Risk assessment; Urban soils; Contaminants of emerging concern (CEC); Heavy metals; Persistent organic pollutants (POPs), State models

1. Introduction

Integration of urban agriculture (UA) into modern city planning has become increasingly popular in communities across the country. UA has proved to be a promising method to increase access to healthy, nutritious, and low-cost produce. Due to their urban nature, these gardening plots are highly influenced by past and present anthropogenic activities that can threaten both soil health and food safety (Lupolt et al. 2021). The composition of urban soil includes soil contaminants, elements present in the soil at a level that could potentially pose health risks. Exposure to soil contaminants can increase the risk for acute and chronic health problems (Yang and Zhang 2015). Characterization of soil matrices reveals a composition comprised of (i) naturally occurring background soil

levels and (ii) contaminants of emerging concern (CECs). Naturally elevated levels of elements and chemicals vary depending on the region of the country (U.S. EPA 2011). Areas may also show elevated contaminant levels due to poor waste handling practices, spills, and natural disasters. To date, a majority of the literature surrounding soil contamination has been limited to a narrow set of metals (e.g. lead (Pb), arsenic (As)) in areas previously known to be contaminated (Ramirez-Andreotta et al. 2013a, 2013b). This results in a limited generalizability for areas where previous evidence of contamination is absent, and furthermore, a lack of clear safety parameters and guidelines for urban growers (Lupolt et al. 2021). Therefore, we present an extensive research report of current literature regarding the quantification of soil media in UA across the U.S. to better characterize the

levels of contaminants present

2. Identifying Contaminants of Emerging Concern (CECs)

For decades, soil research has primarily been focused on agricultural and forest lands (Lombi et al. 1998). It remains an ongoing challenge for soil scientists to understand and interpret the multifaceted characteristics and properties of soils. With the growing public concern surrounding the environment and human health, it is imperative to identify the contaminants of emerging concern (CECs) that may be found in any given urban gardening site across the United States (Srikanth et al. 2019). A soil contaminant is defined as an element or chemical present in the soil at a level that could potentially pose a risk to human health. Sources of contamination include that of geogenic (naturally occurring) and anthropogenic (human-driven) origin (Soltani-Gerdefaramarzi et al. 2021).

Risks associated with UA soil contamination include plant uptake of contaminants through the soil and bioaccumulation occurring when humans ingest contaminants from vegetation growing in compromised soil (Rosen 2002). Existing guidelines are commonly intended for the clean-up and remediation of highly contaminated sites (Jennings 2013). Their correlation for the safety of food grown in UA soils is unknown. Most urban soils are formed from different parent materials than natural soils and thus require different parameters for use and management. CECs of urban soil are especially important because anthropogenic activities have increased the soil levels of many elements and chemicals (Table 1). Common anthropogenic sources include pesticides, burning fossil fuels, agricultural practices, etc. (Heinegg et al. 2000).

2.1. Trace Elements

Trace elements commonly found in urban soils include heavy metals and metalloids. Heavy metals and metalloids are among the most investigated soil contaminants and their presence in the environment is recognized as a global health problem, making metals such as lead (Pb) a legacy CEC. At high concentrations, they act as systemic toxins that interact with specific biological systems to produce teratogenic, neurotoxic, cardiotoxic, and/or nephrotoxic effects. Metals enter the body via inhalation, ingestion, and dermal routes, where they can be store in both soft and

Table 1. Common anthropogenic sources of CECs.

Anthropogenic Source	Contaminant Type	
	Trace Elements	*Persistent Organic Pollutants (POPs)*
Paint (before 1978)	Pb	
High traffic areas	Pb, Zn	PAHs
Treated lumber	As, Cr, Cu	
Burning wastes		PAHs, dioxins
Contaminated manure	Cu, Zn	
Coal production	Mo, S, Se	PAHs, dioxins
Sewage sludge	Cd, Cu, Zn, Pb	
Petroleum refining/spills	Pb	Petroleum products (PAHs, MAHs)
Pesticides	Pb, As, Hg	OCPs
Commercial/industrial site use	Pb, As, Ba, Cd, Cr, Hg, Zn	PAHs, MAHs, PBDEs, PCBs, PFAS

Adapted from Heinegg et al. (2000).

Pb: lead; Zn: zinc; As: arsenic; Cr: chromium; Cu: copper; Mo: molybdenum; S: sulfur; Se: selenium; Hg: mercury; Ba: barium; PAHs: polycyclic aromatic hydrocarbons; MAHs: monoaromatic hydrocarbons; OCPs: organochlorine pesticides; PBDEs: polybrominated diphenyl ethers; PCBs: polychlorinated biphenyls; PFAS: per- and polyfluoroalkyl substances.

hard tissues (Lupolt et al. 2021). Biological organisms are incapable of degrading metals because of their nonbiodegradable nature and long half-life (Amaral and Rodrigues 2005; Nabulo et al. 2011). They are released into solids from lithogenic (parent material) and anthropogenic sources. Nearly any heavy metal and metalloid can be potentially toxic to soil biota depending upon the concentration and duration of exposure. Regarding their roles in biological systems, heavy metals and metalloids can be classified as essential or nonessential (Table 2).

Essential metals function as protein cofactors in various biological processes and are considered non-toxic when present in trace amounts (Apostoli 2002; Antoine et al. 2012). Nonessential metals have no biological function and are considered toxic in trace amounts (Chang 2000; Nies 1999). Nonessential metals pose a threat to human health because of their ability to

hijack cellular transport mechanisms of essential metals (Martinez-Finley et al. 2012). These nonessential metals act as systemic toxins that interact with specific systems to produce teratogenic, neurotoxic, cardiotoxic, and/or nephrotoxic effects (Jaishankar et al. 2014; Järup 2003). Both nonessential and high concentrations of essential metals disrupt metabolic processes by altering the number of homeostatic processes (e.g. antioxidant balance; binding to free sulfhydryl groups; competing for enzyme binding sites, receptors, and transport proteins) (Martinez-Finley et al. 2012).

Table 2. Classification of essential and nonessential heavy metals/metalloids (Lupolt et al. 2021).

