Scuola di Agraria e Medicina Veterinaria
dell'Università degli Studi di Napoli Federico II

IL caffè SCIENTIFICO

IL SISTEMA SUOLO-PIANTA IN AMBIENTI TERRESTRI ED EXTRATERRESTRI E LE INTERAZIONI CON L'UOMO

Relatore:

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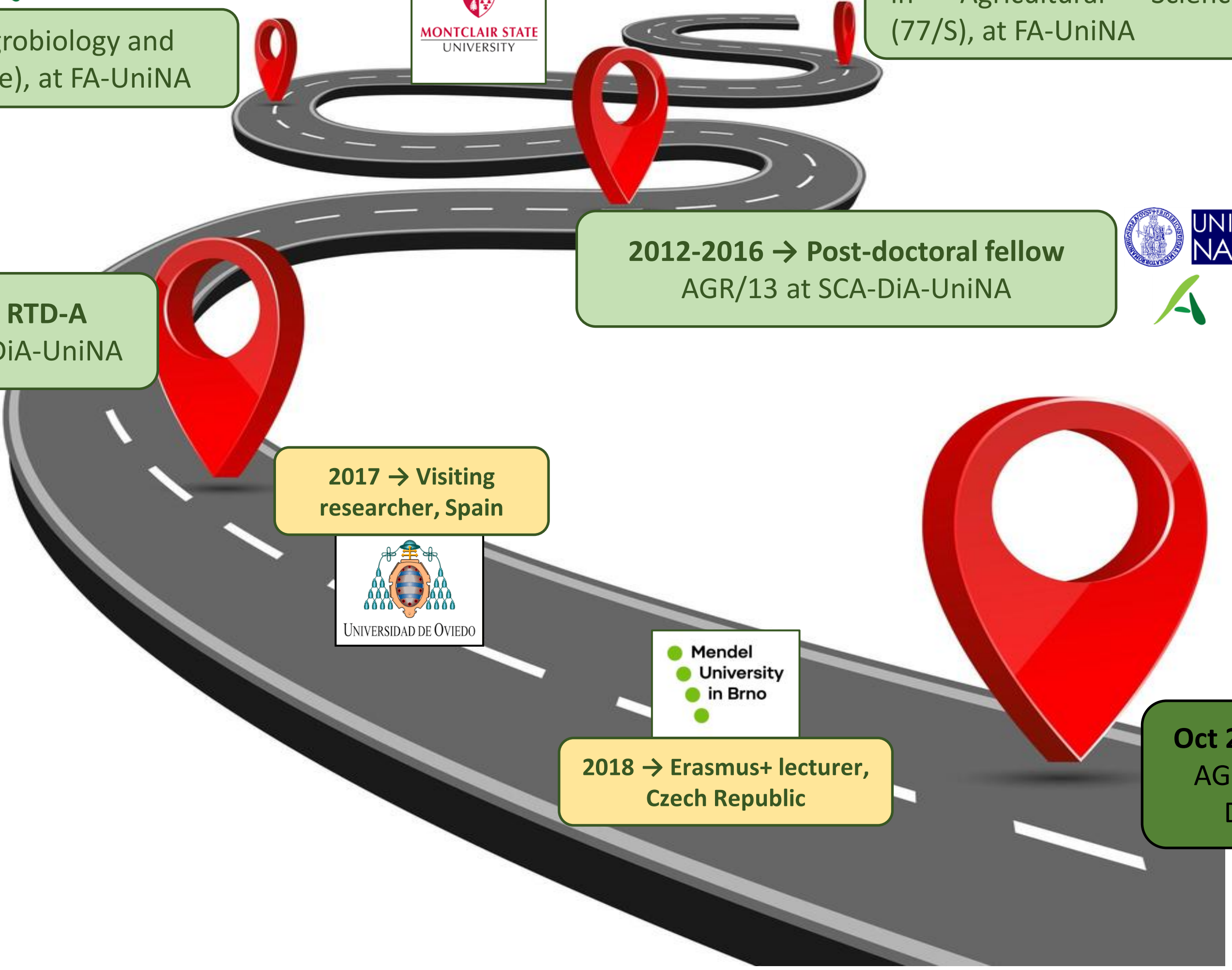
RTDB AGR/13 (*ag.caporale@unina.it*)

Sezione SCA, DiA-UniNA

UNI NA

My education path



Oct 2008 → Master's degree in Agricultural Sciences (77/S), at FA-UniNA

2010 → Visiting Ph.D. student, USA

MONTCLAIR STATE UNIVERSITY

Feb 2012 → Ph.D. in Agrobiology and Agrochemistry (XXIV cycle), at FA-UniNA

2012-2016 → Post-doctoral fellow AGR/13 at SCA-DiA-UniNA

2016-2021 → RTD-A AGR/13 at SCA-DiA-UniNA

2017 → Visiting researcher, Spain

UNIVERSIDAD DE OVIEDO

Mendel University in Brno

2018 → Erasmus+ lecturer, Czech Republic

Oct 2021 → RTD-B AGR/13 at SCA-DiA-UniNA

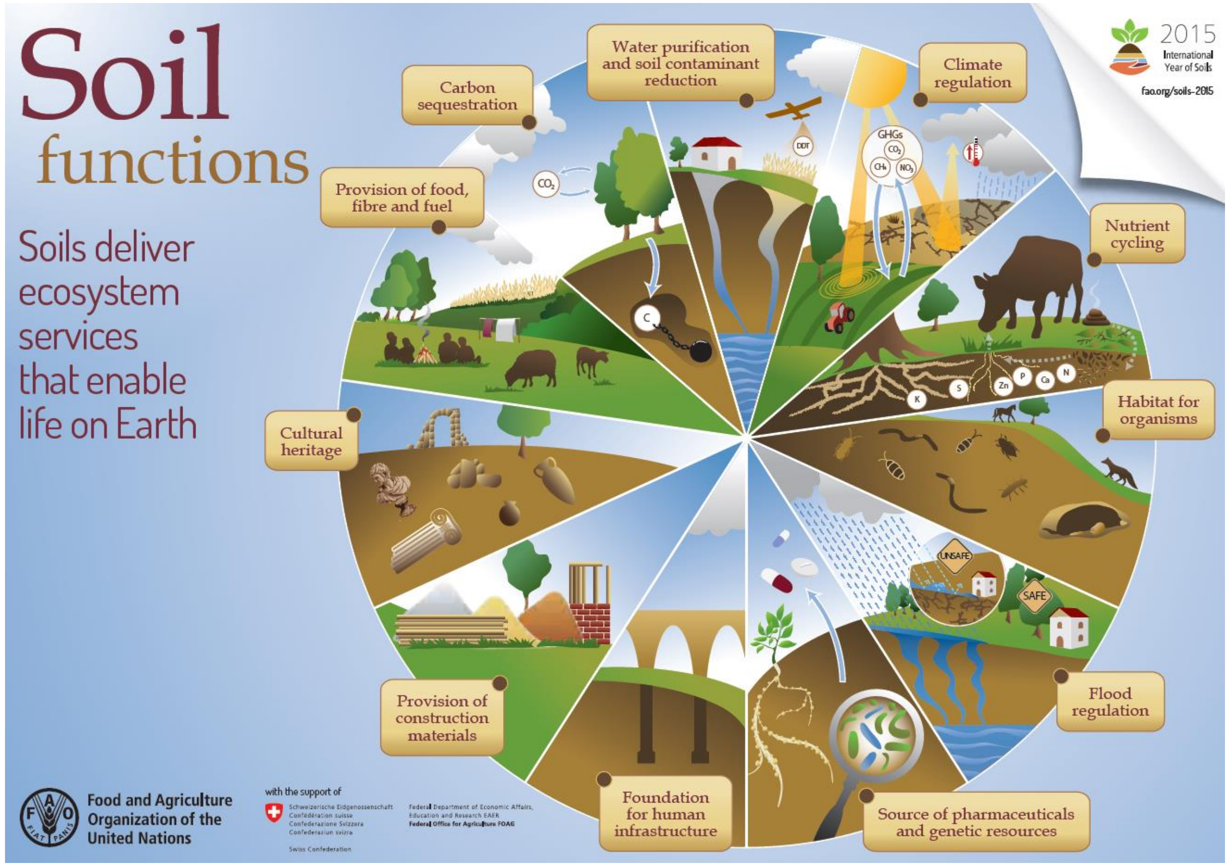
Soil-plant systems

Lab scale

Greenhouse scale

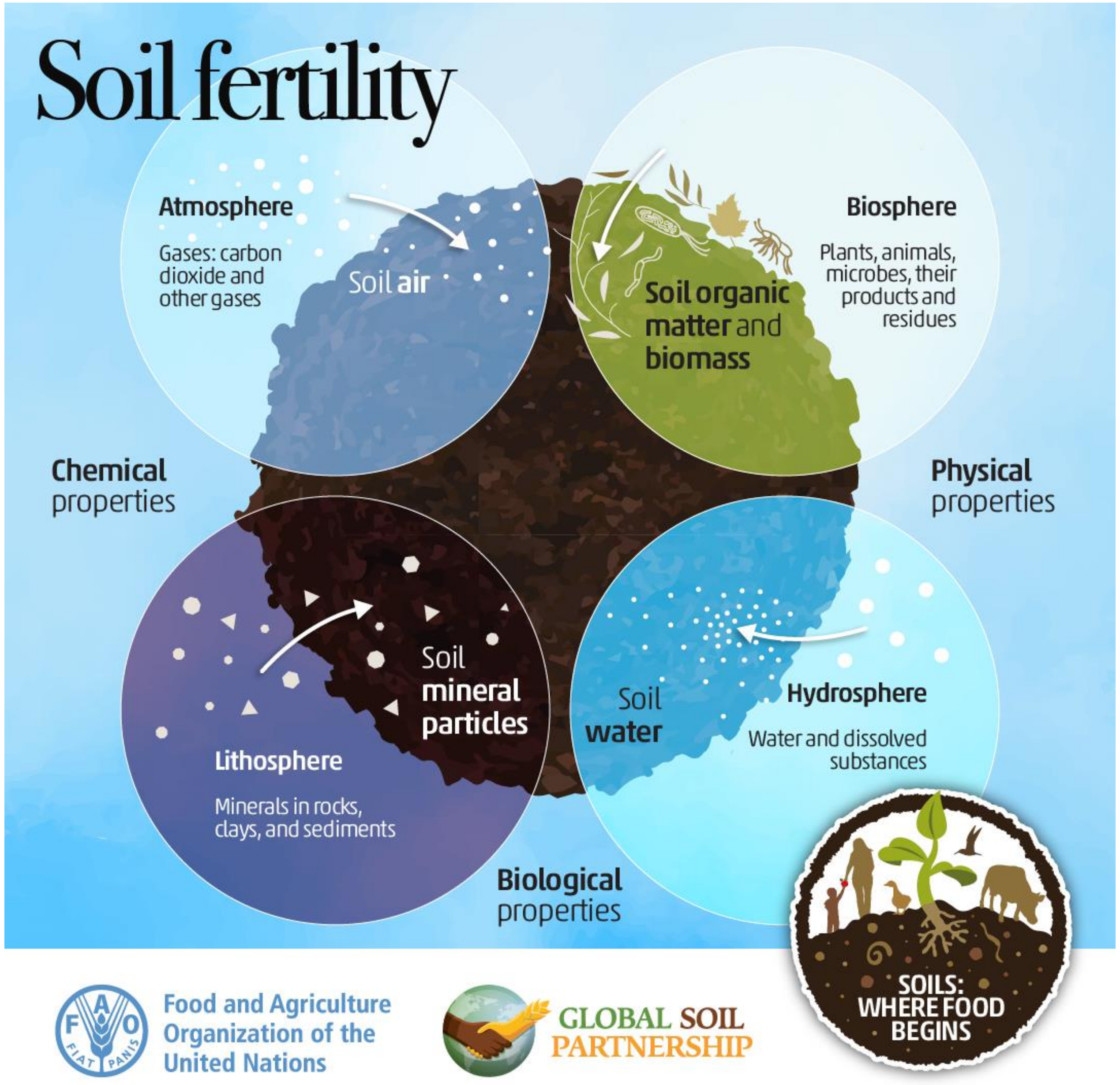
Field scale

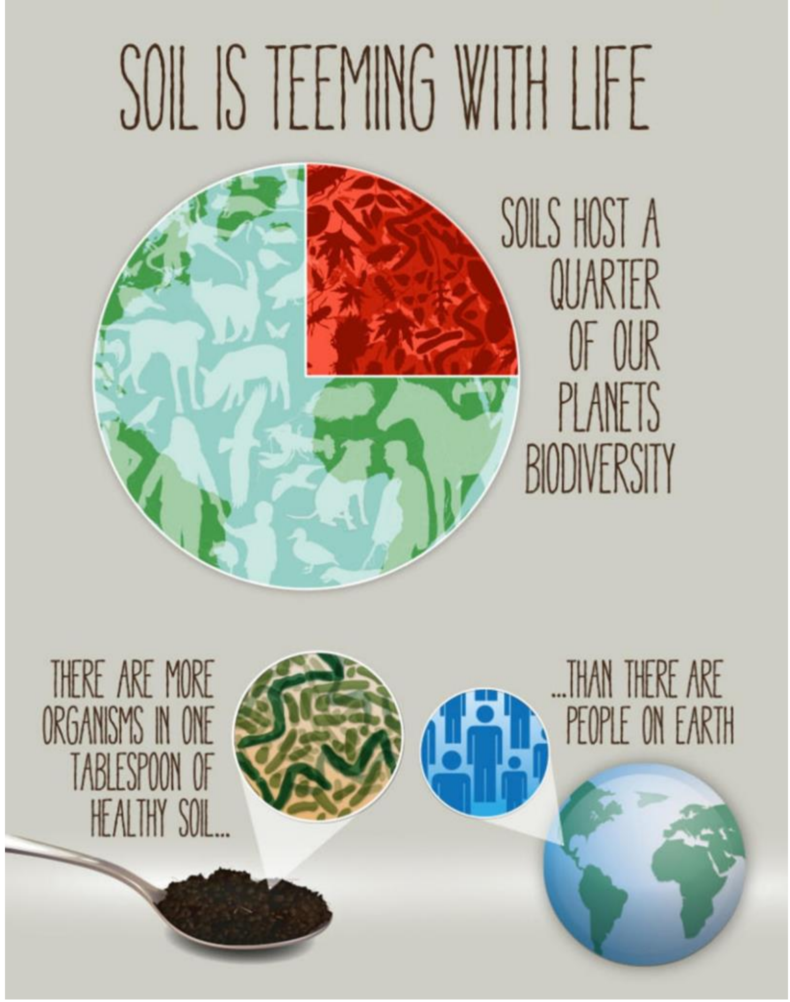
The soil: a key and non-renewable resource for humankind



World Soil Day (WSD) is held annually on 5 December (from 2002, promoted by IUSS: International Union of Soil Sciences) to focus attention on the importance of healthy soil and to advocate for the sustainable management of soil resources

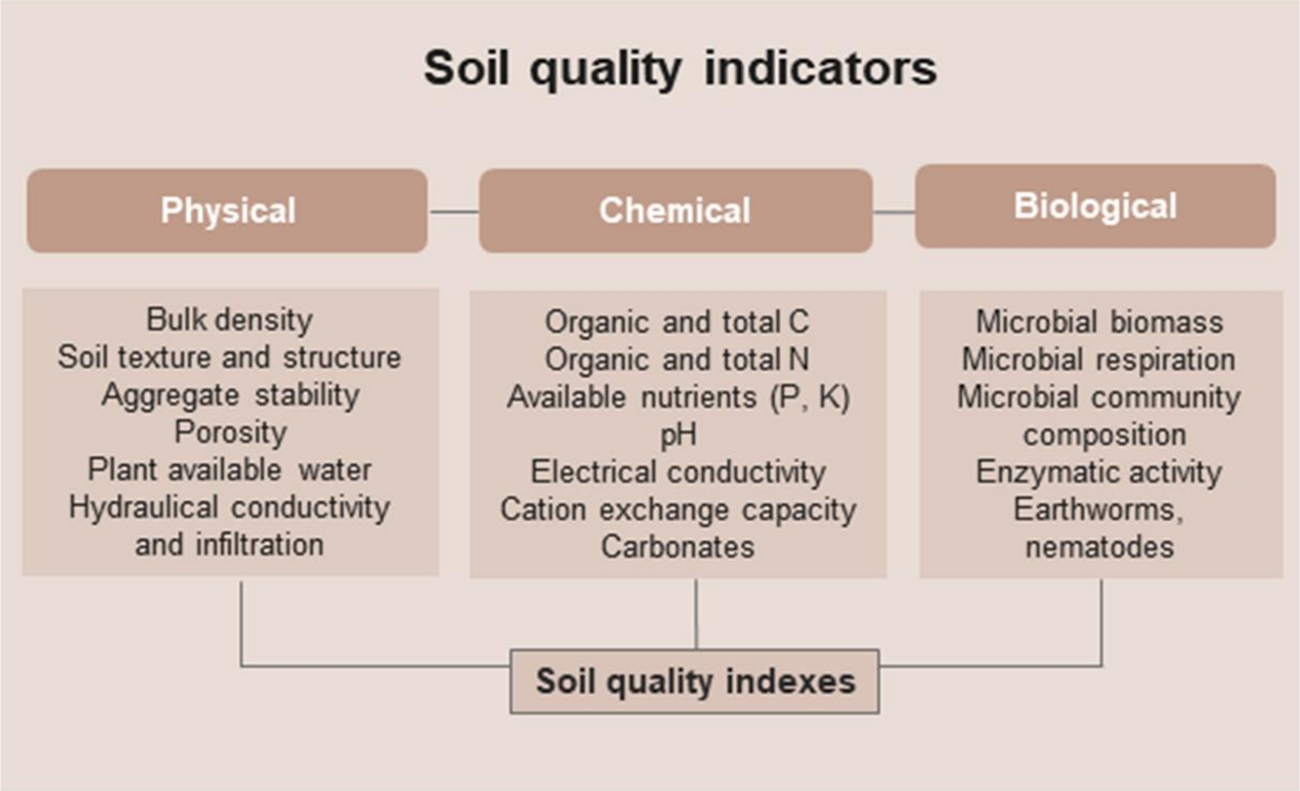
The soil: a true cradle of life enables to feed humanity

