

Understanding and Controlling Metal Contamination in Urban Gardens

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Outline

- What are soil contaminants?
- Heavy metal contaminants in urban areas.
- How to determine metal contaminants in soils.
- Newark urban gardens as a case study.

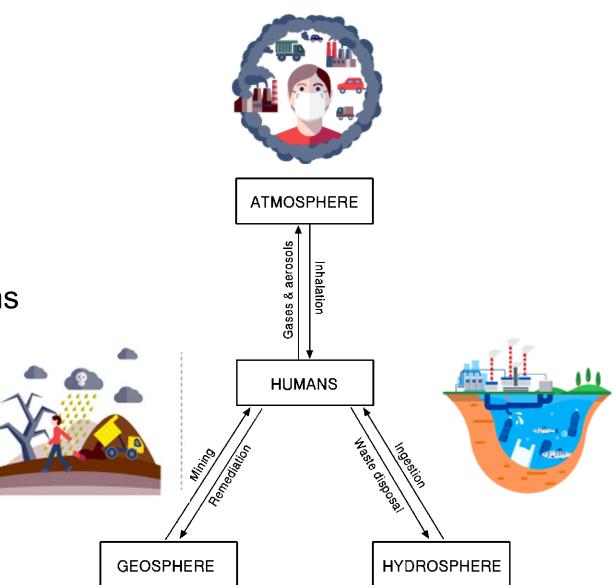
Soil Contaminants

- Contaminant
 - Unwanted substance added to a system
 - Present higher than natural concentrations
 - Changes the natural composition of the system
- Pollutant
 - Contaminant that has a net negative impact on the environmental system
- Toxic Pollutant

- Pollutant that has a negative impact on biota and/or human health

Soil Contaminants

- (Toxic) Pollutants:
 - Substances identifiable in excess
 - Can be produced by both natural and anthropogenic processes
 - Known to be harmful to living organisms
- Include:
 - Pathogens
 - Nutrients
 - Synthetic organic chemicals
 - Heavy metals



Heavy Metals

- Have a high atomic number, atomic weight and a specific gravity greater than 5.0
- Include
 - Metalloids
 - Transition metals
 - Basic metals
 - Lanthanides
 - Actinides

1 IA 1A						Perio	odic 1	Table	of the	e Elen	nents						18 VIIIA 8A 2
Hydrogen 1.008	2 11A 2A							Atomic Number	_			13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012							Syn	nbol			5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15,999	9 Fluorine 18.998	10 Neon 20.180
11 Na sodium 22.990	12 Mg Magnesium 24.305	3 111B 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 	c Mass	11 IB 1B	12 IIB 2B	13 Aluminum 26.982	14 Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca calcium 40.078	21 Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51,996	25 Mn Manganese 54.938	26 Fe Iron 55,845	27 Co Cobalt 58,933	28 Ni Nickel 58,693	29 Cu Copper 63,546	30 Zn 2inc 65.38	31 Ga Gallium 69.723	32 Germanium 72.631	33 As Arsenic 74.922	34 Se selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92,906	42 Mo Molybdenum 95.95	43 TC Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn 118,711	51 Sb Antimony 121,760	52 Te Tellurium 127.6	53	54 Xe xenon 131.294
55 Cs (Cs 132,905	56 Ba Barium 137,328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180,948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190,23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 TI Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208,980	84 Po Polonium [208.982]	85 At Astatine 209,987	86 Rn Radon 222.018
87 Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	¹⁰⁹ Mt	110 Ds	111 Rg Roentgenium [280]	¹¹² Cn	¹¹³ Nh	114 Fl Flerovium [289]	¹¹⁵ Mc	116 LV Livermorium [293]	¹¹⁷ Ts	118 Oganesson [294]
	Lanth Ser	ies			Pr N						bium 66 Dysp						-U etium
	Actii Ser	nide ies Act	8.905 140 90 T tinium Tho	116 14 14 14 91 Fium Prota	0.908 144 Pa 92 Ura	242 144 93 J N nium Nept	11 11 11 11 11 11 11 11 11 11 11 11 11	50.36 151 Pu A tonium Ame	1964 1 96 ricium C	57.25 158 97 Berk	98 98 elium Califo	2.500 16 Df 99 Einst	4.930 16 ES JOO Fer Fer	7.259 168 101 mium Mende	8.934 17: 102 102 Nob	3.055 17 103 103 Lawr	4.967
		22	7.028 232 Alkali Metal	.038 23 Alkali Eart	ne Trans	sition	Basic	Semimetal	Nonmet		N	oble	nthanide	Actinide	58.1 251	9.101 [3	262]
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RUTGERS Sources of Heavy Metals in Urban areas