Essential	Nonessential
Zinc (Zn)	Cadmium (Cd)
Nickel (Ni)	Lead (Pb)
Copper (Cu)	Mercury (Hg)
Molybdenum (Mo)	Chromium (Cr)
Selenium (Se)	Arsenic (As)
	Barium (Ba)

2.2. *Persistent Organic Pollutants (POPs)*

Persistent organic pollutants (POPs) are toxic chemicals that bioaccumulate and persist in the environment for long periods of time (CEC 2015). The primary concern surrounding the adverse effects of POPs on environmental and human health is linked to their ability to bioaccumulate and be transferred across species via the food chain (Alharbi et al. 2018). Although most POPs are no longer produced in the U.S., the risk associated with environmental persistence of intentionally and unintentionally produced POPs remains. Intentionally produced POPs include chemicals currently or previously used in agriculture, disease control, manufacturing, or industrial processes. Whereas, unintentionally produced POPs result from some industrial processes and combustion (e.g. burning wastes) (U.S. EPA 2009).

2.2.1. Petroleum Products

Petroleum based products function as a major source of energy in the era of industrialization (Lu et al. 2009;

Bonfa et al. 2011; Macaulay and Rees 2014; Varjani and Upasani 2016a, 2017a). Exploration activities of the petroleum industry produce petroleum hydrocarbons that pose potential environmental and human health risks (Bachmann et al. 2014). POPs found in petroleum refinery wastes include (i) monoaromatic hydrocarbons (MAHs) and (ii) polycyclic aromatic hydrocarbons (PAHs). These hydrocarbon contaminants induce mutagenic, carcinogenic, immunotoxic, and teratogenic effects in soil biota and humans alike. The complexity of the different chemicals found in crude oil and other petroleum products make it difficult to measure each one individually. Rather, it is effective to measure the total amount of these compounds at contaminated sites. The term total petroleum hydrocarbon (TPH) is used to measure the mixture of PAHs and MAHs found at contaminated sites (Sui et al. 2021).

(i) *Monoaromatic Hydrocarbons (MAHs)*

Monoaromatic hydrocarbons (MAHs) are comprised of four alkyl benzene volatile organic compounds (VOCs): benzene, toluene, ethylbenzene, and the ortho, meta, and para substituent positions of xylene. This class of contaminants, commonly referred to as the BTEX compounds, are among the five most regulated soil contaminants in the United States and worldwide (Jennings 2009). BTEX compounds are among the most harmful volatile organic compounds (VOCs) present in air, water, and soil media. As common constituents of petroleum fuels, the petroleum industry utilizes the term BTEX to represent the sum of the concentrations of these four compounds in measuring the quality of fuels. This parameter has been adapted for use by the EPA and state agencies to serve as a measure of effluent quality of these contaminants in water (U.S. EPA 2005).

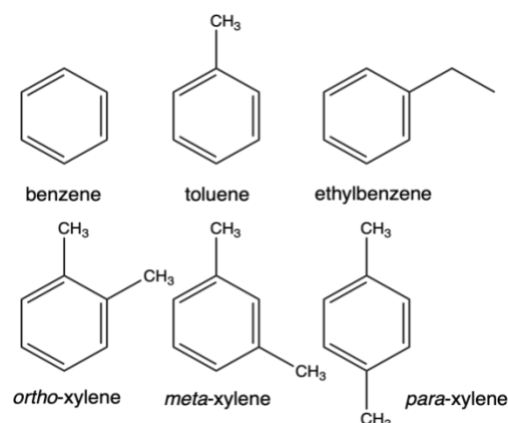**Figure 1.** BTEX Compounds. Via ChemDraw 20.1.

Individual anthropogenic sources of the BTEX compounds include (MDE 2007):

(a) Benzene: synthetic rubber, plastics, nylon, insecticides, paints, and cigarettes.
(b) Toluene: solvent for paints, coatings, gums, oils, and resins.
(c) Ethylbenzene: paints, inks, plastics, and pesticides.
(d) Xylenes: solvent in printing, rubber and leather industries.

Acute exposures to high levels of BTEX components have been associated with skin/sensory irritation, central nervous system depression, and adverse effects on the respiratory system. Prolonged exposure to BTEX compounds has effects on the kidney, liver, and blood systems (ATSDR 2007). According to the U.S. EPA Integrated Risk Information System (IRIS) (2009), sufficient evidence from both human and animal studies reported benzene to be a human carcinogen.

(ii) *Polycyclic Aromatic Hydrocarbons (PAHs)*

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in the environment. Anthropogenic sources of PAHs include the burning of fossil fuels, coal production, oil manufacturing, oil spills, wood preservation (creosote), tobacco smoke, manufactured gas plants, asphalt plants and their corresponding byproducts, and various forms of cooking (Hussar et al. 2012). Natural sources include volcanoes and forest fires. Of the hundreds of known PAHs, seventeen have been designated High Priority Pollutants by the Agency for Toxic Substances and Disease Registry (ATSDR). These 17 PAHs are of environmental concern because of their potential toxicity in humans and other organisms and their prevalence and persistence in the environment (ATSDR 1995).

The unique physiochemical properties specific to PAHs contribute to their prevalence in terrestrial systems. PAHs can be characterized by their low water solubility, low vapor pressure, and high melting/boiling points (Lee and Vu 2010). The presence of dense pi electrons on both sides of the ring structure gives PAHs biochemical persistence, making them more resistant to degradation than any other hydrocarbons in the environment (Haritash and Kaushik 2009). Molecular weight (MW) of PAHs largely influences their prevalence in soil media. and the presence of benzene rings. PAHs with a higher MW have increased hydrophobicity and lipophilicity. PAHs with high MW are poorly bioavailable and more resistant to microbial degradation when compared with low MW PAHs. This

results in high MW PAHs being more carcinogenic, mutagenic, and teratogenic than low MW PAHs (Okere and Semple 2012).

Table 3. 17 Designated High Priority PAH Pollutants (Adapted from ATSDR 1995).