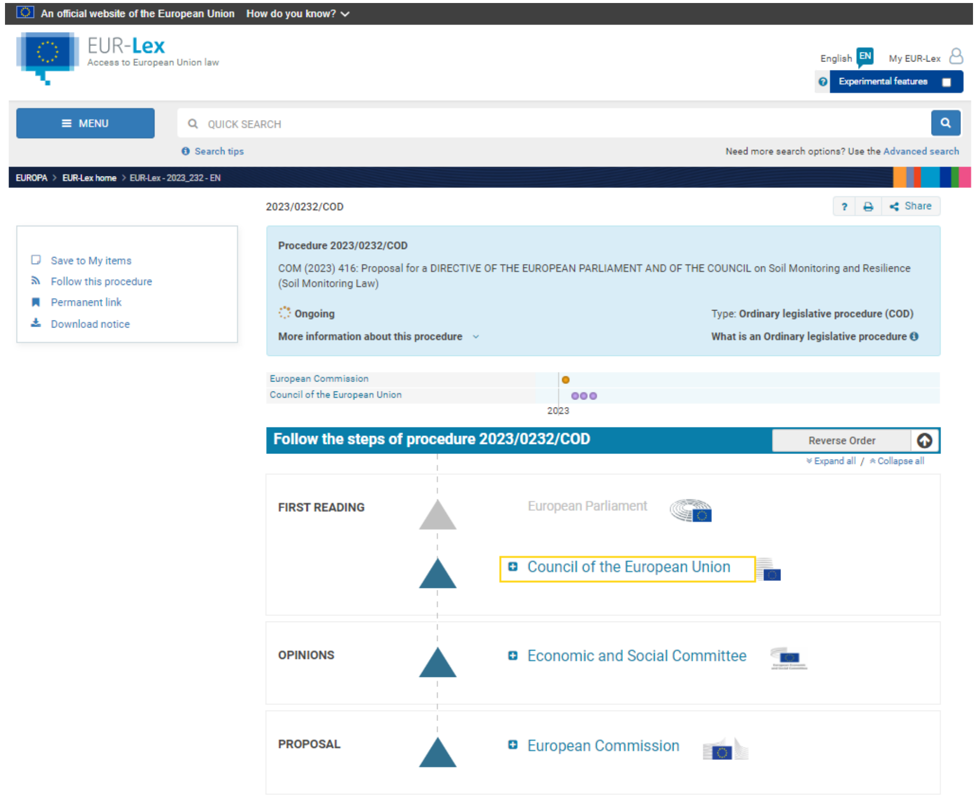


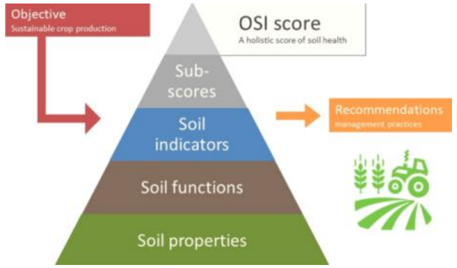


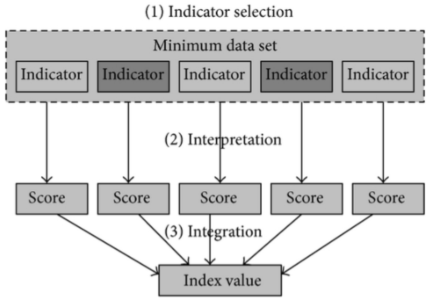
Soil produces 95% of our food, be it the crops we eat, or forages and other plants to feed animals for meat (FAO, International Year of Soils 2015)

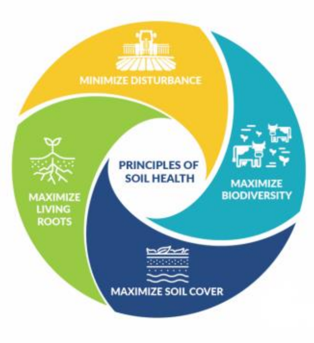
INDICATORS → DESCRIPTORS







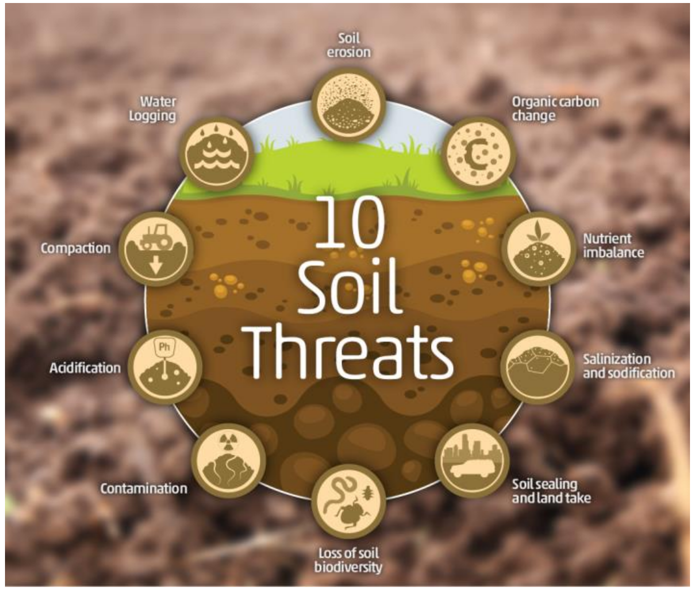


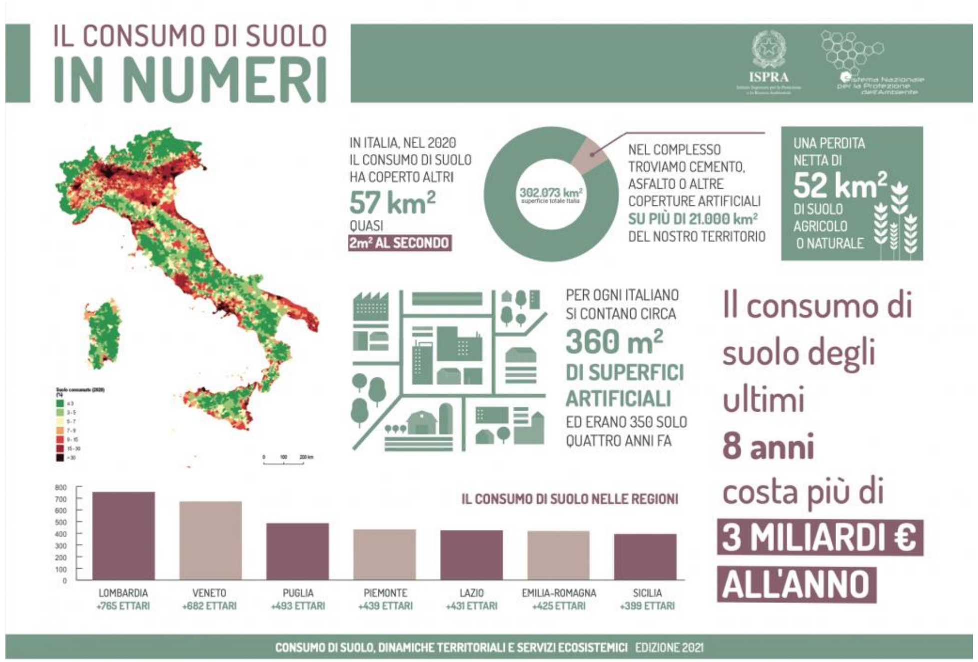


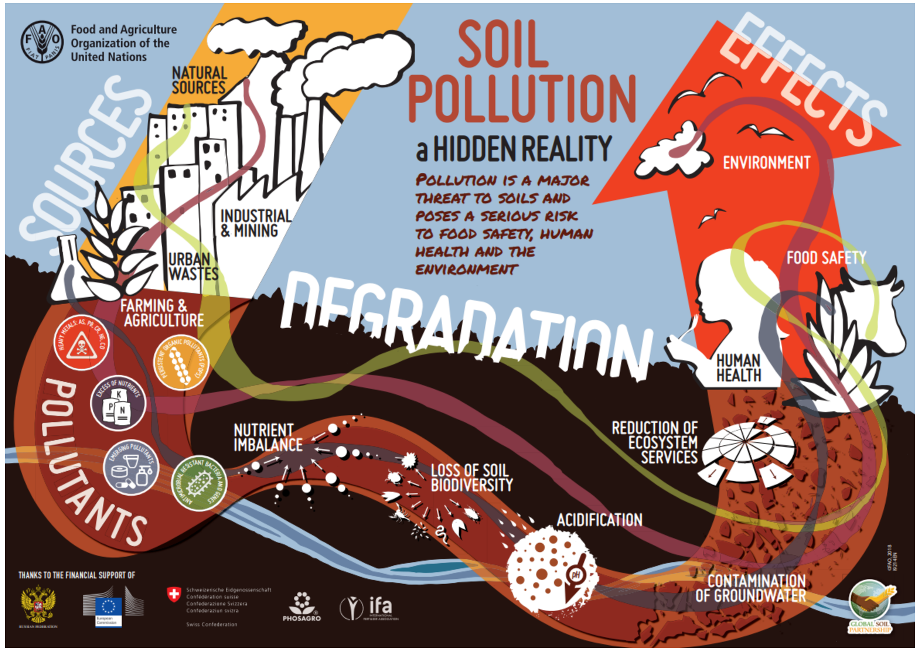
Procedure 2023/0232/COD

COM (2023) 416: Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on **Soil Monitoring and Resilience (Soil Monitoring Law)**

Soil threats







Italian legal benchmark

Supplemento ordinario alla "Gazzetta Ufficiale" n. 88 del 14 aprile 2006 - Serie generale

Spediz. abb. post. 45% - art. 2, comma 20/b
Legge 23-12-1996, n. 662 - Filiale di Roma

GAZZETTA UFFICIALE
DELLA REPUBBLICA ITALIANA

PARTE PRIMA — Roma - Venerdì, 14 aprile 2006 — SI PUBBLICA TUTTI I GIORNI NON FESTIVI

DIREZIONE E REDAZIONE PRESSO IL MINISTERO DELLA GIUSTIZIA - UFFICIO PUBBLICAZIONE LEGGI E DECRETI - VIA ARENULA 70 - 00100 ROMA
AMMINISTRAZIONE PRESSO L'ISTITUTO POLIGRAFICO E ZECCA DELLO STATO - LIBRERIA DELLO STATO - PIAZZA G. VERDI 10 - 00100 ROMA - CENTRALINO 06 85081

DECRETO LEGISLATIVO 3 aprile 2006, n. **152.**

Norme in materia ambientale.

Decreto legislativo 03.04.2006 , n. 152			
	Allegato 4/14 - Allegato 5 al Titolo V della Parte quarta - Valori di concentrazione limite accettabili nel suolo e nel sottosuolo riferiti alla specifica destinazione d'uso dei siti da bonificare	**A**	**B**
	Concentrazione soglia di contaminazione nel suolo, nel sottosuolo e nelle acque sotterranee in relazione alla specifica destinazione d'uso dei siti	Siti ad uso Verde pubblico, privato e residenziale	Siti ad uso Commerciale e industriale
	Tabella 1: Concentrazione soglia di contaminazione nel suolo e nel sottosuolo riferiti alla specifica destinazione d'uso dei siti da bonificare	(mg kg^{-1} espressi come ss)	(mg kg^{-1} espressi come ss)
	Composti inorganici		
1	Antimonio	10	30
2	**Arsenico**	20	50
3	Berillio	2	10
4	**Cadmio**	2	15
5	**Cobalto**	20	250
6	**Cromo totale**	150	800
7	**Cromo VI**	2	15
8	**Mercurio**	1	5
9	**Nichel**	120	500
10	**Piombo**	100	1000
11	**Rame**	120	600
12	Selenio	3	15
13	Stagno	1	350
14	Tallio	1	10
15	Vanadio	90	250
16	**Zinco**	150	1500
17	Cianuri (liberi)	1	100
18	Fluoruri	100	2000
	Aromatici		
19	Benzene	0.01	2
20	Etilbenzene	0.05	50
21	Stirene	0.05	50
22	Toluene	0.05	50
23	Xilene	0.05	50
24	Sommatoria organici aromatici (da 20 a 23)	1	100

MINISTERO DELL'AMBIENTE E DELLA TUTELA DEL TERRITORIO E DEL MARE

DECRETO 1° marzo 2019, n. **46.**

Regolamento relativo agli interventi di bonifica, di ripristino ambientale e di messa in sicurezza, d'emergenza, operativa e permanente, delle aree destinate alla produzione agricola e all'allevamento, ai sensi dell'articolo 241 del decreto legislativo 3 aprile 2006, n. 152.

ce in studio, il codice assegnato all'area è ripetuto e seguito da un numero sequenziale (A1, A2...An) che indica il punto di campionamento; ciò premesso, si procede come segue:

nell'area individuata per il campionamento di suolo relativo ai prodotti vegetali, a meno dei frutteti, in base all'estensione della zona da investigare, si prelevano, lungo i percorsi definiti, da 5 a 15 punti fino a profondità di 30-50 cm (profondità di rimescolamento o rivoltamento), mediante uso della vanga; il suolo campionato deve essere setacciato in campo mediante vaglio a maglia di 2 cm;

la quantità di suolo campionato per ciascun punto deve essere, indicativamente, pari a 3-5 kg, una parte della quale è utilizzata per formare il campione globale, mentre la restante è conservata e sarà eventualmente utilizzata in seguito per effettuare analisi di controllo sul campione elementare; tale campione elementare potrebbe essere codificato mediante la Sigla Campione costituita come segue:

lettera A(maiuscola), numero sequenziale, suolo (cioè il nome della matrice stessa) =

A1_suolo, A2_suolo..., An-suolo

dai singoli punti di campionamento verrà costituito, previa miscelazione e quartatura delle singole aliquote, il campione globale individuato dalla sigla:

Atot_suolo.

Nel campo NOTE della relativa scheda di campionamento dovranno essere specificate tutte le SIGLE CAMPIONE dei campioni elementari, per esempio:

Atot_suolo
A1_suolo (con eventuale georeferenziazione)
A2_suolo
... ...
An_suolo

N.B. All'interno di terreni con presenza di colture varie (alberi da frutta, foraggio, ortaggi, ecc.) si individuano i punti di campionamento nelle vicinanze delle colture stesse.

5. Procedura di campionamento di soil-gas.

Per il campionamento del soil-gas si può fare riferimento alle procedure stabilite dagli enti di controllo. In assenza di procedure specifiche è possibile fare riferimento ai protocolli approvati per aree SIN.

ALLEGATO *2*

Art. 3.
Concentrazioni soglia di contaminazione (CSC) per i suoli delle aree agricole

		CSC (mg kg^{-1} espressi come ss)
	Composti inorganici	
1	Antimonio	10*
2	Arsenico	30*
3	Berillio	7*
4	Cadmio	5*
5	Cobalto	30*
6	Cromo totale	150*
7	Cromo VI	2*
8	Mercurio	1*
9	Nichel	120*
10	Piombo	100*
11	Rame	200*
12	Selenio	3*
13	Tallio	1*
14	Vanadio	90*
15	Zinco	300*
16	Cianuri (liberi)	1
	Aromatici policiclici	
17	Benzo(a)antracene	1
18	Benzo(a)pirene	0,1
19	Benzo(b)fluorantene	1
20	Benzo(k)fluorantene	1
21	Benzo(g,h,i)perilene	5
22	Crisene	1
23	Dibenzo(a,h)antracene	0,1
24	Indenopirene	1
	Fitofarmaci	
25	Alaclor	0,01
26	Aldrin	0,01
27	Atrazina	0,01
28	alfa-esacloroesano	0,01
29	beta-esacloroesano	0,01
30	gamma-esacloroesano (lindano)	0,01
31	Clordano	0,01
32	DDD	0,01
33	DDT	0,01
34	DDE	0,01
35	Dieldrin	0,01
36	Endrin	0,01
	Diossine e furani	
37	Sommatoria PCDD, PCDF + PCB Dioxin-Like (PCB-DL) **(conversione T.E.)	6 ng/kg SS WHO-TEQ
38	PCB non DL ***	0,02
	Idrocarburi	
39	Idrocarburi C10-C40 (1)	50

	L.D. 152/2006	M.D. 46/2019
	mg kg^{-1}	
As	20	30
Cd	2	5
Cu	120	200
Zn	150	300

1. Approfondimento della caratterizzazione dell'area.

Qualora, nella fase di caratterizzazione dell'area, non si riscontrino, nel terreno, superamenti delle Concentrazioni soglia di contaminazione (CSC), non si rende necessario alcun tipo di intervento, ne' alcun approfondimento di caratterizzazione delle matrici ambientali.