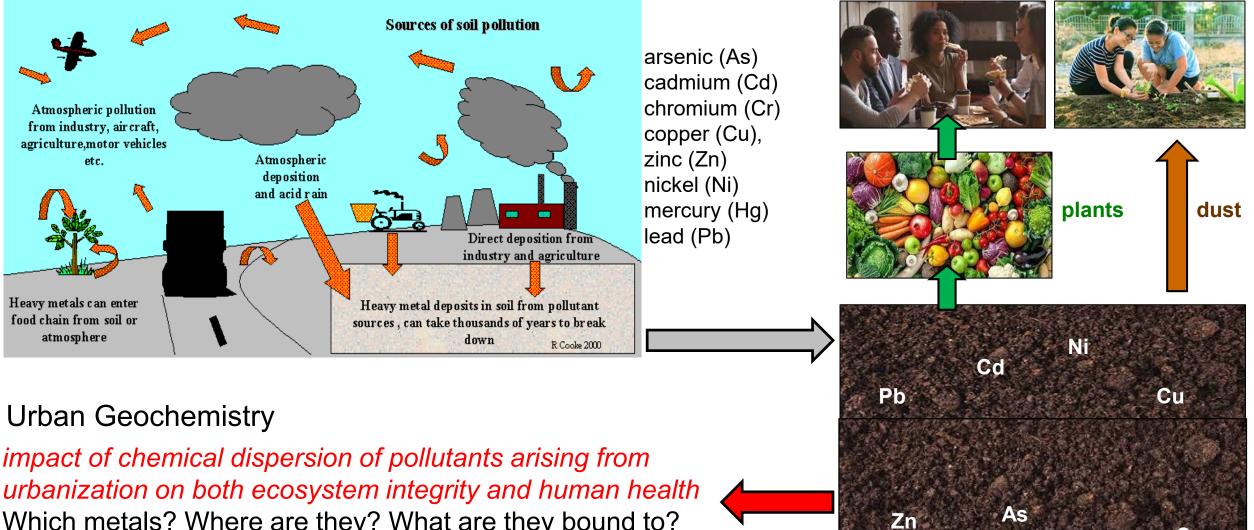
- Transportation
 - Traffic and vehicles emissions
 - Brake and tyre wear
 - Weathering of asphalt and roadside material
- Industrial activities
 - industrial discharge
 - power and desalination plants,
 - fuel combustion
- Household
 - Consumer products
 - Roofing materials
 - Paint







Urban soil quality



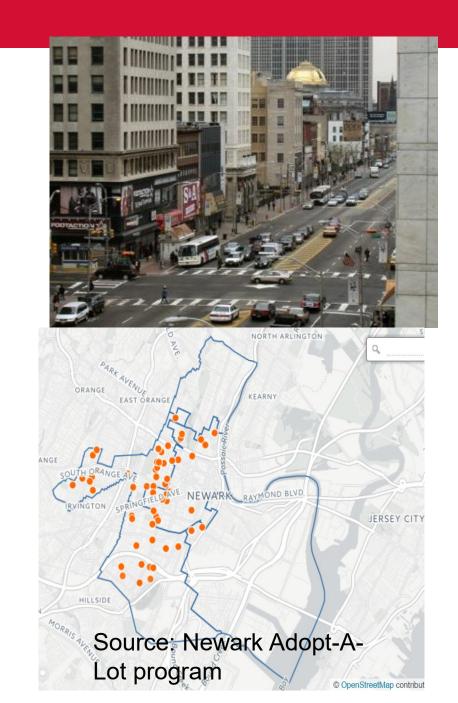
Pollutant transfer pathways

Cr

Which metals? Where are they? What are they bound to? Are they mobile and/or bioavailable?