17 Priority PAHs	
Acenaphthene (ACE)	Benzo[k]fluoranthene (B[k]F)
Acenaphthylene (ACY)	Chrysene (CHRY)
Anthracene (ANTH)	Dibenz[a,h]anthracene (D[ah]A)
Benzo[a]anthracene (B[a]A)	Fluoranthene (FLTH)
Benzo[a]pyrene (B[a]P)	Fluorene (FLU)
Benzo[e]pyrene (B[e]P)	Indeno[1,2,3-c,d]pyrene (IND)
Benzo[g,h,i]perylene (B[ghi]P)	Phenanthrene (PHEN)
Benzo[b]fluoranthene (B[b]F)	Pyrene (PYR)
Benzo[j]fluoranthene (B[j]F)	

2.2.2. Dioxins

Dioxins and dioxin-like compounds are highly toxic byproducts of common manufacturing processes (e.g. herbicide production, paper bleaching). Classified as a persistent environmental pollutant, these thermally stable, lipophilic, and halogenated aromatic compounds can be classified into two main groups: (i) polychlorinated dibenzodioxins (PCDDs), and (ii) polychlorinated dibenzofurans (PCDFs) (Hites 2011; U.S. EPA 2022). In addition to PCDDs and PCDFs, some dioxin-like polychlorinated biphenyls (PCBs) are considered dioxins. Historically, dioxins are produced as byproducts of combustion processes (e.g., waste incineration) and industrial manufacturing processes (e.g., pesticide production). (Hites 2011; Japan Govt report) Urban areas experience the highest levels of dioxin contamination in all environmental mediums due to relative location to industrial sites. The principal source of dioxins in urban soils and plants is atmospheric deposition of dioxins from coal burning and municipal waste incineration. Uptake of PCDD/Fs from soil is heavily influenced by the octanol-water partition coefficient (Kow) of each compound. Briggs et al. (1982) concluded that uptake of a contaminant in the roots increased with increasing log Kow values or increasing lipophilicity. It is important to note that, while root uptake via adsorption varies between

congeners, transfer from root to shoot varies between plant species (Zhang et al. 2022). Overall, assessment of crop contamination of crops is both compound and crop specific.

In terms of public health, exposure to dioxins can lead to cancer, hormone interference, and reproductive, developmental, and immunological effects. (U.S. EPA 2022) PCDDs and their corresponding PCDF congeners often produce the same acute and chronic health effects, with levels of toxicity varying between congener pairs. (Hites 2011) In general, only dioxins with chlorines located in the 2, 3, 7 and 8 positions on their aromatic rings are deemed toxic to human health. (U.S. EPA 2022)

(i) Polychlorinated dibenzodioxins (PCDDs)

The most notable dioxin, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), also known as the "most toxic man-made chemical," belongs to the PCDD subgroup. (Hites 2011) There are 75 identified PCDD congeners, with only 7 being toxic (EQS 2011; see Table 4).
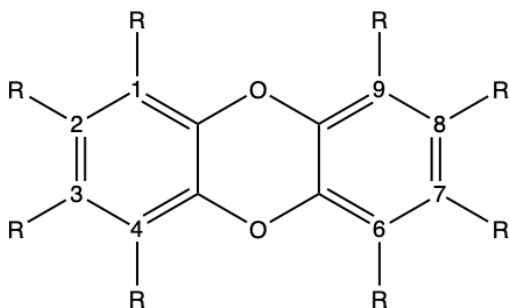

Figure 2. General structure of PCDDs. R = chlorines or hydrogens. Via ChemDraw 20.1.

Table 4. List of Toxic PCDD Congeners. Adapted from EQS 2011.

Compound	CAS Number
2,3,7,8-TCDD	1746-01-6
1,2,3,7,8-PCDD	40321-76-4
1,2,3,4,7,8-HCDD	39227-28-6
1,2,3,6,7,8-HCDD	57653-85-7
1,2,3,7,8,9-HCDD	19408-74-3
1,2,3,4,6,7,8-HCDD	35822-46-9
1,2,3,4,6,7,8,9-OCDD	3268-87-9

(ii) Polychlorinated dibenzofurans (PCDFs)

There are 135 identified PCDF congeners; however, only 10 of the 135 are considered toxic. (EQS 2011; see Table 5)
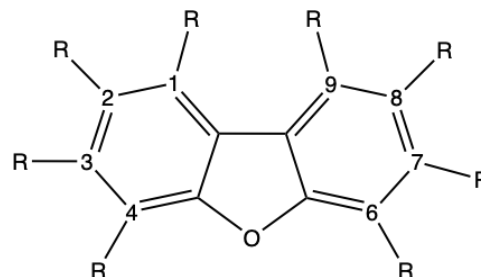

Figure 3. General structure of PCDFs. R = chlorines or hydrogens. Via ChemDraw 20.1.

Table 5. List of Toxic PCDF Congeners. Adapted from EQS 2011.

Compound	CAS Number
2,3,7,8-TCDF	51207-31-9
1,2,3,7,8-PCDF	57117-41-6
2,3,4,7,8-PCDF	57117-31-4
1,2,3,4,7,8-HCDF	70648-26-9
1,2,3,6,7,8-HCDF	57117-44-9
1,2,3,7,8,9-HCDF	72918-21-9
2,3,4,6,7,8-HCDF	60851-34-5
1,2,3,4,6,7,8-HCDF	67562-39-4
1,2,3,4,7,8,9-HCDF	55673-89-7
1,2,3,4,6,7,8,9-OCDF	39001-02-0

2.2.3. Organochlorine Pesticides (OCPs)

Organochlorine pesticides (OCPs) are fat-soluble, chlorinated hydrocarbon compounds which were first developed in the 1940s (ECOTOX; U.S. EPA ROE; DHSS 2015). Most uses of OCPs have been banned in the United States since the 1970s and 1980s, due to the persistence of OCPs in the environment (U.S. EPA ROE). These chemicals are also associated with central nervous system and carcinogenic effects, alongside convulsions, dizziness, nausea, tremors, slurred speech (U.S. EPA ROE; DHSS 2015). Structurally, OCPs can be grouped into five categories: (i) hexachlorocyclohexane (HCH), (ii) cyclodienes and similar compounds, (iii) toxaphene and similar compounds, (iv) mirex and chlordecone (caged structures), and (v) dichlorodiphenyltrichloroethane (DDT) and its analogs (ECOTOX). Here, we examine the most notable OCPs:

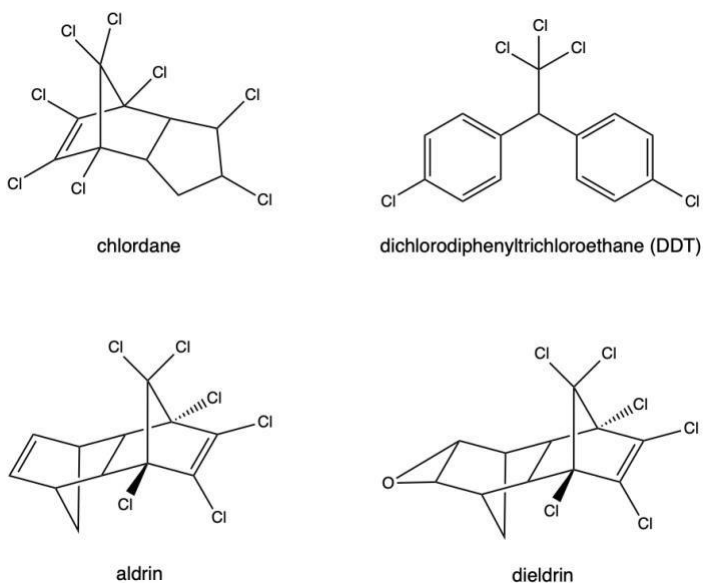chlordane, DDT, aldrin, and dieldrin (Fig. 4).

Figure 4. OCP structures Via ChemDraw 20.1.

(i) *Chlordane*

Chlordane was used as a synthetic pesticide on crops, lawns, and gardens from the 1940s until it's ban by the U.S. EPA in 1988. Acute exposure of chlordane mainly affects the nervous system, but can induce headaches, confusion, dizziness, and tremors in some cases. Prolonged exposure may result in convulsions or death. There is no sufficient evidence on the carcinogenic effects of exposure to chlordane. The U.S. EPA-determined reference dose (RfD) for chlordane is 0.0005 mg/kg-day (ATSDR 2018). Figure 5 shows the frequency of National Priorities List (NPL) sites across the United States where chlordane has been detected.
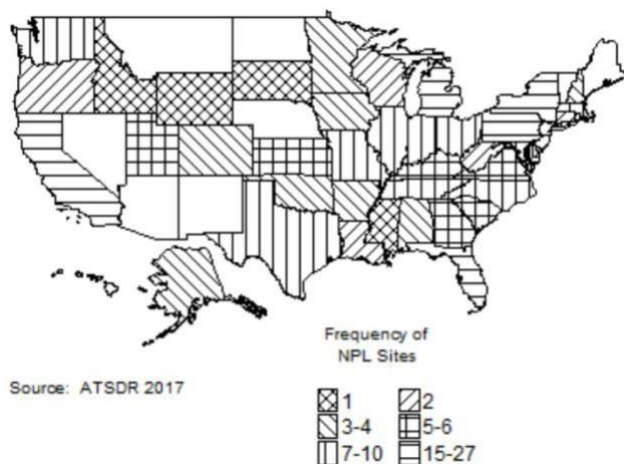

Figure 5. Frequency of NPL Sites with Chlordane Contamination (ATSDR 2018).

(ii) *Dichlorodiphenyltrichloroethane (DDT)*

For more than 30 years, DDT was used as an agricultural insecticide until banned by EPA in 1972 (CDC 2021). While it is no longer used as an insecticide, it is still used to control mosquitoes to limit the spread of malaria in some countries. Often grouped with DDT are the degradation products and metabolites dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE) (ATSDR 2022). In a similar fashion to DDT, DDD was also manufactured for use as an insecticide, while DDE only exists as a byproduct during DDT production (ATSDR 2022). There are many isomers of DDT and its metabolites, but here we focus on the *p,p*-DDT isomer.

While previously celebrated for its impact in reducing malaria, the persistence of DDT in the environment and the human body in combination with its adverse health effects soon began to outweigh the benefits it produced. DDT and its metabolites are slow to biodegrade in the environment, like most OCPs (Turusov et al. 2002). This persistence leads to bioaccumulation in the food chain and is the main reason why DDT became a public health threat. DDT is not alarmingly acutely toxic, but with its ability to accumulate in fatty tissues and resistance to degradation within the body, it can lead to alarming chronic toxicity effects (Turusov et al. 2002). Exposure to large doses of DDT can lead to vomiting, tremors, and seizures (CDC 2021). Studies show consistent evidence for the following adverse health effects related to exposure to DDT and its metabolites: increased prevalence for wheeze in infants or children when the mother was exposed, increased risk of Type 2 diabetes, and increased risk of liver cancer (ATSDR 2022). Some studies also indicate that DDT is an endocrine disruptor (Turusov et al. 2002). The RfD for DDT is 0.0005 mg/kg-day (ATSDR 2022). Figure 6 shows the frequency of NPL sites across the United States where DDT and its metabolites have been detected.
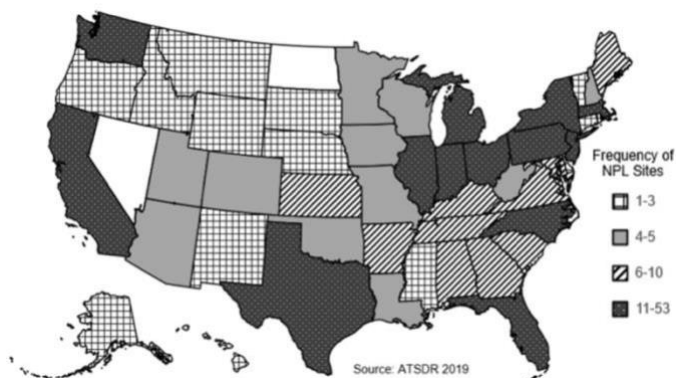

Figure 6. Frequency of NPL Sites with DDT, DDE, and DDD Contamination (ATSDR 2022).