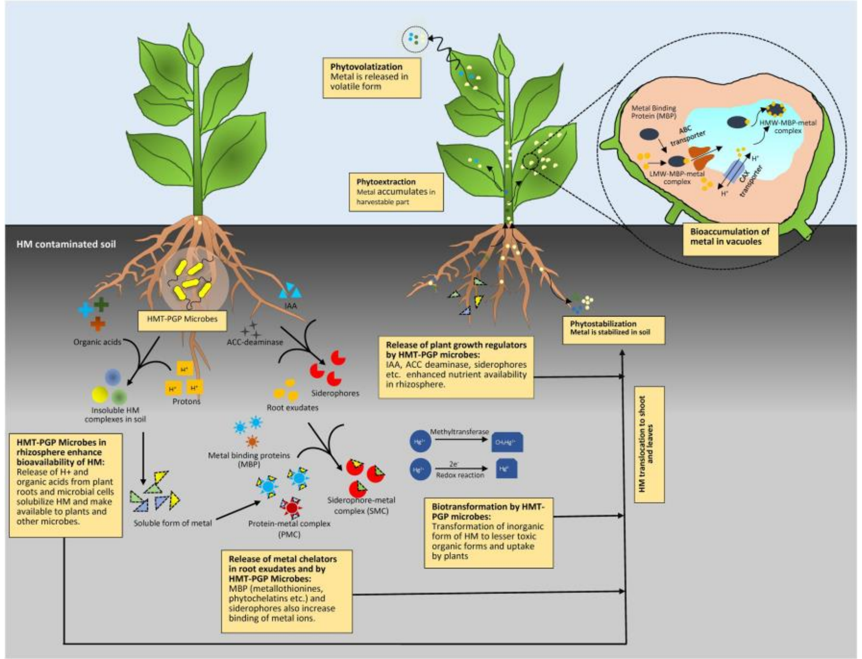
Di contro, qualora venga accertato il superamento delle CSC, anche per un solo parametro, devono essere attuate delle misure di prevenzione e di salvaguardia dell'area interessata, secondo quanto segue:

deve essere evitato l'incremento del livello di contaminazione del suolo, verificato mediante opportuni controlli analitici;

si effettuano ulteriori accertamenti analitici sul suolo (es. test di bioaccessibilità e/o biodisponibilità, test di estrazione con chelanti ecc);

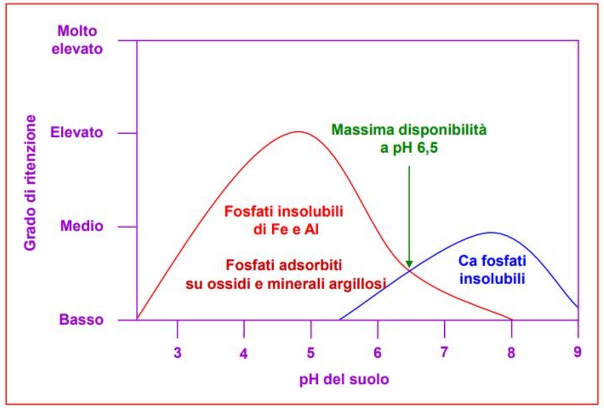
Bioavailability of potentially toxic elements (PTEs)

Bioavailable pool of a PTE can be defined as the fraction of its total content in the soil that can interact with a biological target (Geebelen et al., 2003)

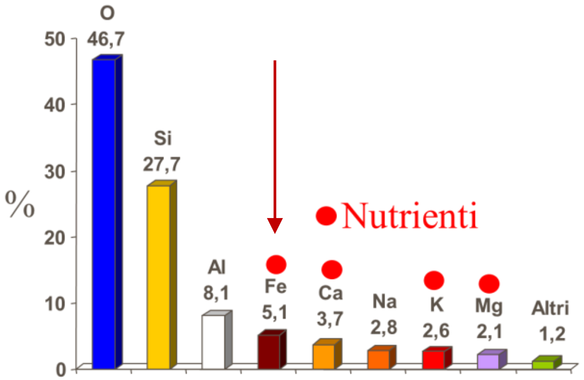


Source: Mishra et al., 2017. Front Microbiol 8, 1706

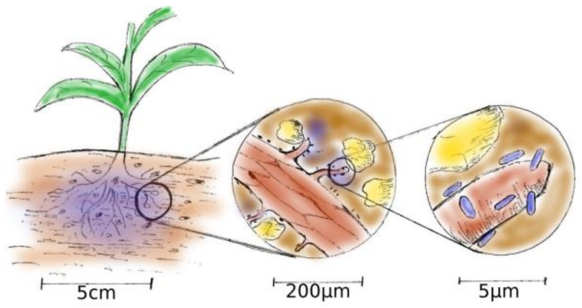
Bioavailability to plants is governed by the dynamic equilibrium between aqueous and solid soil phases, rather than by the total metal content



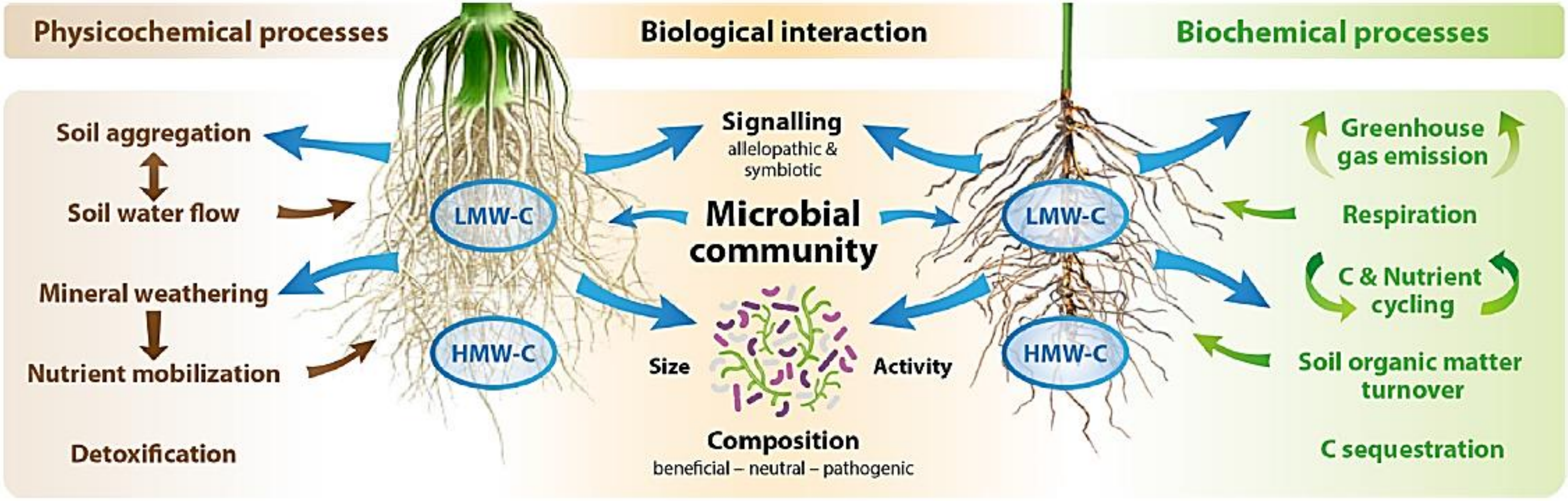
	Total content	Bioavailable pool
	mg kg^{-1}	
Fe	30000-50000	30-500
P	1000-4000	10-150



The influence of rhizosphere activity



In the rhizosphere, many physical, chemical and biochemical processes occur as a consequence of root growth, water and nutrient uptake, respiration, rhizodeposition and enhanced microbial activities

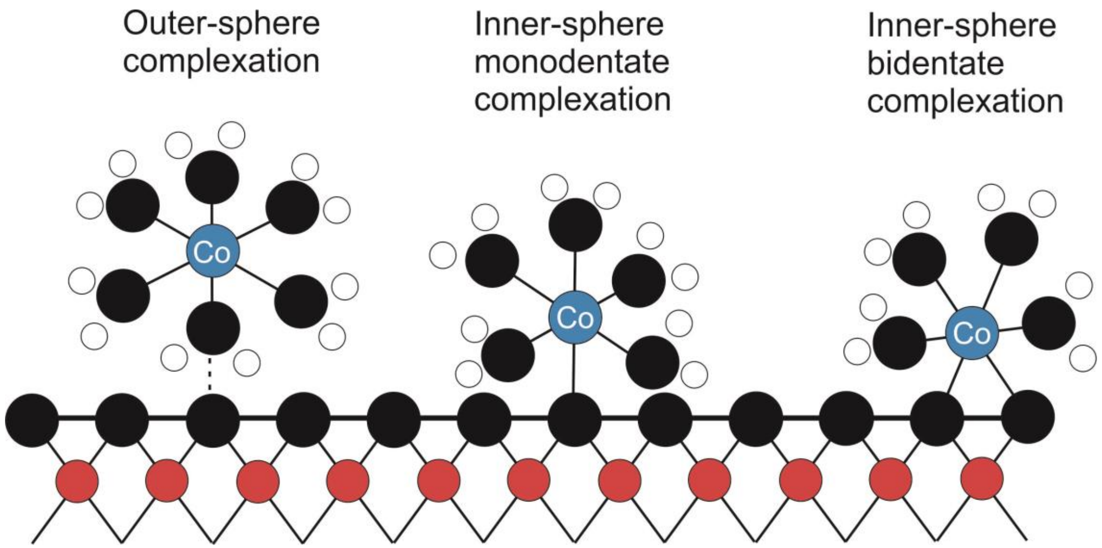


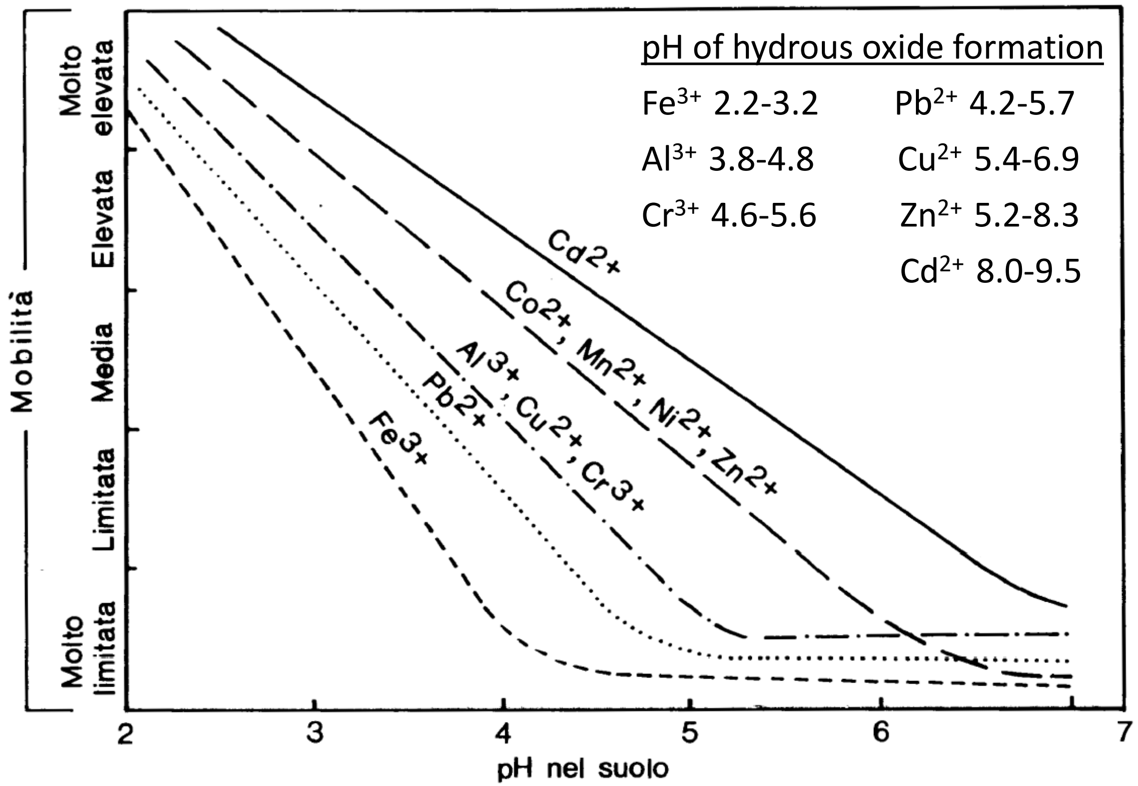
The different bioavailable pools are in a dynamic equilibrium → if the most easily bioavailable fraction is taken up from the soil, the less available fraction can rapidly reintegrate the easily available pool

Theorical sequence of PTE mobility in the soil

Comments	Metal sequence	Reference
Theoretical sequence according to…		
…Electronegativity	Hg > Pb > Cd > Co > Ni > Zn > Cu > Cr	*Antoniadis et al., 2017. Earth Sci Rev 171, 621-645*
…Hydroxyl formation constants	Hg > Pb > Cu > Zn > Cr > Co > Ni > Cd	

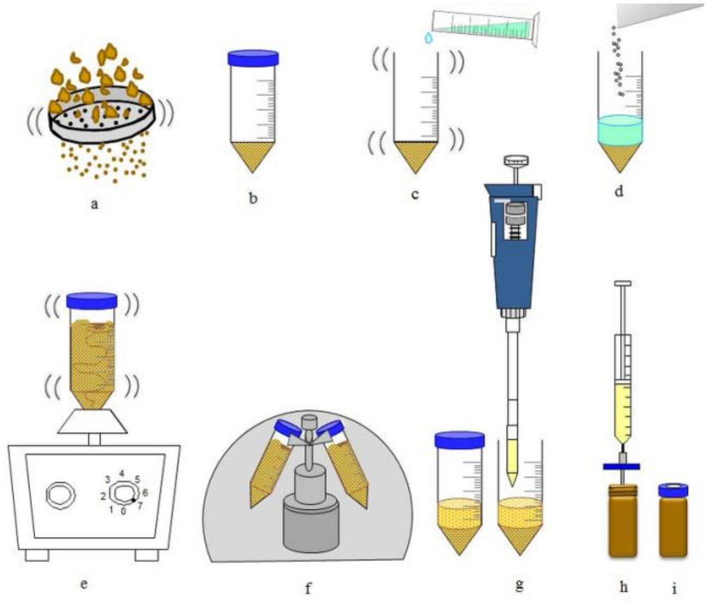
INCREASING MOBILITY AND AVAILABILITY →





Assessment of bioavailability

In vitro tests must enable quantification of the metal dissolution under realistic conditions, by extractions with one or more reagents simulating soil solution



In vivo tests are generally considered the best bioavailability tests, as the plant uptake measured in these tests is believed to resemble the natural conditions. However, these assays are time- and resource-consuming

Assessment of PTE bioavailable fractions

Rhizon-sampler → to monitor metal dissolved in pore water over time

Single-step extractions

- 1M NH_4NO_3 (ISO 19730, 2008) or 0.01M $CaCl_2$ (Houba *et al.*, 2000), to address the soluble and non-specifically adsorbed fractions
- 0.05M EDTA at pH 7 (Rauret *et al.*, 2001) or DTPA (Lindsay and Norvell, 1978), to quantify the potentially bioavailable fraction of metals organically-bound or specifically adsorbed by oxides and secondary clay minerals

Sequential extractions → 4-step EU-BRC (Rauret *et al.*, 1999) or Wenzel procedure (Wenzel *et al.*, 2001), to estimate the distribution of metals in presumed geochemical fractions

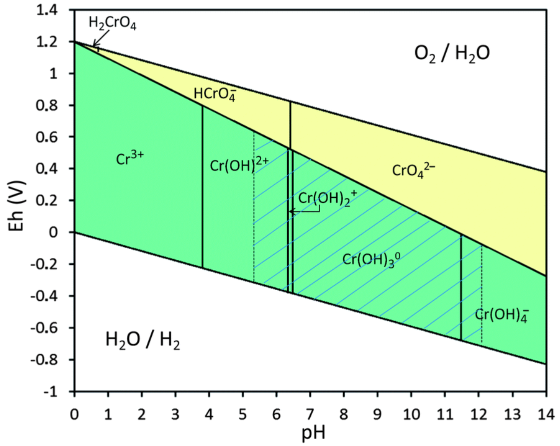
Fraction	Extracting agent	Extracting conditions	
		Shaking time	Temperature
Fr I- Exchangeable, water and acid soluble	0.11 mol·L^{-1} CH_3COOH (pH= 7)	16 h	20 - 25°C
Fr II- Reducible e.g. bound to iron and manganese oxyhydroxides	0.5 mol·L^{-1} NH_2OH-HCl (pH = 1.5)	16 h	20-25°C
Fr III- Oxdisable e.g. bound to organic matter and sulfides	30% H_2O_2 (pH=2.0) and then 1.0 mol·L^{-1} CH_3COONH_4 (pH=2.0)	1, 2, 16 h	20-25, 85, 20-25°C
Fr IV- Residual, non-silicate bound metals	*Aqua regia*	2.5 h	60-70°C