Newark: A Case Study

- Newark is the most populous city in NJ, and is the second largest city of the NYC Metropolitan area – a Megacity
- Major air, shipping, and rail hubs and industry and residences
- Suffers from legacy and current pollution from toxic wastes, manufacturing & industry, transportation; several superfund sites.
- Numerous organizations manage urban farming initiatives that involves local community residents, school children and corporate partners



Soil Quality Standards

Residential Soils				
Contaminant	mg/kg			
Ag	390			
As	19			
Cd	78			
Со	1,600			
Cu	3100			
Hg	23			
Ni	1600			
Pb	400			
Se	390			
Zn	23,000			

- Minimum standards for remediation of residential and non-residential direct contact soils, NJDEP
- Sets levels at which metals may pose a threat to human health via ingestion, dermal and inhalation pathways
- Protects human health but also the environment

Methods to Determine Heavy Metal Contamination

- In-situ analysis
 - Portable X-ray fluorescence analyzer



- Sampling and ex-situ analysis
 - Inductively-coupled optical emission spectrometer



Limits of Detection

XRF LOD for Contaminants in Soil (ppm, mg/kg) for a Standard Reference Material (SRM).

Element	SRM	Element	SRM
Ca	500	Rb	10
Sc	400	Sr	11
Ti	160	Zr	15
V	70	Мо	15
Cr	85	Ag	10
Mn	85	Cd	12
Fe	100	Sn	30
Со	260	Sb	30
Ni	65	Ba	100
Cu	35	Hg	10
Zn	25	Pb	13
As	11	Th	20
Se	20	U	20

ICP-OES LOD with different configurations ug/L

Zn 213.857	0.7	0.2	0.2
Te 214.282	13	15	11
Pt 214.424	11	1.8	1.8
Cd 214.439	0.5	0.1	0.1
Pb 220.353	9.2	2.2	2.2
Bi 223.061	9.1	2.2	2.3
lr 224.268	7.9	1.7	1.8
Re 227.525	5.6	1.5	1.5
In 230.606	26	5.6	6.0
Ni 231.604	4.5	0.9	0.9
Fe 238.204	1.6	0.2	0.3
Co 238.892	2.7	0.6	0.6
Au 242.794	3.1	1.1	1.2
B 249.772	0.6	0.3	0.3
Si 251.611	4.4	0.9	0.9
Mn 257.610	0.2	0.1	0.1
Lu 261.541	0.2	0.05	0.05
Ta 263.558	5.0	1.5	1.5
Hf 264.141	3.7	0.9	0.8
Cr 267.716	1.1	0.2	0.2