(iii) *Aldrin*

First produced in 1948, aldrin was widely used as a pesticide and insecticide (ECOTOX). While aldrin was banned for agricultural use by the U.S. EPA in 1970, it was still used for termite extermination until 1987 (ECOTOX). Aldrin is classified as a semi-volatile compound and is known to be resistant to biodegradation due to its low mobility in soil (ATSDR 2022). The most common route of exposure to aldrin is ingestion of contaminated drinking water or foods (ATSDR 2022). Risk associated with aldrin exposure has decreased due to the halt in manufacturing of the compound in the United States (ATSDR 2022). Acute exposure to aldrin may lead to skin irritation, headaches, dizziness nausea, vomiting, convulsions and/or death (NJDOH 2010). Chronic exposure to aldrin may lead to cancer and reproductive effects, as aldrin is suspected to be a carcinogen and teratogen (NJDOH 2010). The RfD for aldrin is 0.00003 mg/kg-day (ATSDR 2022). It is also important to note that, with a log Kow of 6.50 aldrin is expected to bioconcentrate and has high potential for bioaccumulation (ATSDR 2022). Figure 7 shows the frequency of NPL sites across the United States where aldrin has been detected.
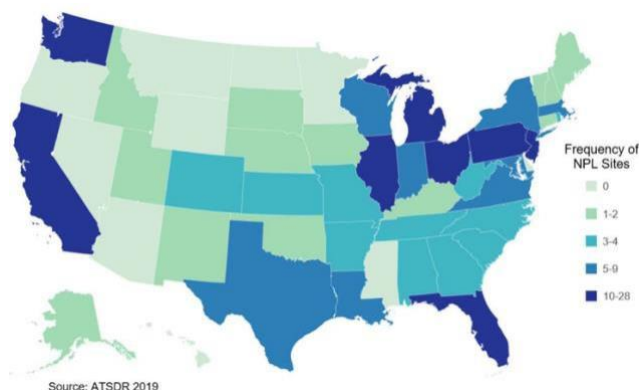

Figure 7. Frequency of NPL Sites with Aldrin Contamination (ATSDR 2022).

(iv) *Dieldrin*

Dieldrin was first used as a pesticide in 1950, shortly after the introduction of aldrin (ATSDR 2022). Dieldrin is readily produced in the environment and in the human body via the epoxidation of aldrin (ATSDR 2022). When examining the OCPs, dieldrin and aldrin are often grouped together due to their similarities in structure and human health effects. Dieldrin is

suspected to be a carcinogen and teratogen, with exposure yielding similar health outcomes as exposure to aldrin. Dieldrin has high potential for bioaccumulation and bioconcentration in aquatic and terrestrial systems (ATSDR 2022). The RfD and log Kow of dieldrin are 0.00005 mg/kg-day and 6.2, respectively (ATSDR 2022). Figure 8 shows the frequency of NPL sites across the United States where dieldrin has been detected.
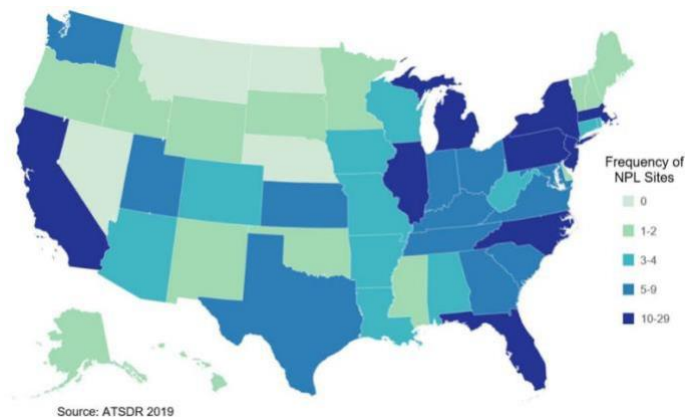

Figure 8. Frequency of NPL Sites with Dieldrin Contamination (ATSDR 2022).

2.2.4. Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are considered POPs due to their widespread presence across the United States, long-term persistence, bioaccumulative abilities, and high toxicity. Due to their distribution and transfer via the food chain, PCBs have been reported to induce adverse effects on the procreation of both humans and animals as a hormone interferon (Ulbrich and Stahlmann 2003). PCBs have optimal chemical/thermal stability and dielectric (insulating) properties for a variety of electrical applications such as dielectric fluid in transformers, heat-transfer fluids, and hydraulic fluids (IARC 2016).

The following characteristics result in the persistence of PCBs in soils: high hydrophobicity, low volatility, low water solubility, and resistance to degradation (Strek and Weber 1982). Strek and Weber (1982) found a positive, linear correlation with total organic carbon (TOC), indicating that TOC was the most influential factor on PCB mobility and persistence in soil. Due to their high hydrophobicity, PCBs tend to bioconcentrate in roots, where they remain bound to lipids found in the membrane organelles and cell walls (Paterson et al.

1990). Adsorption through the roots is the dominant mechanism for uptake of PCBs in plants (Strek and Weber 1982).

2.2.5. Polybrominated Diphenyl Ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) are a class of chemicals used in consumer products, such as furniture foam padding, draperies, upholstery, and small appliances, to decrease their flammability. There are three commercial PBDE mixtures that have been used: pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), and decabromodiphenyl ether (decaBDE); where decaBDE is the most widely used (U.S. EPA 2017). PBDEs are structurally like PCBs, and thus, they reflect many of the same properties. PBDEs with fewer bromines tend to bioaccumulate more than those with more bromines (U.S. EPA 2017). Like PCBs, research indicates that PBDEs will strongly partition to sediments rather than water (ATSDR 2017).

In terms of food, exposure to PBDEs is more likely to occur to those with omnivorous diets, rather than vegetarian diets (ATSDR 2017). This is due to the high contamination of fish, meat, and dairy products (ATSDR 2017). Additionally, uptake of PBDEs varies between plant species, but it is noted that leafy vegetables may contain higher contaminant concentrations due to deposition of PBDE-contaminated air particles (ATSDR 2017). Whereas root vegetables are only influenced by contaminated soils and water.