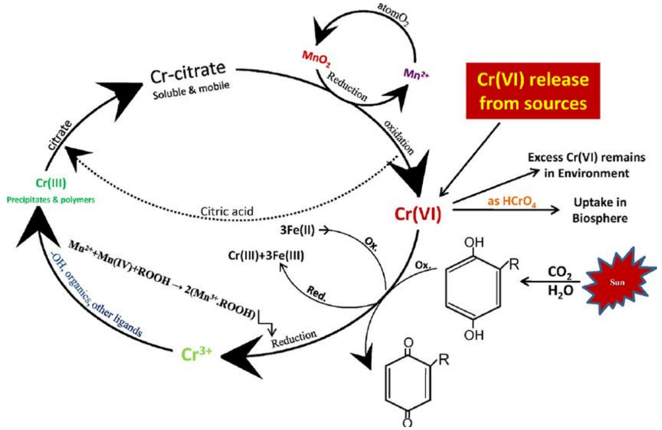
Passive sampler → diffusive gradients in thin films (DGT) or semipermeable membrane, to measure the freely dissolved concentration of organic pollutants in equilibrium with the rapidly desorbing fraction

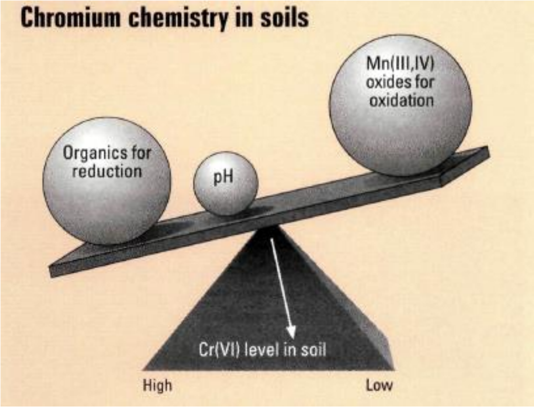
Non-exhaustive techniques → mild solvent extraction, solid sorbents (e.g. Tenax) and hydroxypropyl-β-cyclodextrin (HPCD), to extract the rapidly desorbing fraction of organic pollutants from soil

The assessment of PTE chemical species

The bioavailability of the PTEs is closely interlinked with their chemical speciation, i.e. the distribution of elements among their various chemical forms







Cr(III)

↓

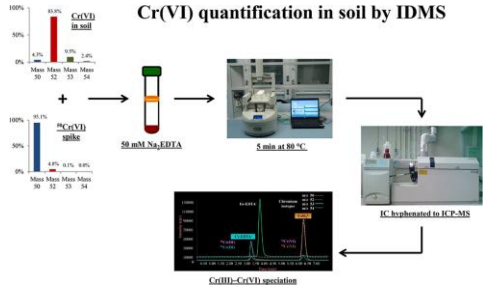
500 to 1000x less toxic than

↓

Cr(VI)

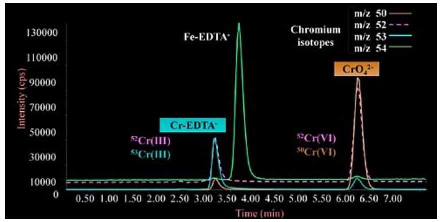
Isotope dilution mass spectrometry (IDMS)

- ✓ correction of Cr redox interconversions
- ✓ low detection limits
- ✓ *Cr extraction phase at high temperature*



IC coupled to ICP-MS

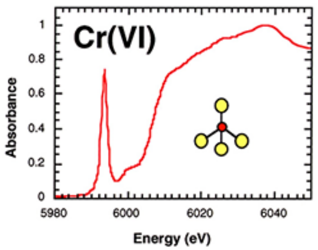
→

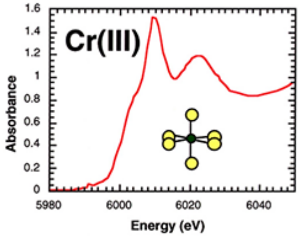


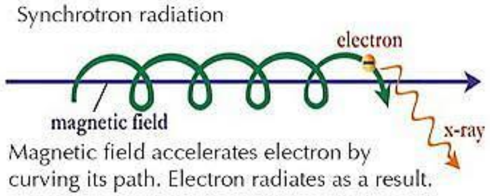
Cr(III) – Cr(VI) speciation

Synchrotron X-ray absorption spectroscopy (XAS)

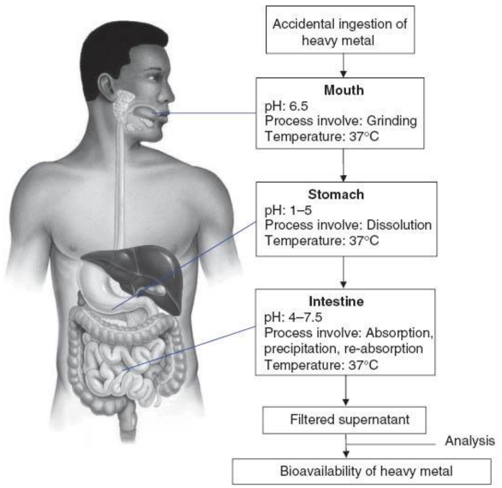
- ✓ high element specificity
- ✓ limited sample preparation
- ✓ *high level of expertise*
- ✓ *high detection limits*

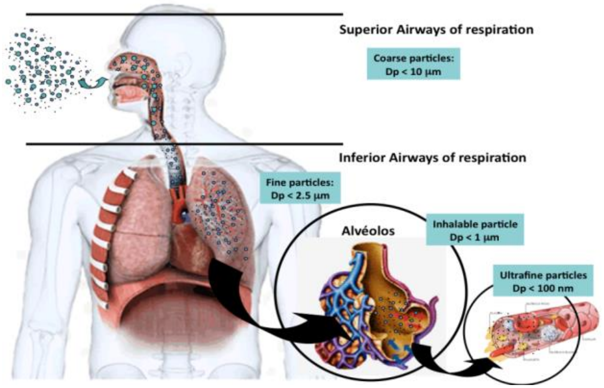


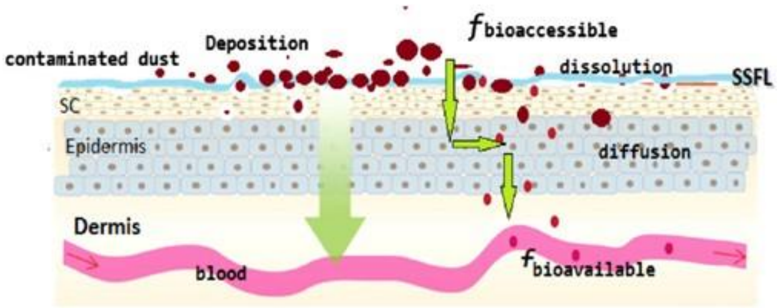


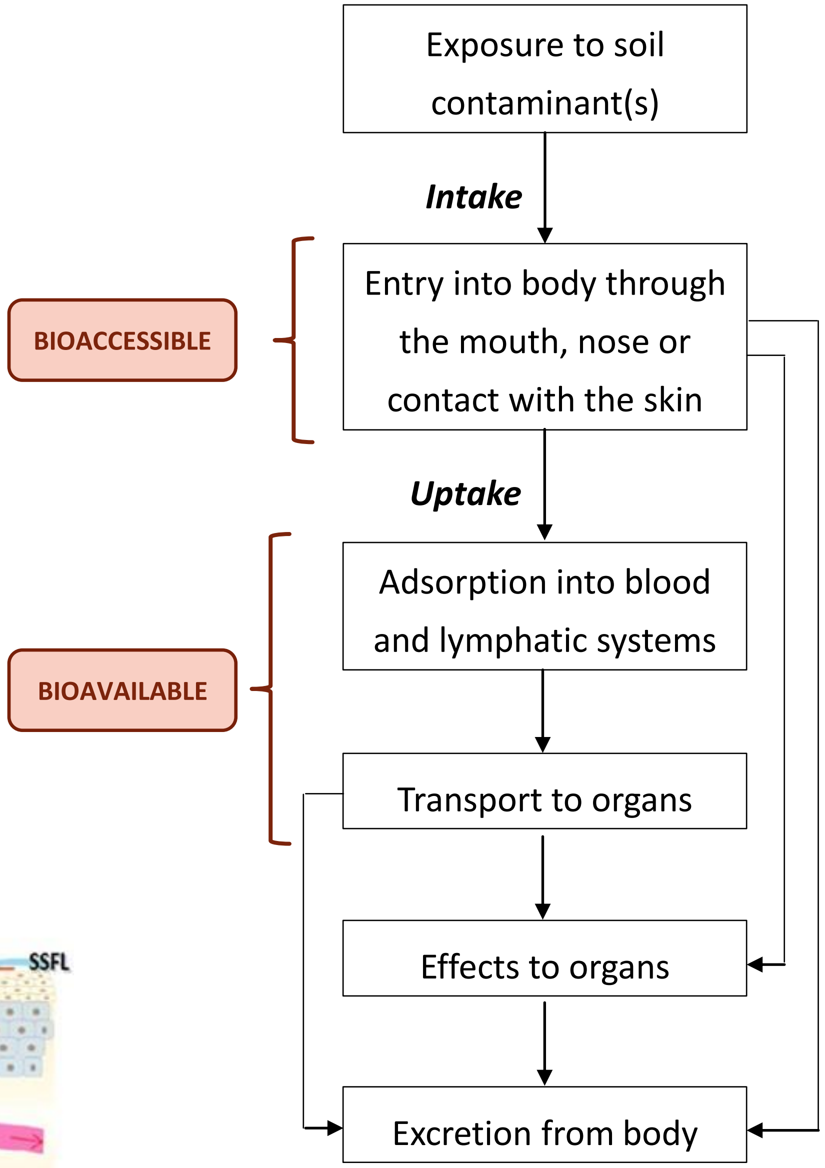


Bioaccessibility *vs* bioavailability of soil contaminants

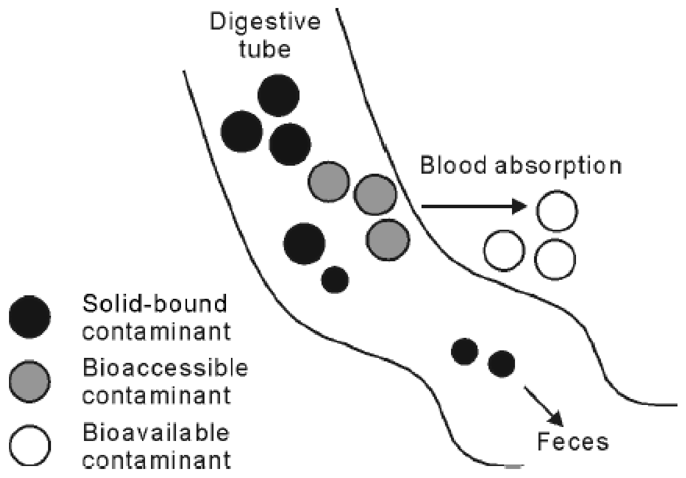








The International Union of Pure and Applied Chemistry (IUPAC) defines as <u>bioaccessible</u> a substance *'able to come in contact with a living organism and interact with it'* and <u>bioavailable</u> a substance '*able to be absorbed by living organisms'*

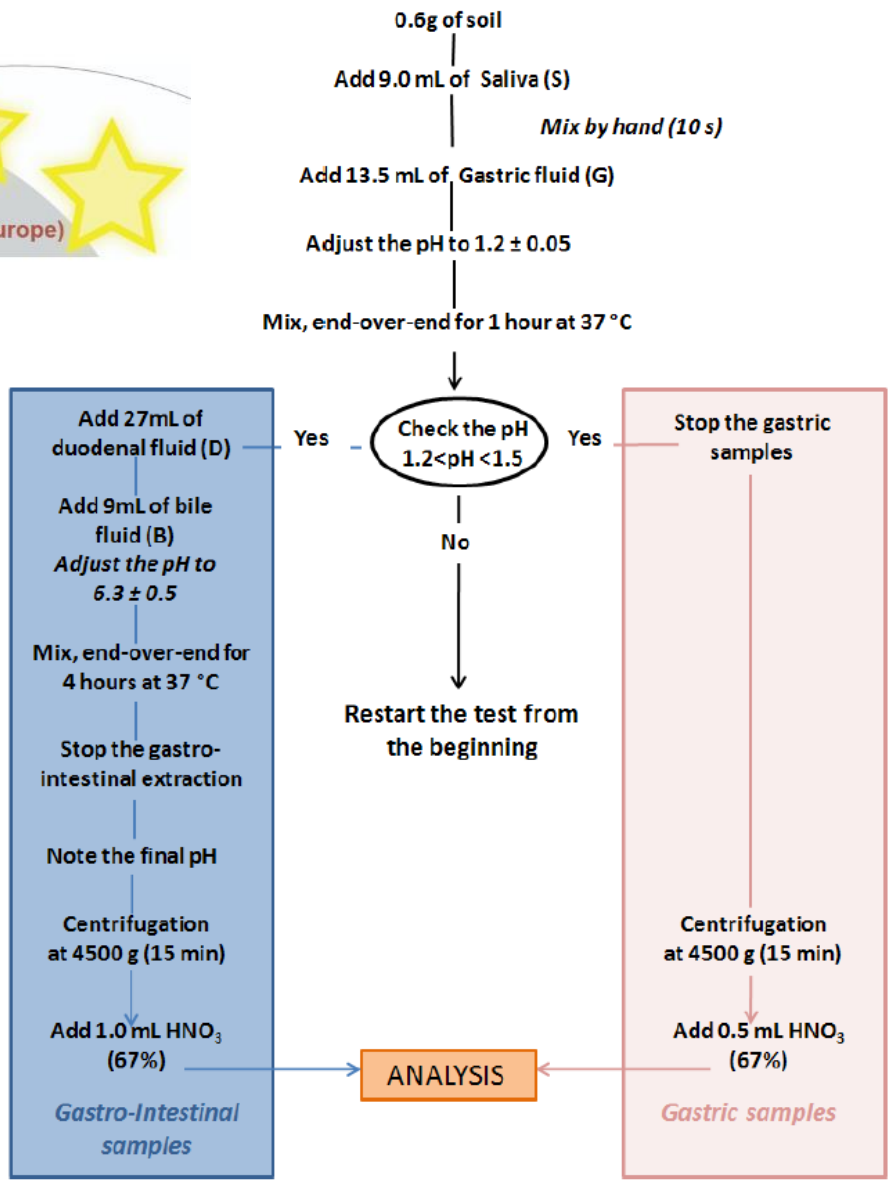


Source: Kumpiene et al., 2017. Pedosphere 27(3): 389-406

Methodological complexity of in-vitro assays

BARGE (the Bioaccessibility Research Group of Europe)

	REAGENTS	Saliva (S)	Gastric (G)	Duodenal (D)	Bile (B)	Volume (mL)
Inorganic (I)	KCl	448	412	282	188	250
	NaH_2PO_4	444	133	-	-	
	KSCN	100	-	-	-	
	Na_2SO_4	285	-	-	-	
	NaCl	149	1376	3506	2630	
	$CaCl_2$	-	200	-	-	
	NH4Cl	-	153	-	-	
	$NaHCO_3$	-	-	2803.5	2893	
	KH_2PO_4	-	-	40	-	
	$MgCl_2$	-	-	25	-	
	NaOH (1M)	0.9 mL	-	-	-	
	HCl (37%)	-	4.15 mL	90 uL	90 uL	
Organic (O)	Urea	100 mg	42.5	50	125	250
	Glucose		325	-	-	
	Glucuronic acid		10	-	-	
	Glucosamine hydrochloride		165	-	-	
Enzymes	Alpha amylase	72.5 mg	-	-	-	250+250= 500
	Mucin	25 mg	1500	-	-	
	Uric acid	7.5 mg	-	-	-	
	Bovine Serum Albumin	-	500	500	900	
	Pepsin	-	500	-	-	
	$CaCl_2$	-	-	100	111	
	Pancreatin	-	-	1500	-	
	Lipase	-	-	250	-	
	Bile	-	-	-	3000	
pH	I+O	6,5 +/- 0,5	1,1 +/- 0,1	7,4 +/-0,2	8 +/- 0 .2	



Highly-contaminated case studies

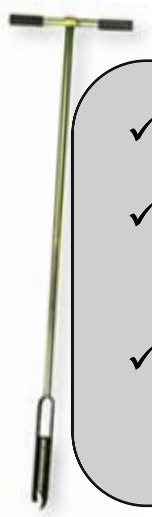
6 ha of farmland currently confiscated by the Italian Judiciary due to past illegal burial of industrial wastes

Main pollutants: Cr (max 4500 ppm)
and Zn (1850) and hydrocarbons C>12 (1800)

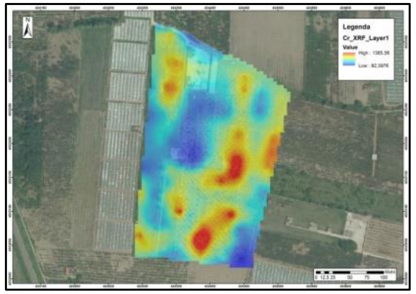
3.5 ha of industrial soil inside an automobile-battery recycling plant in operation since 1970

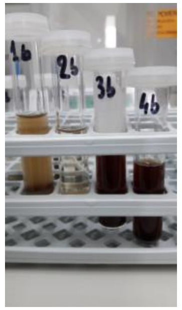
Main pollutants: Pb (max 80000 ppm),
Sb (1475), As (312) and Cd (235)

Soil characterization and phytoremediation plants



- ✓ Sampling grid: **20 x 20 m**
- ✓ Depths at site A:
  0-20, 30-60, 70-90 cm
- ✓ Depths at site B:
  0-10, 10-40 cm