NJDEP Limits

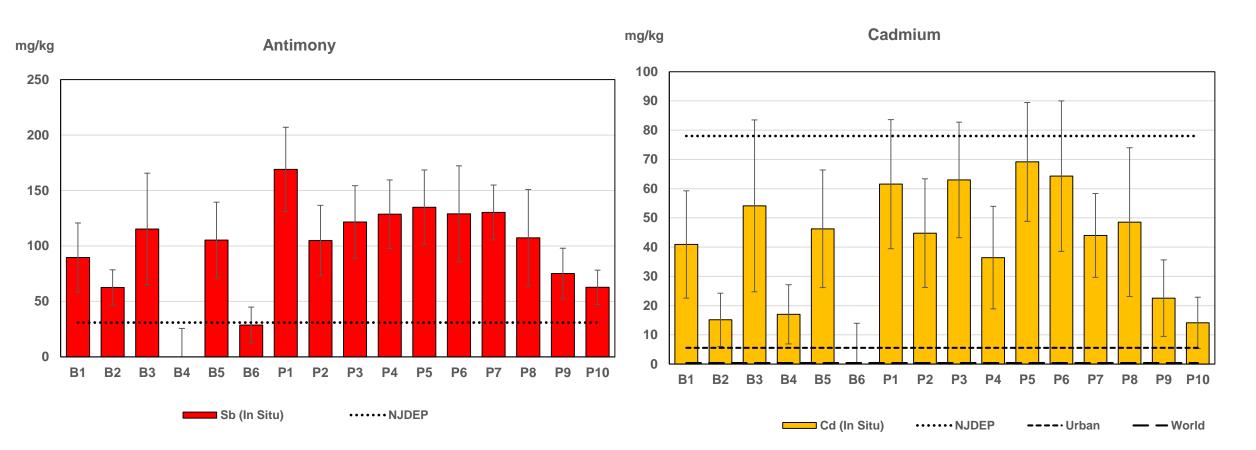
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In-Situ XRF for Heavy Metals

- XRF Analysis using EPA Method 6200
- Remove large debris from the soil surface e.g. rocks, pebbles, leaves, vegetation, roots, and concrete.
- Smooth with a stainless-steel trowel and/or compact the soil
- Soil should not be saturated with water ($\leq 20\%$).
- Position the analyzer on the desired analysis spot, ensure the nose of the analyzer is making contact with the soil, and then initiate a reading.
- Sample in a grid, or areas of most concern



In-Situ XRF for Heavy Metals

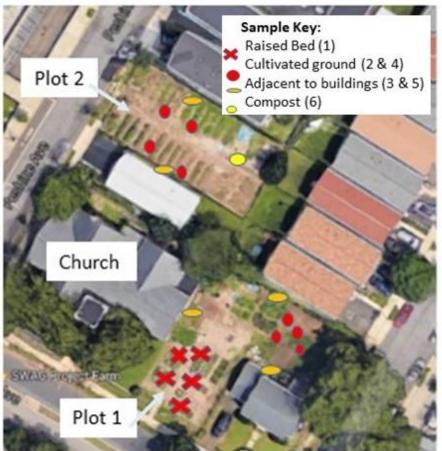


Unit Name

Sampling and Ex-Situ Analysis for Heavy Metals







Located in the South Ward

Unit Name

Methods

Sampling

- 4 subsamples of soil were collected at 20-30 cm depth
- Subsamples were mixed into a single composite soil sample

Sieving, drying

- Samples were air dried and sieved (2 mm)
- Dried in a muffle furnace at 105 °C for 24 hours

Total metal extraction

- A portion of dried <2mm fraction was digested with 1 M nitric acid¹(with continuous shaking) for 2 hours
- Extractant was filtered using a 0.45 µm PES syringe filter and stored for analysis

Tessier scheme of extraction

To determine metal associated with the various fractions of soil².

	Fraction	Description	Mineral/Organic matter association		
	1	Exchangeable	Hydrated Fe-Mn oxides and humic acids		
	2	Acid Soluble	Carbonates		
	3	Reducible	Fe-Mn oxides		
	4	Oxidizable	Organic matter (humic and fulvic acids)		

Reagent
1 M MgCl2 (pH 7)
1 M NaOAc (pH 5)
0.04 M NH2OH.HCI (in 25% HOAc)
H2O2/HNO3 (pH 2), NH4OAc (3.2 M)

1. Carter, M. R., ed. 1 M HNO₃ Extraction. Soil Sampling and Methods of Analysis, edited by Carter, M. R. Boca Raton, FI: Lewis Publishers, 1993

2. Tessier, P. G. C. Campbell, and M. Bisson Sequential extraction procedure for the speciation of particulate trace metals, Analytical Chemistry 1979 51 (7), 844-851