2.2.6. Per- and poly-fluoroalkyl Substances (PFAS)

The persistent, bioaccumulative, and toxic properties of per- and poly-fluoroalkyl substances (PFAS) are of increasing concern. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are common PFAS used in industry and consumer products (e.g., cookware, packing materials, stain repellents). Like PCBs, PFAS are considered POPs due to their persistence in the environment, bioaccumulation in humans, and toxicity in small doses.

Sorption and uptake trends are difficult to define for the entire class of PFAS. Rather trends may be seen amongst groups of PFAS, such as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). Similarly, PFSAs and PFCAs will tend to partition and associate with the organic carbon found in sediment (ITRC 2020). Additionally, retention in soil increases with increasing tail length (Costello and Lee 2020). However, PFSAs will be retained in soil more strongly than their PFCA counterparts of the same tail length (Costello and Lee 2020). The uptake of PFAS in plants most significantly occurs through exposure to contaminated soil and groundwater, but bioaccumulation and partitioning varies from structure to structure and depending on the plant species. In general, long-chain PFAS are found in the roots, while short-chain PFAS partition to other parts of the plant, due to their increased solubility (ITRC 2020).

3. State Specific CECs

Identifying state specific CECs was done in attempt to provide a more generalized visual representation of chemical contaminants across the U.S. Nationwide data was limited and further research on the remaining states will produce a more cohesive representation of regional and state specific CECs. This will allow for the identification of geographical trends that may be a useful resource for urban growers. Such trends are anticipated based on the various soil media and terrain that make up the terrestrial systems across the U.S. CECs specific to each state and corresponding EPA region have been identified in Table 6.

Table 6. Regional and State Specific Contaminants of Emerging Concern (CECs)

EPA Region	State Name	State Abbr.	Contaminants of Emerging Concern (CECS) Subtypes	
			Trace Metals	**POPs**
1	Connecticut	CT	Hg, As, Ba, Cd, Pb	BTEX, Naphthalene, benzo(a)pyrene, PCE, TCE
	Maine	ME	Cd, Pb, Zn, Hg, Ba, Ag	Chlordane, DDT/DDE/DDD, PCBs
	Massachusetts	MA	Pb, Hg	1,4-dioxane, perchlorate, PFAS, PBDEs, PCE, TCE,
	New Hampshire	NH		

	Rhode Island	RI		
	Vermont	VT		
2	New Jersey	NJ		PFNA, PFOA, PFOS
	New York	NY		
3	Delaware	DE		
	Maryland	MD	As, Cr	
	Pennsylvania	PA		
	Virginia	VA		
	West Virginia	WV		
	Washington D.C.	DC		
4	Alabama	AL		
	Florida	FL		Benzo(a)pyrene
	Georgia	GA		
	Kentucky	KY	Pb, As, Hg, Ba	Benzo(a)pyrene, PFAS, PAHs
	Mississippi	MS		
	North Carolina	NC	Pb, As, Ba, Cd, Cr, Hg, Se, Zn	Atrazine, BTEX, benzo(a)pyrene, carbaryl, chlordane, PCDD, PAHs, PERC, PCE, PCB, TCE
	South Carolina	SC		Benzo(a)pyrene
	Tennessee	TN		Benzo(a)pyrene
5	Illinois	IL		
	Indiana	IN		
	Michigan	MI		
	Minnesota	MN	Pb, Cd, As	PAHs, PHCs, BTEX
	Ohio	OH		
	Wisconsin	WI		
6	Arkansas	AR		
	Louisiana	LA		
	New Mexico	NM		
	Oklahoma	OK		
	Texas	TX		

7	Iowa	IA		
	Kansas	KS		
	Missouri	MO		
	Nebraska	NE		
8	Colorado	CO		
	Montana	MT		
	North Dakota	ND		
	South Dakota	SD		
	Utah	NT		
	Wyoming	WY		
9	Arizona	AZ		
	California	CA		
	Hawaii	HI		
	Nevada	NV		
10	Alaska	AK		
	Idaho	ID		
	Oregon	OR		
	Washington	WA		

4. Plant Uptake of CECs from Urban Soil

Urban soil systems differ from their rural counterparts in terms of their physical and chemical properties (Wortman and Lovell 2013). Urban agricultural soils are highly variable chemically and physically at fine geographic scales, reflecting the various management history of individual sites (Beniston and Lal 2012). Consequently, plant uptake findings from rural agricultural soils do not directly apply for risk assessment of urban soil media. When evaluating the environmental fate of chemicals in terrestrial ecosystems, the bioavailability of the chemical and the effects of soil characteristics are both important considerations in determining the potential for intercompartment transfer as well as the bioaccumulation potential of a chemical. Bioavailability of organic compounds in terrestrial environments is complicated by many factors that will also influence the outcome of bioaccumulation tests (Hoke et al. 2014).

In the work of Semple et al. (2003) a bioavailable chemical "is freely available to cross an organism's cellular membrane from the medium the organism inhabits at a given time that is available now (no constraints)." A chemical is thought to be bioaccessible if it "is available to cross an organism's cellular membrane from the environment it inhabits, if the organism has access to the chemical" (Semple et al. 2003). The bioavailable fraction is a subset of the bioaccessible fraction (ECETOC 2013b) and is likely the fraction of greatest importance for conducting urban exposure studies (Semple et al. 2003).

Soil acts as a universal sink for terrestrial systems therefore bearing the greatest burden of environmental pollution. Pollutants have a higher accumulation rate by soil/sediment in comparison to air and water (Ockenden et al. 2012; Armitage et al. 2007). Accumulating evidence show that the uptake of CECs by crop plants may be influenced by a variety of factors,

both biotic and abiotic ([Christou et al. 2019a](#)). The main biotic factors that may influence the uptake of CECs by crop plants are the plant itself (encompassing the species, the variety and cultivar, the genotype, and the physiological state of the plant), and the soil microorganisms, which constitute the main cause for the biodegradation and biotransformation of CECs within the soil. Climatic conditions and other environmental perturbations (such as temperature, wind speed, UV radiation, salinity, drought, environmental pollution, etc.), the physio-chemical properties of CECs and soil composition make up the main abiotic factors that influence the likelihood for CECs uptake by crop plants in urban soil media ([Christou et al. 2019a](#)). Plants serve as a primary vehicle for the transfer of CECs into the food chain. CECs enter plant systems through two key processes: uptake and translocation. Uptake and translocation of pollutants by plants are affected by (i) plant physiology, (ii) soil properties, (iii) environmental factors, and (iv) the physiochemical properties of the pollutants.