IMPLEMENTATION OF ECO-COMPATIBLE PROTOCOLS FOR AGRICULTURAL SOIL REMEDIATION IN LITORALE DOMIZIO-AGRO AVERSANO NIPS (LIFE11/ENV/IT/275 – ECOREMED)

Phytoremediation plants consisting of poplar trees (*Populus nigra* L.) and permanent grass cover, assisted by compost amendment and irrigation system, were then implemented on both sites years ago

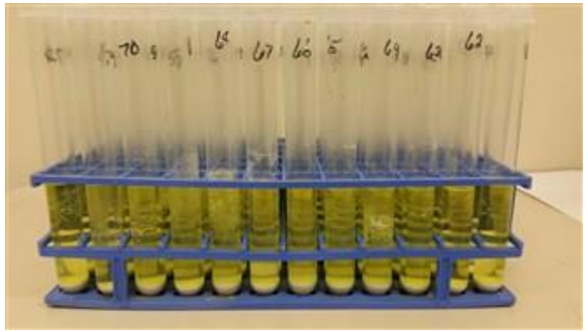
Site A

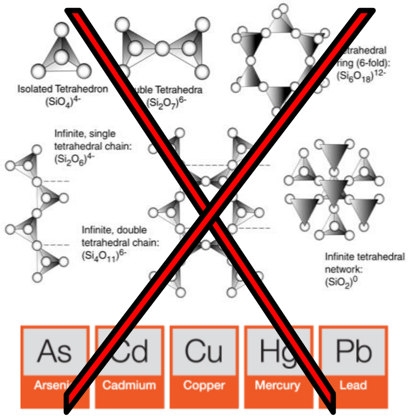
Site B

Benchmark lab-based technique

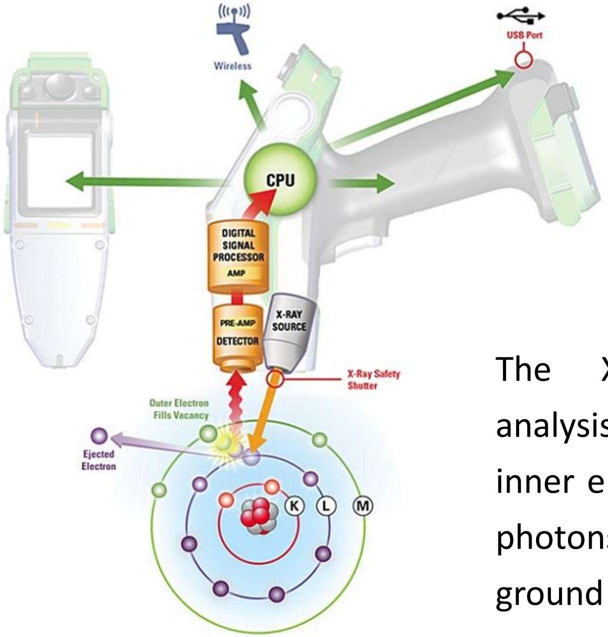
Portable-XRF technique

Microwave-assisted soil digestion by *aqua regia* (3:1 v/v, HCl to HNO_3), followed by analysis of metal-containing extracts by AAS or ICP-OES/MS (ISO standard 54321, USEPA method 3051A), determines the **pseudo total content** of the analysed elements

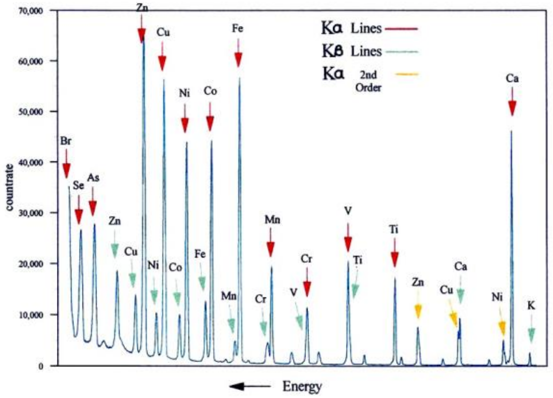




Aqua regia does not produce a complete soil digestion because the least acid-soluble components as **metal-bearing silicates are not completely dissolved** and are thus not included within the analytical measure

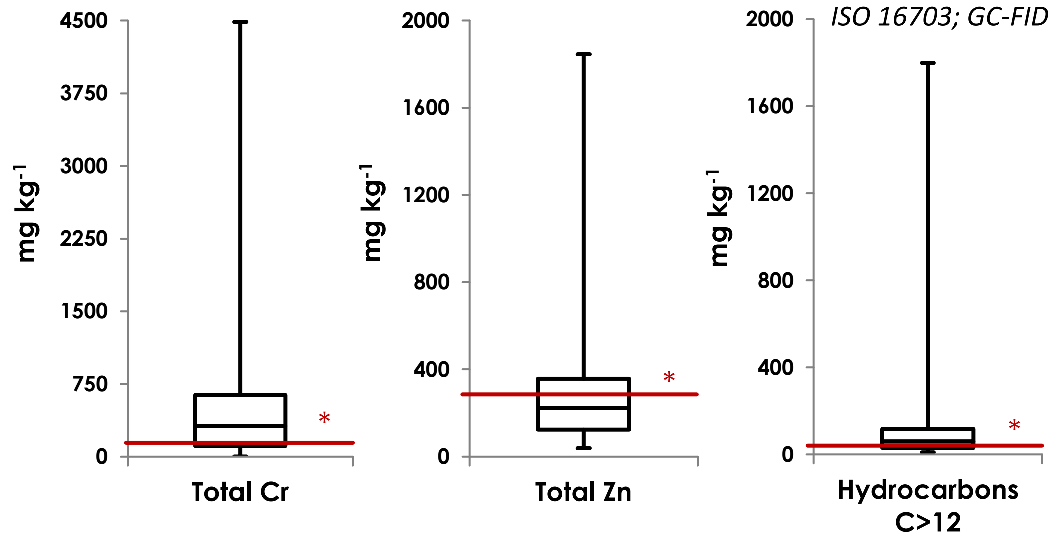


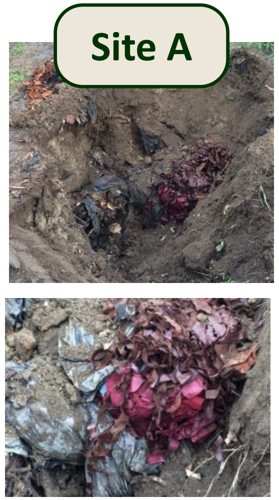
The X-ray fluorescence (XRF) analysis is based on the excitation of inner electrons and the emission of photons after they relax to their ground state (fluorescence)



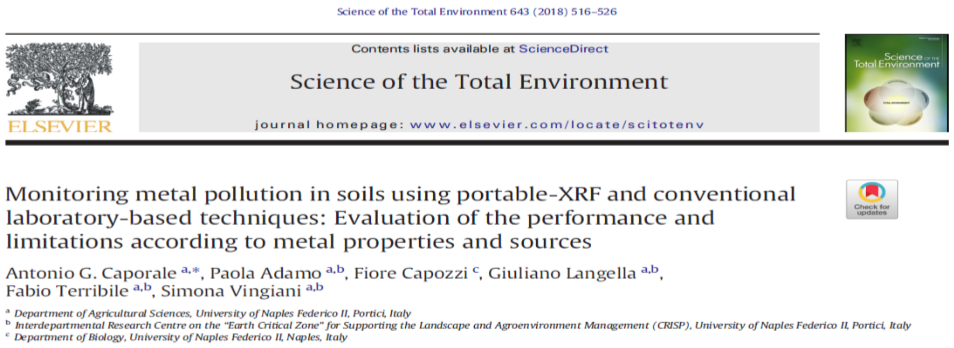
In short time, pXRF provides accurate total elemental contents in soil samples (USEPA method 6200), although it does not have very sensitive detection limits

Main soil pollutants





** Italian screening values for agricultural (site A) and industrial (site B) soils (M.D. 46/2019 and L.D. 152/2006, respectively)*


Science of the Total Environment 643 (2018) 516–526

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journal homepage: www.elsevier.com/locate/scitotenv

Monitoring metal pollution in soils using portable-XRF and conventional laboratory-based techniques: Evaluation of the performance and limitations according to metal properties and sources

Antonio G. Caporale [a,*], Paola Adamo [a,b], Fiore Capozzi [c], Giuliano Langella [a,b], Fabio Terribile [a,b], Simona Vingiani [a,b]

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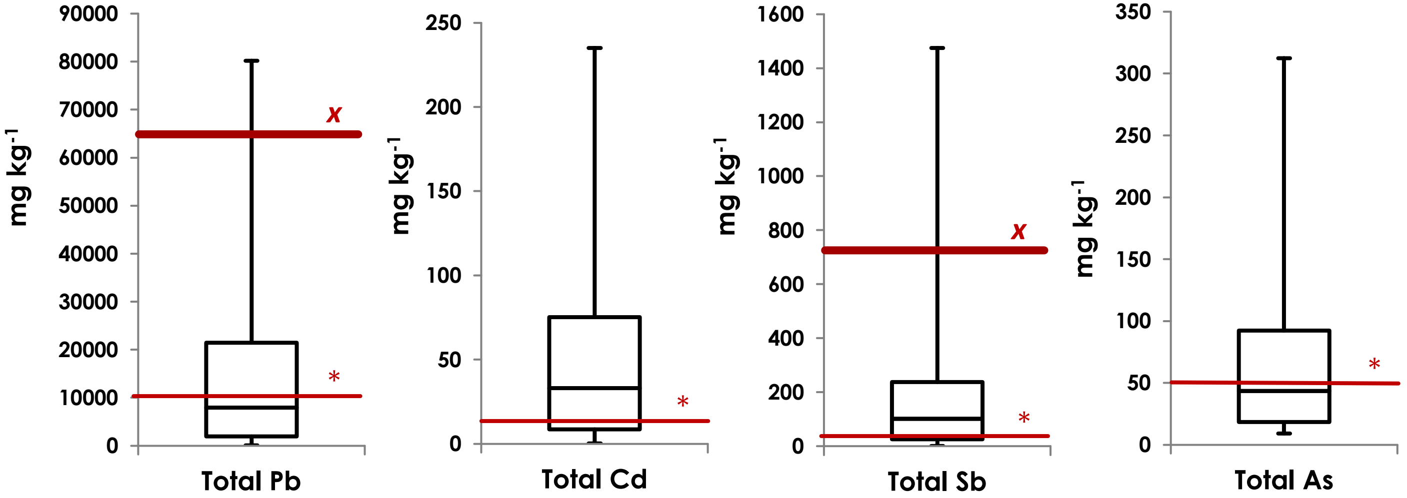
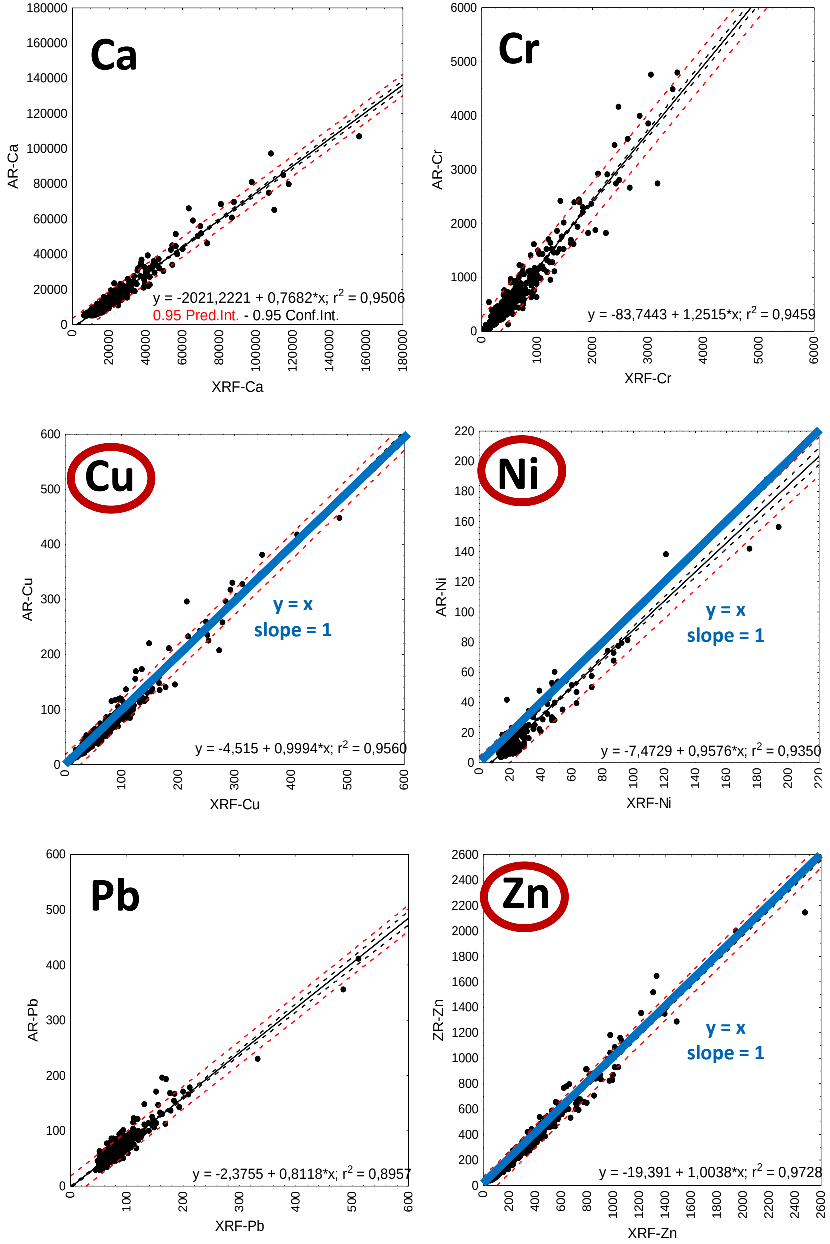


***x* Risk trigger values obtained by site-specific risk assessment**

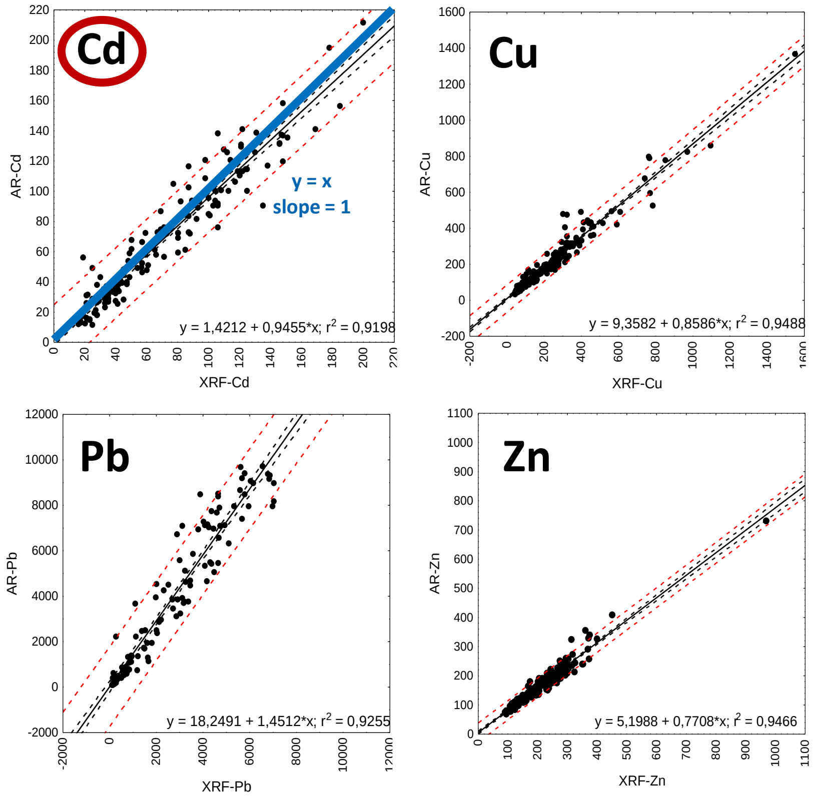
Best linear regression fits

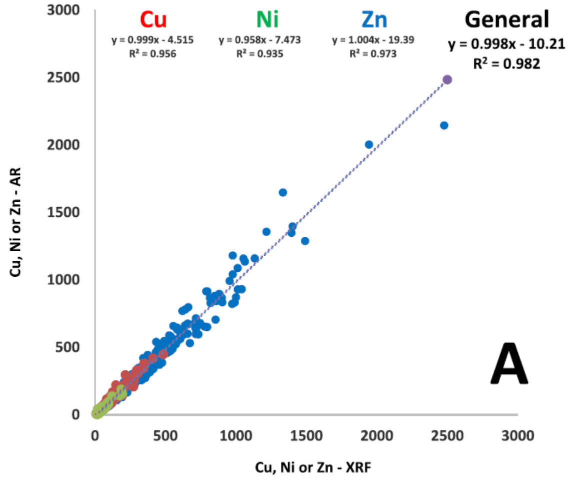
Very satisfying correlations (R^2>0.90) were observed between AR and pXRF contents of …