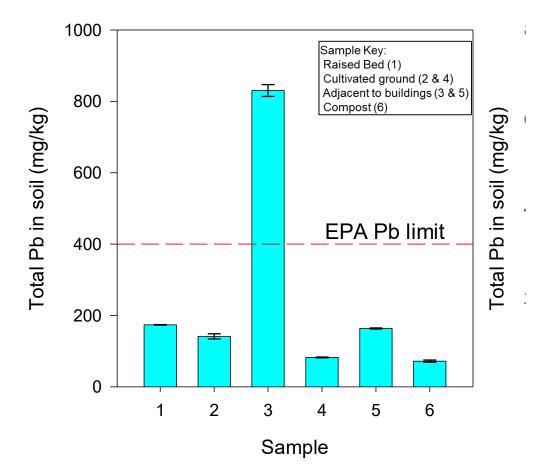
Methods

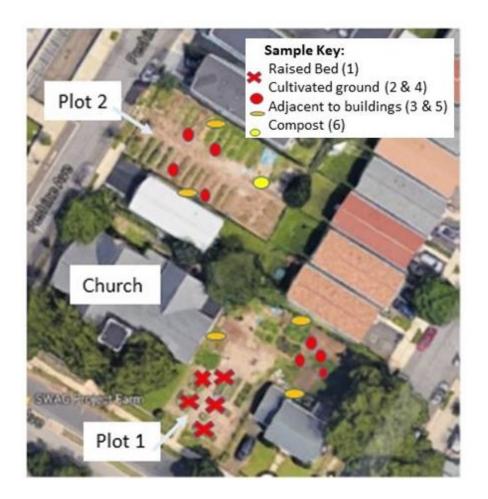
Analysis

- All extractants were analyzed for Pb (also zinc, nickel, copper and cadmium), using an Agilent 5100 SVDV ICP-OES*
- Standards for analysis were prepared in matrices consistent with the samples



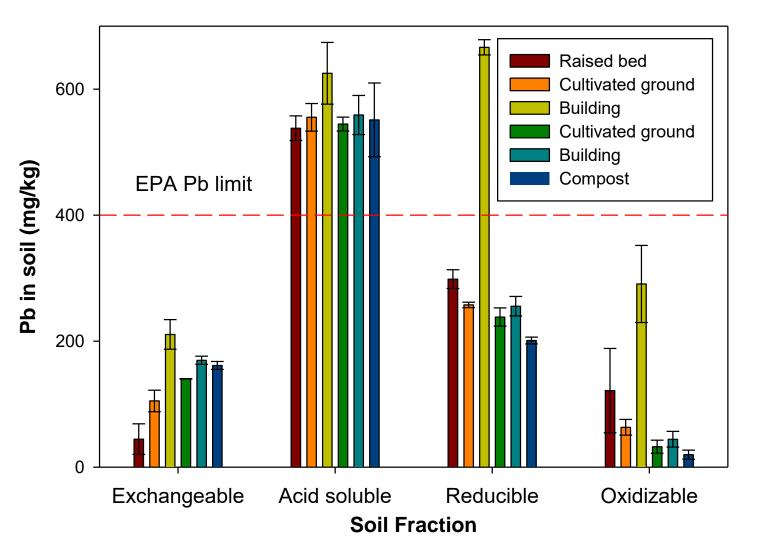
Lead in Bulk Soil





One sample exceeds EPA & NJDEP Pb limit of 400 ppm

lead in Soil Fractions



- The sample collected near the building has the highest concentration of Pb in all fractions
- In this site, most of the Pb is bound to the acid soluble carbonate minerals, and the reducible fraction
- Metal in carbonate fraction has high mobility and can be released by changes in pH
- The likely source of Pb is from old paint on the building

Summary

- Metals are common pollutants in urban soils as a result of concentrated human activity
- There are known levels at which metals may become toxic to humans and require remediation.
- A combination of in-situ and ex-situ analyses can be combined to determine spatial distribution of metals and mobility.
- Results equip urban farmers with quantitative scientific data regarding the environmental health of their soils, facilitating informed decision making.