(i) *Plant Physiology*

Vascular plant tissue is composed of the xylem and phloem. The xylem is a unidirectional transport system for water and minerals, whereas the phloem is a bidirectional transport system for organic molecules. When water and solutes enter the plant root through the epidermis, organic contaminants in solution either cross the root membranes and transport through the vascular pathways to the aerial tissues or accumulate in the plant roots ([Doucette et al. 2017](#)). The accumulation of contaminants in plant roots and edible tissues is measured by root concentration factor (RCF) and fruit concentration factor (FCF) ([Doucette et al. 2017](#)). There is a positive correlation between organic pollutant content and lipid content in plant roots ([Gao and Zhu 2004](#)). Root uptake of polychlorinated dibenzofurans (PCDD/Fs) from nutrient solution was dominated by lipophilic adsorption, and root accumulation of PCDD/Fs from soil solutions could be predicted by extractable lipid content in plant root ([Zhang *et al.* 2009](#)). Most polycyclic aromatic hydrocarbons (PAHs) were detected in plant cell walls which consist mostly of carbohydrate. Therefore, the carbohydrate content of plant cells played a leading role in the uptake of PAHs by plants ([Chen *et al.* 2009](#); [Zhang and Zhu 2009](#)).

Evidence of varying bioaccumulation of CECs across plants species is presented by their growth, reproduction, occurrence, and survival in the contaminated soil ([Doucette et al. 2017](#)). Various plant species can present different toxicity to identical pollutants in the same environmental condition because the mechanisms of elemental uptake by plants are not the same for all plant species. Bryophytes have been used in literature as bioindicators and biomonitors in terrestrial habitats due to their wide range of remarkable anatomical and physiological properties that mirror those of vascular plants (e.g., a plant with roots, stems, leaves) ([Doucette et al. 2017](#)).

Table 7. Plant Physiology Factors Affecting Bioconcentration Factor (BCF) of Plants ([Christou et al. 2019a](#)).

+	-
Plant genotype (genus & species) e.g., leafy vegetables	Crops with small root systems e.g., succulent plants
Summer growing season	Rainy growing season
Healthy plants	Stressed plants
High plant Kc values	Low plant Kc values
High net irrigation requirements	Low net irrigation requirements
Low lipid content in roots	High lipid content in roots

The majority of studies with regard to CECs uptake examined mostly (a) vegetables (leafy vegetables such as lettuce and cabbage, fruit vegetables such as tomato and cucumber, and root vegetables such as carrot and radish) and (b) cereals and fodder crops (e.g. maize, wheat, alfalfa) ([Christou et al. 2019a](#)). Experimental results revealed that the potential for CECs uptake by crop plants decreased in the order of leafy vegetables > root vegetables > cereals and fodder crops > fruit vegetables ([Christou et al. 2019a](#)).

(ii) *Soil Properties*

Inherent properties of natural soils such as pH, fertility, organic matter content, and texture can significantly influence the bioavailability of chemicals ([Christou et al. 2019a](#)). The importance of soil type was demonstrated by Princz et al. ([2014](#)) in an earthworm bioaccumulation study in which uptake of the test chemical in tissue of earthworms exposed in a sandy soil

was significantly greater than that in earthworms exposed to the chemical in clay loam soil where organic matter and clay content were significantly higher.

The transfer capacity of organic pollutants in soil is good in acidic or alkaline media but poor in media with intermediate pH (Sithole and Guy 1987). Increased organic matter content of soil decreased the plant uptake of organic pollutants because some organic pollutants (ionized compounds) might be strongly bound to soil organic matter which is a strong anion/cation exchanger (Trapp and McFarlane 1994). Increased organic matter content of soil decreased the plant uptake of organic pollutants because some organic pollutants (ionized compounds) might be strongly bound to soil organic matter which is a strong anion/cation exchanger (Trapp and McFarlane 1994).

Table 8. Soil Properties Affecting CEC Uptake by Plants (Christou et al. 2019a).

+	-
Low levels of organic matter	High levels of organic matter
Sandy soils	Clay or loamy soils
Acidic pH (pH < pKa of CEC)	Basic pH (pH > pKa of CEC)
Aerated soils (aerobic conditions)	Waterlogged soils (anaerobic conditions)

(iii) *Environmental Factors*

Table 9. Environmental Factors Affecting Evapotranspiration (K_c) by Plants (Christou et al. 2019a).

+	-
High temperature	Low temperature
High wind speed	Low wind speed
Low air humidity	High air humidity
Hot/Dry agricultural areas	Cold/Continental agricultural areas
Adequate soil moisture	Drought conditions

Higher temperature coefficients for diffusion processes of organic pollutants can accelerate passive absorption by the plant. On the other hand, temperature rise stimulated transpiration stream rate and enzyme activity of plants (Korte *et al.* 2000). Further literature

review would provide useful for this factor to better understand the impact environmental factors have on plant uptake.

(iv) *Physiochemical Properties of Pollutants*

+	-
Low MW	High MW
Hydrophilic	Hydrophobic

The physiochemical properties of CECs play a crucial role in the uptake and translocation from soil to plant systems. Some contaminants are highly stable and therefore less likely to undergo conformational change during interactions that occur during the uptake and translocation processes. The transpiration stream concentration factor (TSCF) is defined by Shone and Wood (1974) as "the ratio of chemical concentration in the transpiration stream to the concentration found in the external solution." This factor can be utilized as a tool to determine the overall uptake of CEC from soil to the xylem of plants.