Site A

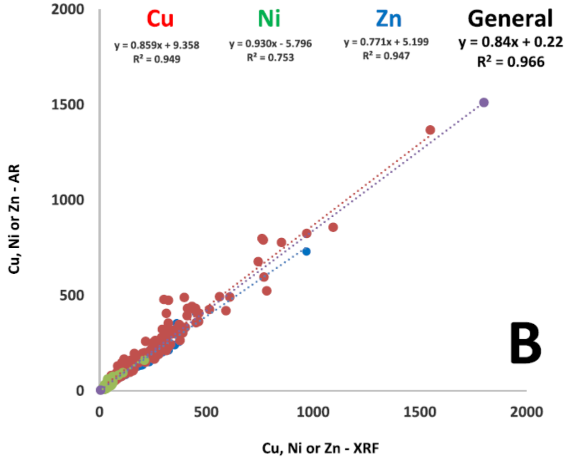


Site B



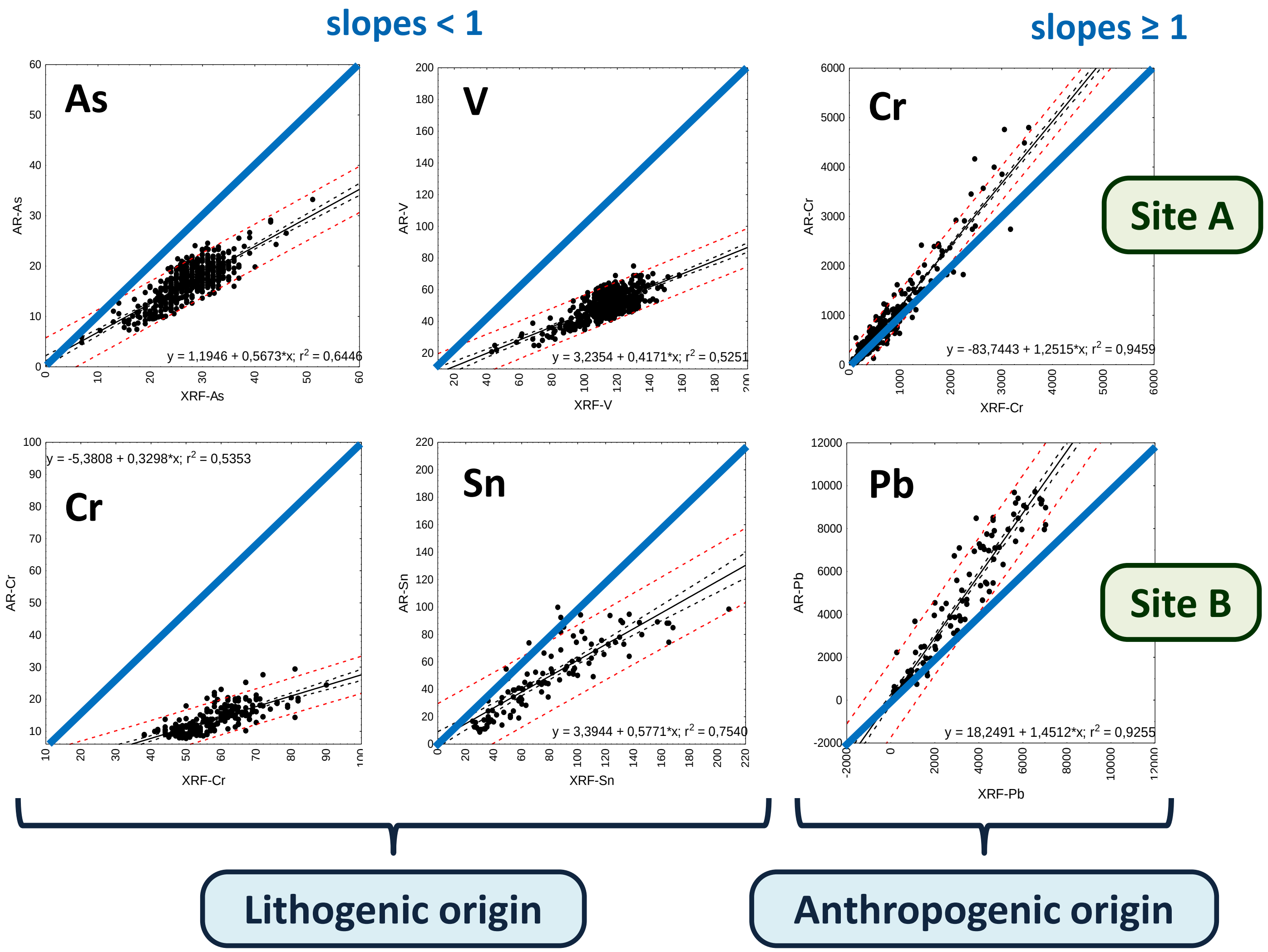


Multielement linear regressions



Metal-dependent and site-specific models

The comparison among different regression parameters revealed that regression models were strongly site-specific and metal-dependent



	Slope		Intercept		R^2	
	Site A	Site B	Site A	Site B	Site A	Site B
As	0.567	0.391	1	19	0.64	0.69
Ca	0.768	1.409	-2021	-12383	0.95	0.73
Cr	1.252	0.330	-84	-5	0.95	0.54
Cu	0.999	0.859	-5	9	0.96	0.95
Fe	0.623	0.420	3901	10248	0.47	0.62
K	0.103	0.235	3913	3808	0.37	0.59
Mn	0.615	0.538	53	244	0.66	0.73
Nb	-0.126	-0.033	13	7	0.17	0.01
Ni	0.958	0.855	-7	-3	0.94	0.83
Pb	0.812	1.451	-2	18	0.90	0.93
Rb	0.316	0.538	15	-18	0.75	0.53
Sn	1.310	0.577	-22	3	0.96	0.75
Sr	0.093	0.288	109	57	0.06	0.39
Th	0.308	0.154	3	6	0.25	0.31
Ti	0.615	0.276	-480	511	0.56	0.57
V	0.417	0.351	3	16	0.53	0.47
Zn	1.004	0.771	-19	5	0.97	0.95
Zr	0.151	0.012	-13	19	0.16	0.02

I_{geo} and EF

The magnitude of the anthropogenic fraction in soil metal contents was estimated by the geoaccumulation index (I_{geo}) and metal enrichment factor (EF)

Anthropogenic pollution categories:

(Igeo≤0) practically uncontaminated

(0<Igeo≤1) uncontaminated to moderately contaminated

(1<Igeo≤2) moderately contaminated

(2<Igeo≤3) moderately to heavily contaminated

(3<Igeo≤4) heavily contaminated

(4<Igeo<5) heavily to very heavily contaminated

(Igeo≥5) very heavily contaminated

$$I_{geo} = \log_2\left[\frac{C_n}{1.5B_n}\right]$$

I_{geo}

	As	Ca	Cr	Cu	K	Ni	Pb	Sn	Zn
I_{geo} site A	-0.10 (0)	1.09 (2)	3.03 (4)	2.13 (3)	0.34 (1)	ND	0.30 (1)	ND	1.84 (2)
I_{geo} site B	1.66 (2)	0.44 (1)	-0.25 (0)	2.83 (3)	-0.17 (0)	0.24 (1)	4.80 (5)	1.04 (2)	0.94 (1)

	Fe	Mn	Nb	Rb	Sr	Th	Ti	U	V	Y	Zr
I_{geo} site A	-0.72 (0)	-0.19 (0)	-0.50 (0)	-0.11 (0)	-0.46 (0)	-0.46 (0)	-0.79 (0)	-0.21 (0)	-0.76 (0)	-0.50 (0)	-0.48 (0)
I_{geo} site B	-0.62 (0)	-0.77 (0)	-0.73 (0)	-0.03 (0)	-0.28 (0)	-0.74 (0)	-0.97 (0)	ND	-0.88 (0)	ND	-0.80 (0)

Metal enrichment categories:

(EF≤2) deficiency to minimal

(2<EF≤5) moderate

(5<EF≤20) significant

(20<EF≤40) very high

(EF>40) extremely high

EF

	As	Ca	Cr	Cu	K	Ni	Pb	Sn	Zn
EF site A	1.40 (<2)	3.19 (2-5)	12.22 (5-20)	6.56 (5-20)	1.91 (<2)	ND	1.84 (<2)	ND	5.37 (5-20)
EF site B	4.84 (2-5)	2.09 (2-5)	1.29 (<2)	10.95 (5-20)	1.36 (<2)	1.81 (<2)	42.61 (>40)	3.15 (2-5)	2.94 (2-5)

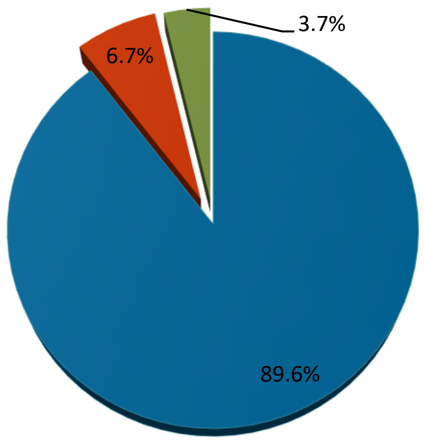
	Fe	Mn	Nb	Rb	Sr	Th	Ti	U	V	Y	Zr
EF site A	0.91 (<2)	1.32 (<2)	1.06 (<2)	1.39 (<2)	1.09 (<2)	1.09 (<2)	0.87 (<2)	1.30 (<2)	0.89 (<2)	1.06 (<2)	1.07 (<2)
EF site B	1.00 (<2)	0.90 (<2)	0.93 (<2)	1.51 (<2)	1.27 (<2)	0.92 (<2)	0.79 (<2)	ND	0.83 (<2)	ND	0.88 (<2)

$$EFs = \frac{C/Fe_{(sample)}}{C/Fe_{(earth's\ crust)}}$$

Site A: soil properties, and bioavailability to plants of main contaminants

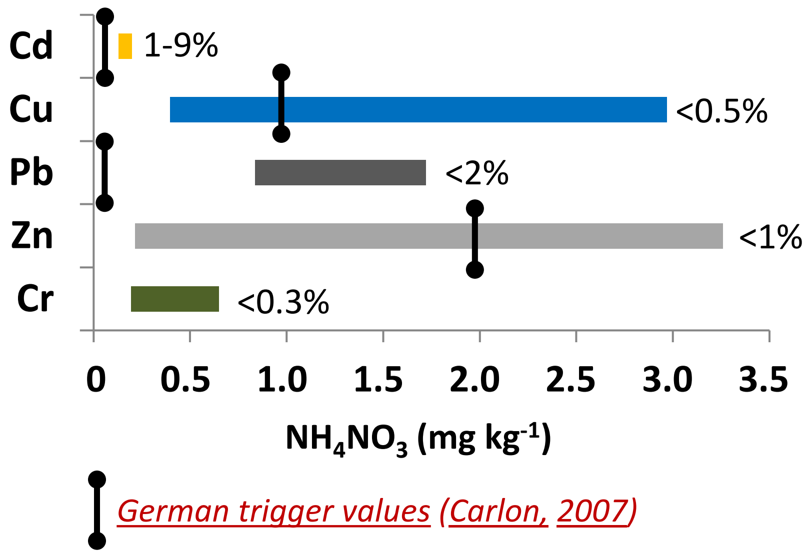
SOIL PROPERTIES	RANGE
Texture	Sandy-loam
pH in H_2O (R=1:2.5)	7.4 – 8.0
O.M. (g kg^{-1})	8 – 50
Carbonates (g kg^{-1})	1 – 79
C.E.C. ($cmol_{(+)}$ kg^{-1})	18 – 29

- ✓ Aliphatic hydrocarbons C_{19}-C_{36}
- ✓ Aliphatic hydrocarbons C_9-C_{18}
- ✓ Other hydrocarbons (PAHs < 0.2%)

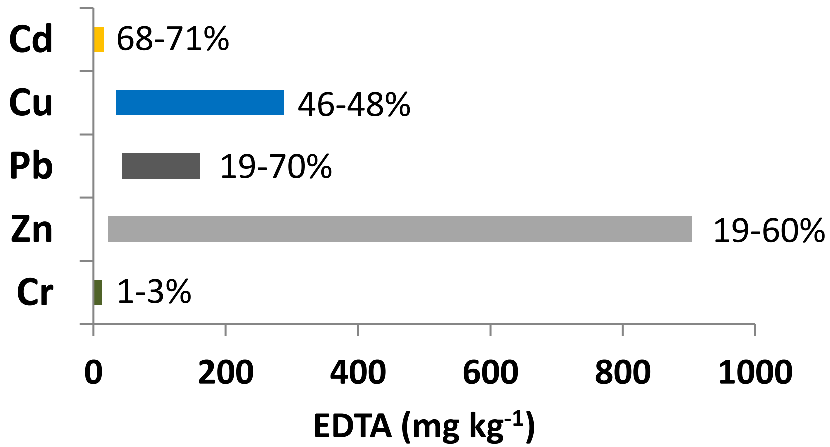


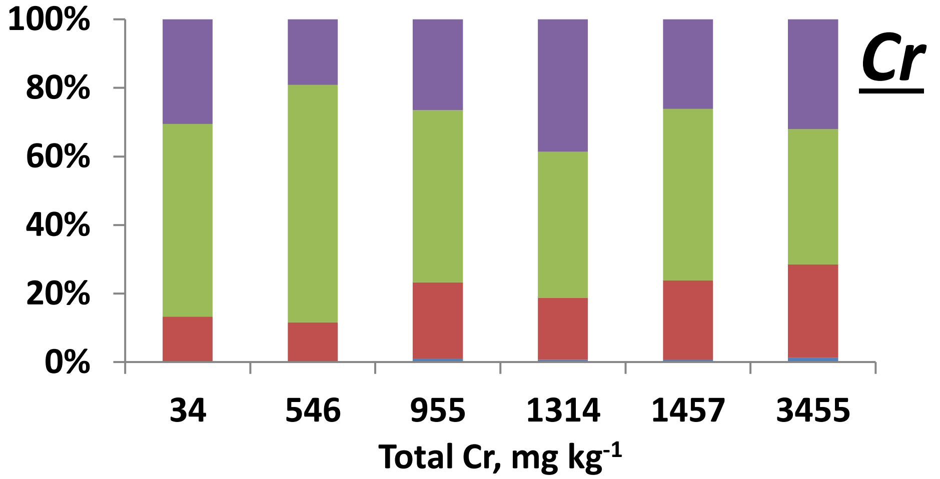
Reference → Agrelli, Caporale, Adamo, 2020. Agronomy 10, 1440

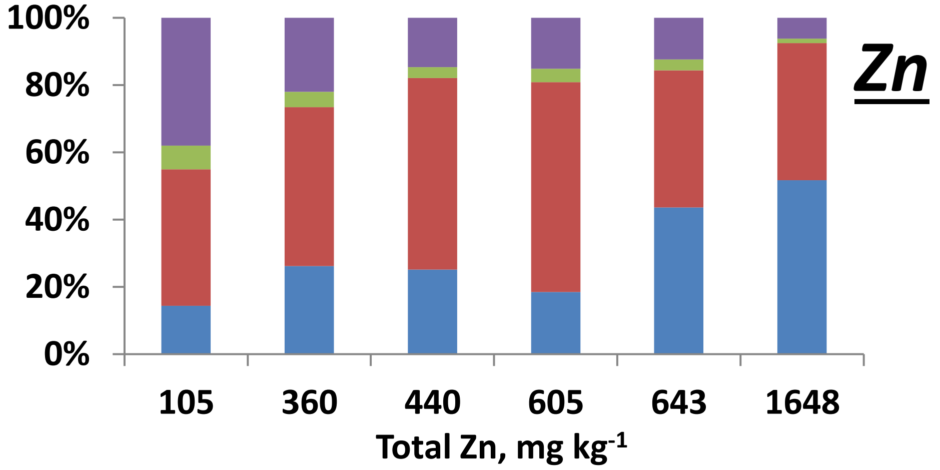
Soil extraction by 1M NH_4NO_3



Soil extraction by 0.05M EDTA (pH 7)







EU-BCR Sequential Extraction

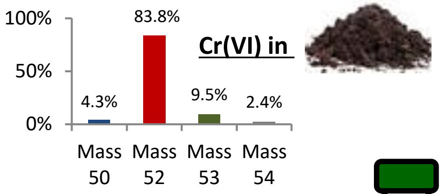
Step 1: easily extractable fraction (soluble, exchangeable, associated to carbonates)

Step 2: reducible fraction (associated to Fe and Mn oxides)

Step 3: oxidasable fraction (associated to organic matter)

Step 4: residual fraction (occluded in non-siliceous minerals)

Chromium speciation by IC-IDMS



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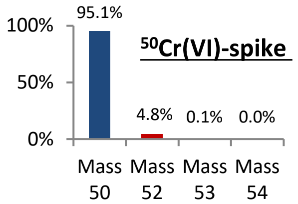

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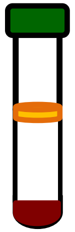


50 mM Na_2EDTA

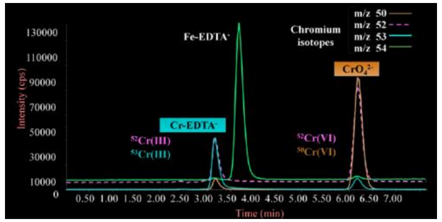
→

5 min at 80°C

→

IC coupled to ICP-MS

→



Cr(III) – Cr(VI) speciation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Hexavalent chromium quantification by isotope dilution mass spectrometry in potentially contaminated soils from south Italy

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[b] CIRAM - Interdepartmental Center for Environmental Research, University of Naples Federico II, Via Mezzocannone 16, 80134, Naples, Italy
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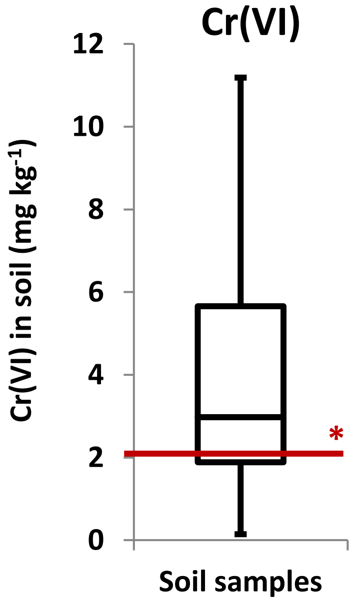
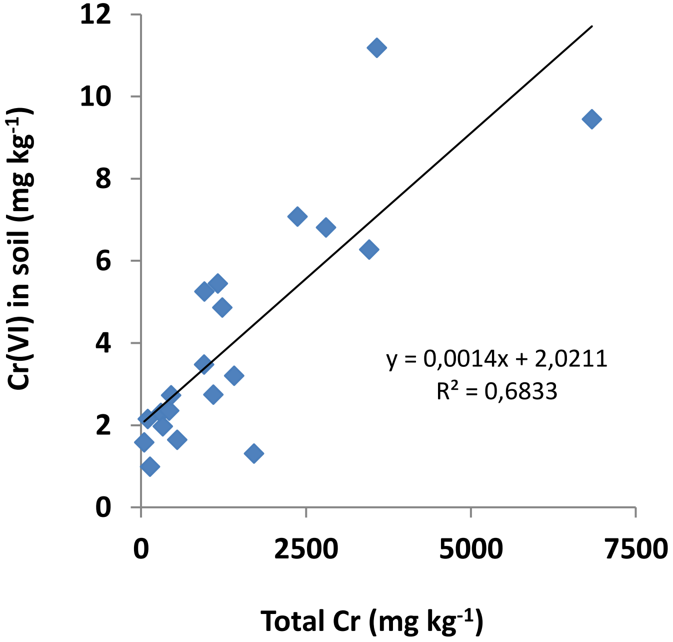
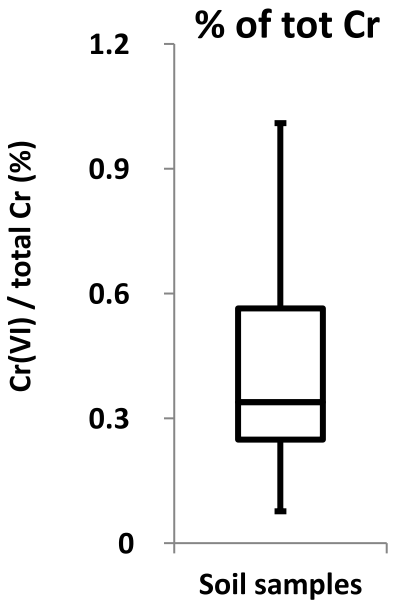
At the Enriched Stable Isotopes of the University of Oviedo (Asturias, Spain)

Universidad de Oviedo



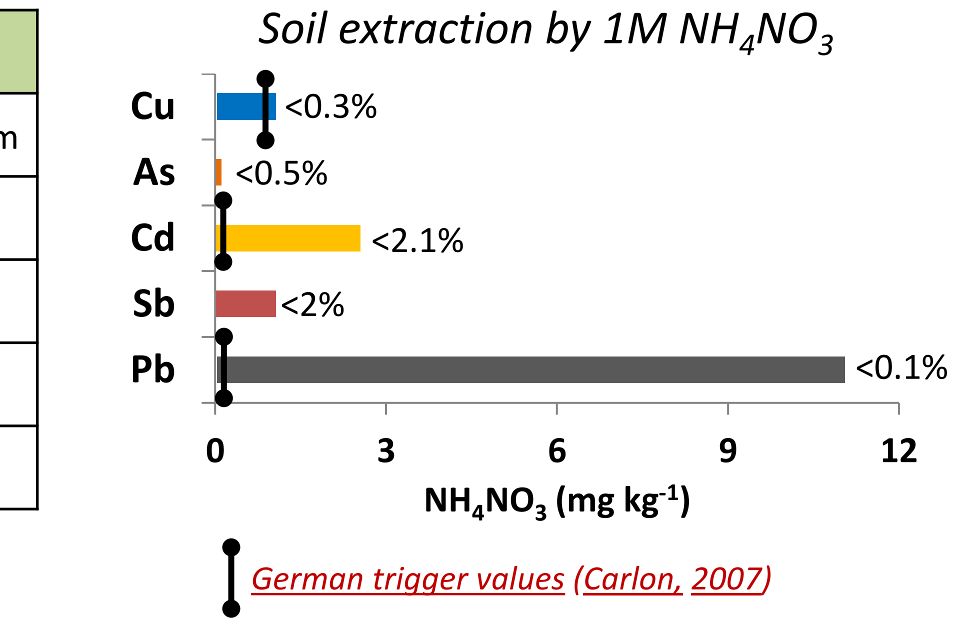
* *Italian screening value for agricultural soils (M.D. 46/2019)*

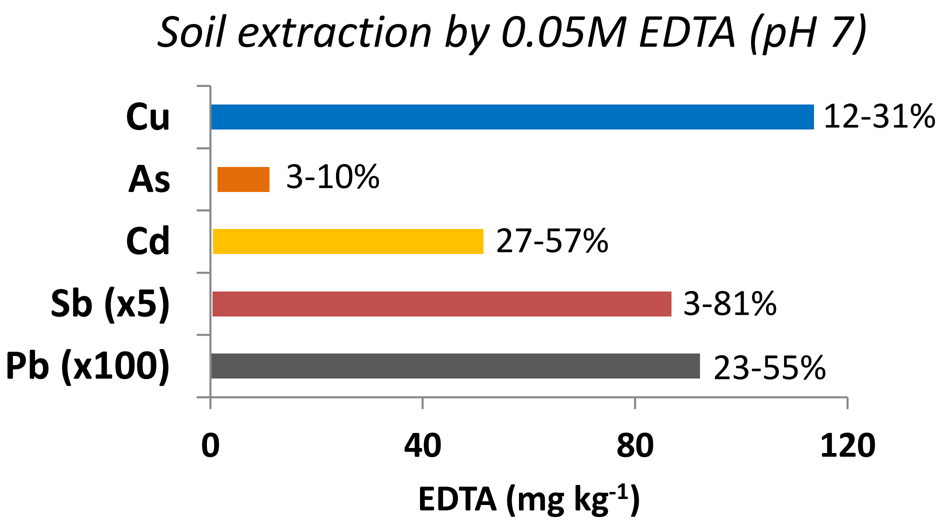


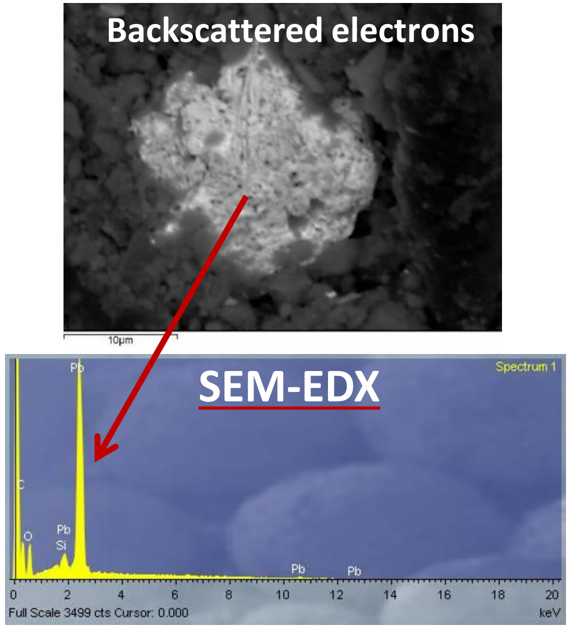


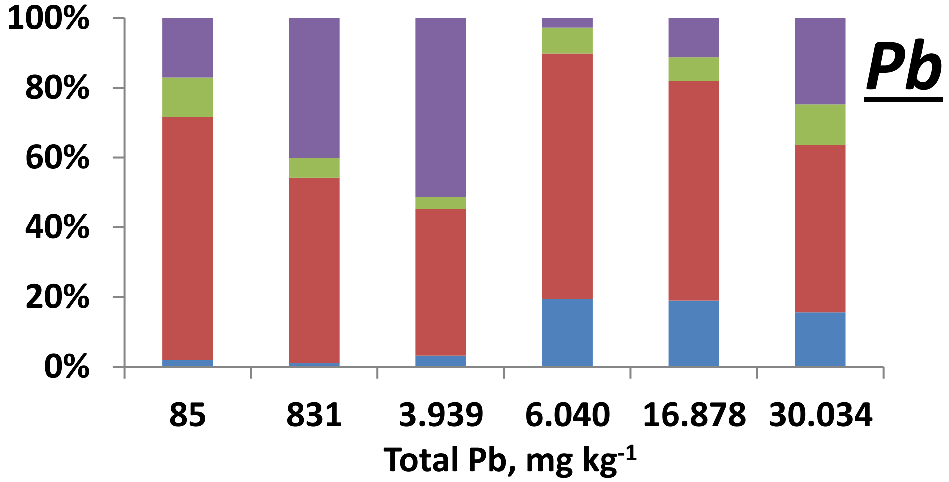
Site B: soil properties, and PTE bioavailability to plants

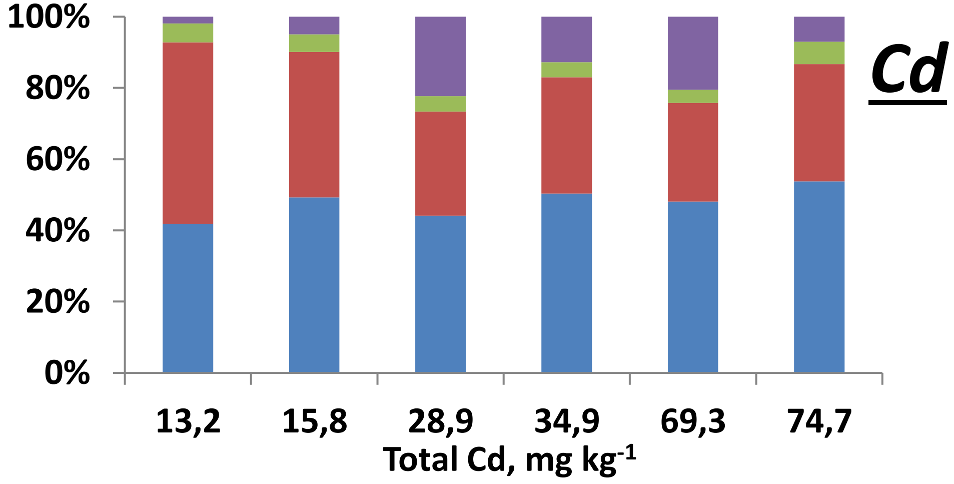
SOIL PROPERTIES	RANGE
Texture	Sandy-loam
pH in H_2O (R=1:2.5)	7.4 – 8.5
O.M. (g kg^{-1})	13 – 31
Carbonates (g kg^{-1})	2 – 151
C.E.C. ($cmol_{(+)}$ kg^{-1})	9 – 27











EU-BCR Sequential Extraction

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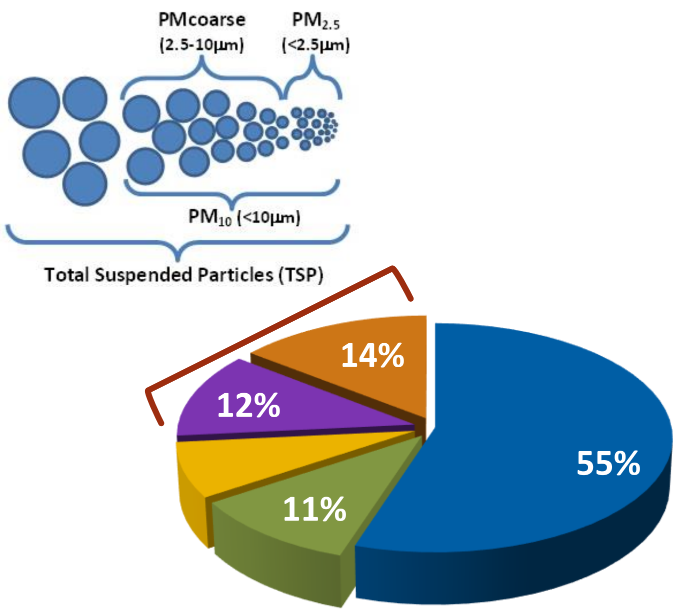
Step 2: reducible fraction (associated to Fe and Mn oxides)

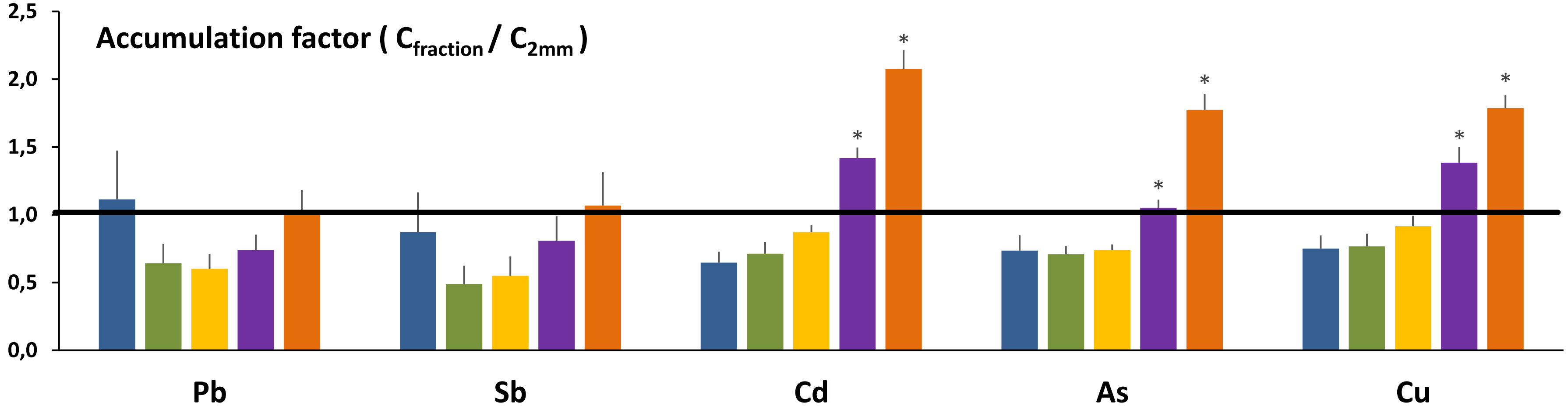
Step 3: oxidasable fraction (associated to organic matter)

Step 4: residual fraction (occluded in non-siliceous minerals)

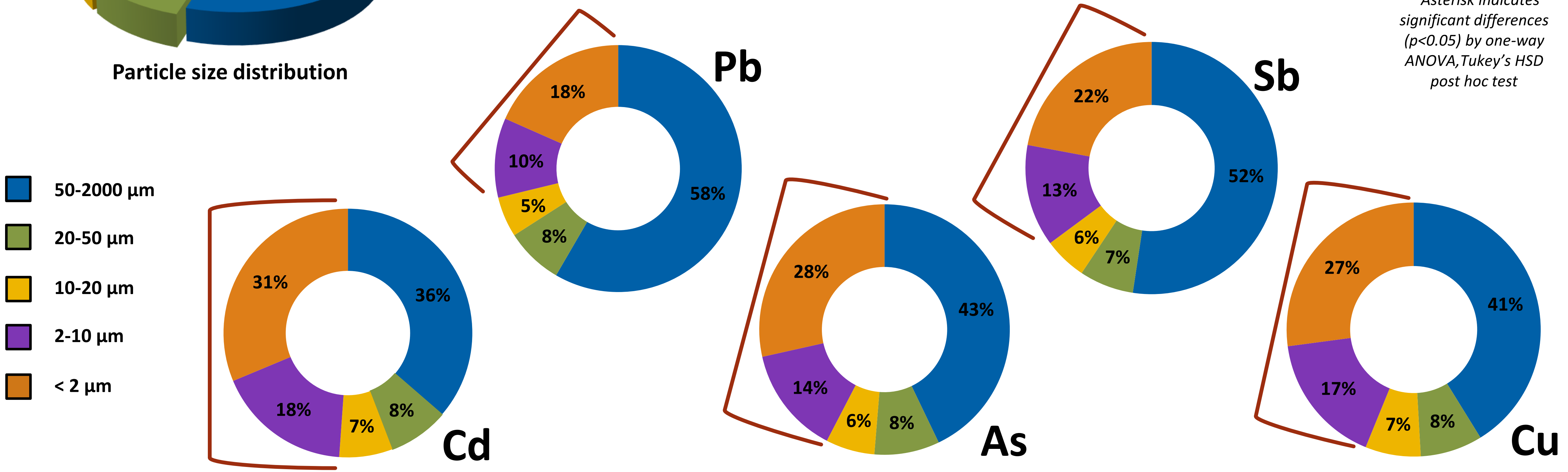
Site B: PTE-distribution in soil particle-size fractions