Molecular mass of CECs is the leading pollutant-specific physiochemical property influencing the plant uptake process. The uptake and transportation of pollutants in plant phloem and xylem depends upon the size of the molecule (e.g., MW). For example, organic pollutants with small molecule size can easily permeate the membrane and hence, easily come in and go out of the phloem and xylem. On the other hand, organic pollutants with large molecule size have low permeability in membranes and therefore cannot be effectively transported in the phloem (Kvesitadze *et al.* 2015). Compounds with low MW are volatile and can be easily absorbed by roots and foliage. However, high MW pollutants, which are nonvolatile and possess strong hydrophobic properties, can only be absorbed by roots (Kvesitadze et al. 2015). A compounds tendency to dissolve in (hydrophilic) or repel (hydrophobic) water can be linked to a higher/lower TSCF (Chen et al. 2009).

5. Plant Uptake Models

Plant uptake models can provide information on the accumulation of chemicals and their transformation products from soil. However, the scope, complexity, and cost of these studies limits their routine application for assessment of terrestrial bioaccumulation. Various studies have been carried out to identify uptake and

translocation mechanisms of CECs by plants. The primary focus of this research surrounds the uptake of CECs by plant roots.

5.1. Mechanism of contaminant uptake by plants

CECs uptake by plants generally follows to main uptake pathways: (i) extracellular uptake and (ii) intracellular uptake. Extracellular uptake depends on the nature of the elements only, as the physiological conditions of the plant have no impact on the rate of uptake. Intracellular uptake is influenced by various aspects of plant metabolism (Cheng et al. 2017). Entry to the cell plasma is determined by affinity for an appropriate carrier, competitive elements, gradients in element concentration, and energy status. Elements located within the cell influence cell metabolism and must be considered when modeling plant uptake. Uptake rates are in general much lower than at the extracellular sites (Cheng et al. 2017).

Studies have shown that contaminants are enriched at the root surface and enter the roots with water. This mechanistic step is in agreeance with previous literature stating that hydrophilic compounds have a higher uptake rate than hydrophobic compounds. CECs penetrate the roots through the cuticle-free cell walls of young root hairs located closely behind the tip of the root. Contaminants then travel to the xylem transport tissue in the root along free intercellular space (apoplastic way) or cells (symplastic way) (Sterling 1994). The cell wall of the root cortex is porous, allowing for CECs to move freely from solution to the interior before they reach the endodermis (Trapp and Mc Farlane 1994). The general approach for examining bioaccumulation of organic chemicals in terrestrial plants includes measuring either root or foliar uptake, depending on the properties of the chemical or the most relevant route of exposure (Hoke et al. 2014). It must be noted that exposure rates may differ depending on consumption of "the root", "the shoot", or "the fruit" of any given plant, therefore potentially posing different health risks. Further research in this area would allow for a more thorough risk-based assessment that takes into account the varying plant species and their subsequent edible parts.

5.2. Mechanism of contaminant translocation by plants

Following uptake by plants, pollutants such as POPs are translocated to different parts of the plants (Lin *et al.* 2007). Generally, two kinds of pollutant transport pathways in higher plants have been reported: (i)

intracellular and intercellular transport (short distance transport) and (ii) conducting tissue transport (long distance transport) (Taiz and Zeiger 2002). Currently, agreement on a formal mechanistic approach for contaminant translocation by plants is not present in literature. Furthermore, literature focusing specifically on urban soil media was not identified.

6. Research Gaps and Concluding Remarks

Data gaps on contaminated lands stem from a variety of factors including the multi-jurisdictional responsibilities for identifying, managing, and cleaning up contaminated risk sites (U.S. EPA 2017). The range of contamination at sites varies along with the range of contaminated sites likely to be proposed for food production or crop cultivation. There has been limited effort to establish a baseline or screening standards for sites oriented for food production or urban agriculture beyond past EPA projects focused on examining urban agriculture from the lens of contaminated sites cleanup or risk-based cleanup standards. Along with the U.S. EPA, other various state and/or federal agencies with authority to protect food supply, agricultural resources, and public health may have key roles to play in delineating and developing baseline standards for food production.

In addition, root uptake and reactive transport are plant- and soil- dependent, making it difficult to generalize results. Concern over the release of a chemical to the environment must consider the toxicity of the chemical, the amount and mode (continuous, intermittent) of release, the environmental compartment to which the chemical is released (soil, atmosphere, water), and fate processes that may ameliorate the potential for exposure or transform the compound to a more a less toxic form (Hoke et al. 2014). Fate processes in terrestrial ecosystems include abiotic and biotic processes (e.g., hydrolysis, photolysis, biodegradation, soil adsorption and mobility, volatilization from water or soil) (Hoke et al. 2014). Future literature research on the impact of these fate processes on the uptake, translocation, bioaccumulation, and bioavailability of CECs in urban soils would provide valuable resources for urban growers.

Another limitation found is that soil testing for contaminants appears to be rare in urban agriculture. Soil testing for agronomic parameters such as pH, organic matter, and cation exchange is commonly done in land grant university soil testing labs. Bridging soil testing practices and disciplines of environmental science and agriculture is of utter importance to better integrate testing for environmental contaminants ubiquitous in urban environments. This has proved it

difficult to provide growers with national or regional specific concentration factor guidelines for possible risk associated with contaminant exposure through produce grown in urban gardens.

The uptake of CECs by important crop plants, such as fruit trees, is not yet sufficiently evaluated (to our findings). Fruit trees, such as citrus, bananas, apple and other fruit bearing trees, have high evapotranspiration rates, which may render them as plants with moderate to high potential for CECs uptake (similar to that of fruit vegetables) (Hoke et al. 2014). Moreover, further research on the quantification of the examined CECs (including their metabolites) in both the edible parts of the examined plants and in the growing medium is of high importance. This specific data gap is in part due to the difficulty in finding state specific plant uptake models on both an industrial and urban agricultural scale. The continuation of this literature

review will allow for a deeper understanding of the potential of urban crop plants to uptake and accumulate CECs, and consequently the assessment of the risk from the consumption of agricultural products grown in urban soils.

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