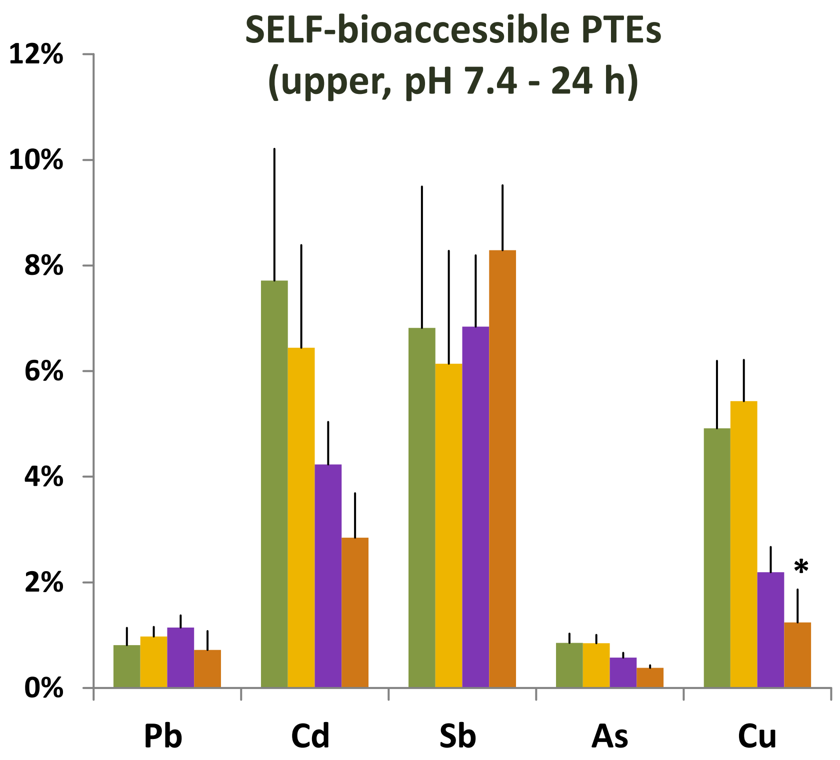
Particle size distribution



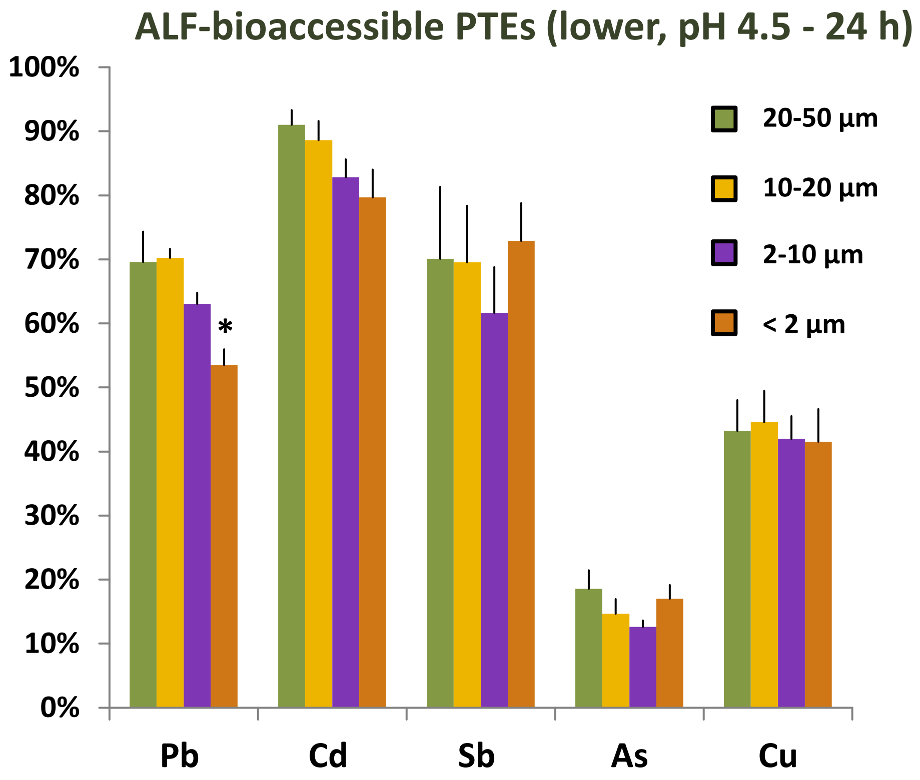
*** Asterisk indicates significant differences (p<0.05) by one-way ANOVA,Tukey's HSD post hoc test***



Lung bioaccessibility test



Bars indicate mean PTE relative bioaccessibility ± SE



** Asterisks indicates significant differences (p<0.05) by one-way ANOVA*

	Pb	Cd	Sb	As	Cu
	mg kg^{-1}				
B1 20-50 µm	4773 (52 d)*	31.1 (88 a)	84.5 (43 d)	4.9 (9 c)	117 (54 b)
B1 10-20 µm	5087 (71 a)	35.1 (84 b)	96.3 (53 b)	4.7 (9 c)	141 (58 a)
B1 2-10 µm	5393 (60 b)	50.0 (72 c)	131 (48 c)	9.7 (13 b)	200 (53 b)
B1 <2 µm	6563 (55 c)	63.3 (65 d)	216 (61 a)	29.4 (24 a)	238 (50 c)

** Values in parenthesis refer to relative bioaccessibility (%). Different letters indicate significant differences (p<0.05) by one-way ANOVA*

Health Risk Assessment

$$ADD_{\text{inhalation}} = C \times \frac{\text{IR} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}}$$

$$ADD_{\text{dermal}} = C \times \frac{\text{SL} \times \text{SA} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6}$$

$$ADD_{\text{ingestion}} = C \times \frac{\text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6}$$

NON-CARCINOGENIC RISKS

$$HQ_{\text{inh}} = \frac{\text{ADD}_{inh}}{\text{RfD}_{inh}}$$

$$HQ_{\text{der}} = \frac{\text{ADD}_{der}}{\text{RfD}_{der}} \qquad \text{NCR} = \text{HI} = \sum HQs$$

$$HQ_{\text{ing}} = \frac{\text{ADD}_{ing}}{\text{RfD}_{ing}}$$

CARCINOGENIC RISKS

$$CR = ADD \times CSF$$

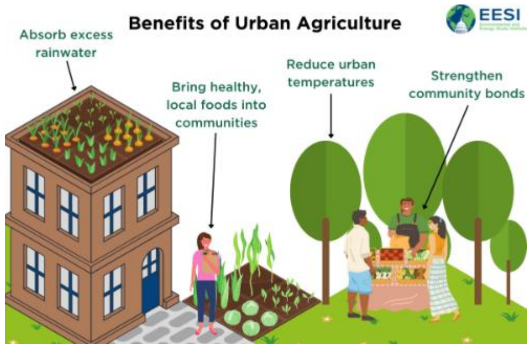
$$CR_{\text{total}} = CR_{\text{ing}} + CR_{\text{inh}} + CR_{\text{der}}$$

Urban soil environment

Soil is a crucial compartment of the urban ecosystem, threatened by anthropic activities, infrastructure sprawl and sealing







Sustainable management strategies of urban soil are strongly encouraged by policy-makers, to preserve urban soil from anthropic degradation/contamination, to enhance its ecosystem functions and services, to produce safe and quality food, and promote social aggregation

- ✓ *Progetto PRIN 2022 (da ottobre 2023): Innovative approach enabling soil and food quality in vegetable gardens of the metropolitan area of Naples (HealthySoil4QualityFood).*
- ✓ *Programma per il Finanziamento della Ricerca di Ateneo (FRA) UniNA, bando 2020, linea d'intervento A (gennaio 2021 - dicembre 2022): Studio multidisciplinare per promuovere la sostenibilità del suolo urbano, per proteggere le sue funzioni e servizi ecosistemici, e per migliorare la sicurezza e la qualità dei prodotti da agricoltura urbana (UrbanSoilGreening).*

Study sites: urban vegetable gardens

Urban soil quality

PHYSICO-CHEMICAL INDICATORS	MIN	MEDIAN	MAX	*Sign. (among study areas)*
Sand (g kg^{-1})	623	728	744	*ns*
Silt (g kg^{-1})	160	171	349	***
Clay (g kg^{-1})	70	97	185	**
pH (in H_20; SSR: 1.2.5)	6.81	7.69	8.03	***
EC (in H_20; dS m^{-1}; SSR: 1.5)	0.08	0.11	0.13	*
Carbonates (g kg^{-1})	0.5	7.4	11.2	***
Organic C (g kg^{-1})	15.5	17.7	28.3	**
Total N (g kg^{-1})	1.2	1.7	2.2	*
C/N	9.6	11.0	14.2	***
Total S (g kg^{-1})	0.57	0.64	0.88	***
CEC (cmol+ kg^{-1})	12.8	18.1	23.1	***
Available P (Olsen; mg kg^{-1})	21.1	46.0	50.2	***

PTE or PAH	MIN	MEDIAN	MAX	*Sign. (among study areas)*	*M.D. 46/2019*
Zn (mg kg^{-1})	80	97	276	***	*300*
Cu (mg kg^{-1})	28	93	139	***	*200*
Pb (mg kg^{-1})	38	57	267	**	*100*
V (mg kg^{-1})	55	67	110	***	*90*
Cr (mg kg^{-1})	5	14	45	***	*150*
As (mg kg^{-1})	11	15	16	***	*30*
Ni (mg kg^{-1})	5	10	20	***	*120*
Cd (mg kg^{-1})	0.2	0.3	0.4	***	*5*
∑ total PAHs (mg kg^{-1})	<0.1	0.3	4.1	***	*10*
Benzo (a) pirene (mg kg^{-1})	<0.01	0.05	0.48	***	*0.1*
∑ heavy/total PAHs (%)	90	96	100	***	-
∑ cancerog/total PAHs (%)	0	48	57	***	-

One-way ANOVA, Tukey's HSD post hoc test (p<0.05; ** p<0.01; *** p<0.001; ns: not significant)*

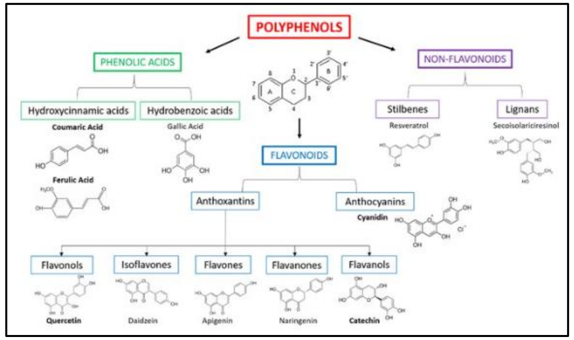
- ✓ Sandy-loam textured soils, with neutral or sub-alkaline pH, low EC, medium-high content of organic matter, bioavailable macro and micronutrients
- ✓ Enhanced soil fertility in organic/synergistic vs. conventional horticultural systems
- ✓ Low-to-moderate soil contamination and bioavailability of PTEs

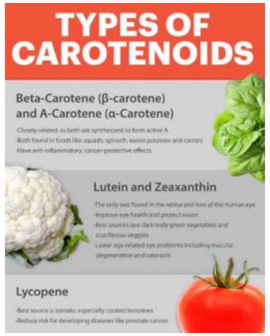
Horticultural food quality and safety

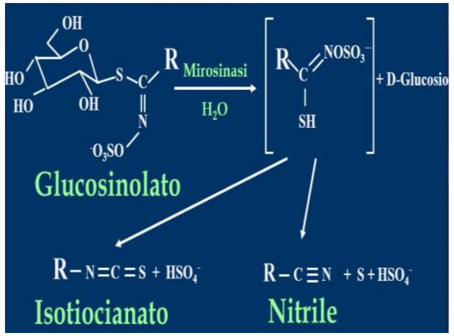


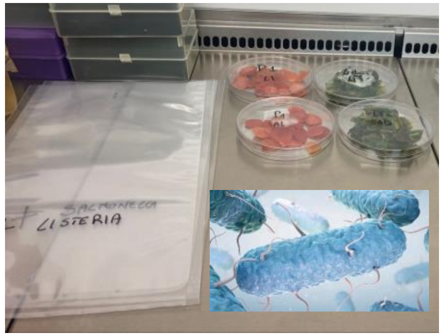
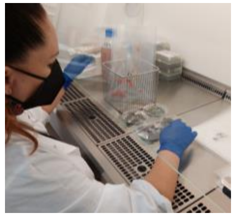

ELEMENTAL PROFILE	N	K	Ca	S	P	Mg	Na	Fe	Zn	Mn	Cu	Pb	V	Cr	Ni	As	Cd
	g kg^{-1} DW							mg kg^{-1} DW									
Mean	25.5	24.5	10.7	5.0	3.1	1.9	0.7	219	23.1	21.4	7.0	0.6	0.5	0.4	0.15	0.11	0.05
Area	ns	**	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Species	***	***	***	**	***	***	***	*	***	**	**	ns	*	*	**	**	***
Area x Species	ns	ns	*	ns	ns	**	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

Two-way ANOVA, Duncan's multiple-range test (p<0.05; ** p<0.01; *** p<0.001; ns: not significant)*



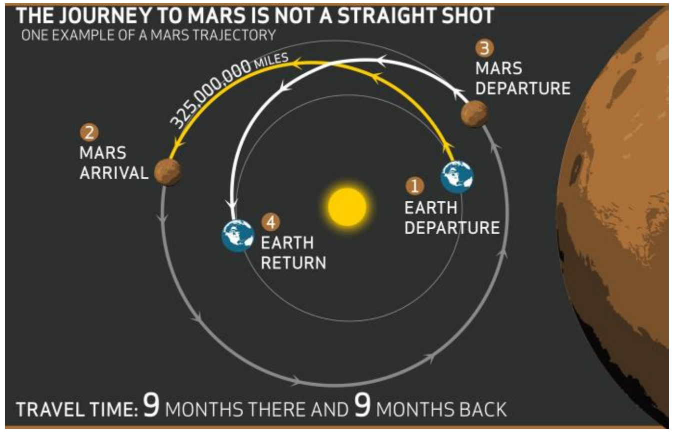


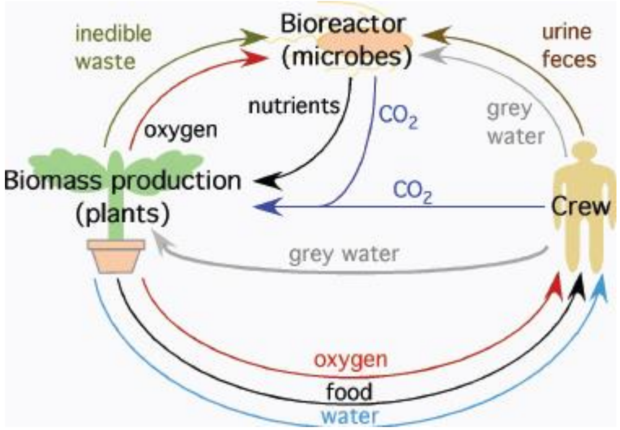


Listeria monocytogenes
&
Salmonella spp.

Extraterrestrial environments





Bioregenerative life support systems (BLSS)

In situ resource utilization (ISRU)

→ use of native materials and waste as primary resources

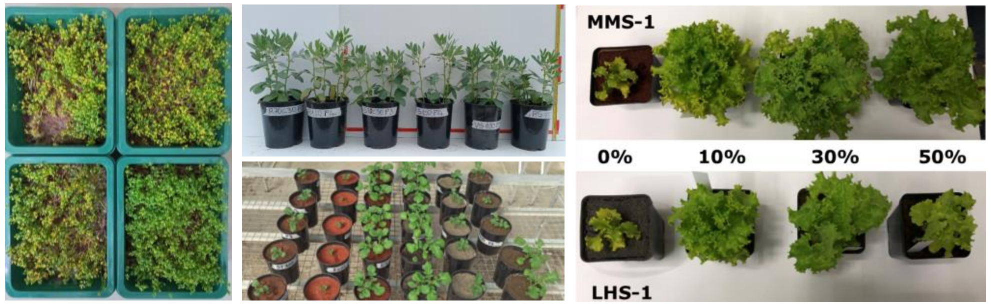
Martian/Lunar simulants

\+

Compost/Manure/SOW

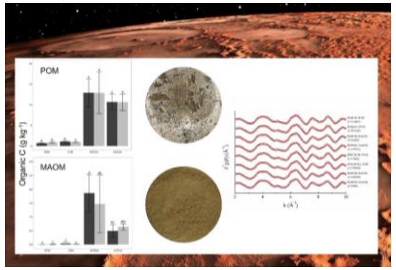
⇨

Plants (e.g., microgreens, lettuce, potato and favabean) growth media



✓ <u>Simulants/amendments and their mixtures:</u> *physico-hydraulic, mineralogical and chemical properties, nutrient biovailability assessment*

✓ <u>Plant biomasses:</u> *biometric and physiological data, productivity, and nutritional/nutraceutical quality*



Article

Evidence of Potential Organo-Mineral Interactions during the First Stage of Mars Terraforming

Beatrice Giannetta [1], Antonio G. Caporale [2], Danilo Olivera de Souza [3], Paola Adamo [2] and Claudio Zaccone [1,4,*]

Soil Systems, 2023, 7, 92.

Stabilisation of exogeneous OM by minerals (e.g., Fe oxides) over time is of paramount importance

References

- ✓ Caporale A.G.*, Adamo P., Capozzi F., Langella G., Terribile F., Vingiani S. (2018). *Monitoring metal pollution in soils using portable-XRF and conventional laboratory-based techniques: Evaluation of the performance and limitations according to metal properties and sources.* Science of the Total Environment 643, 516-526, https://doi.org/10.1016/j.scitotenv.2018.06.178

- ✓ Caporale A.G.*, Agrelli D., Rodríguez-González P., Adamo P., Alonso J.I.G. (2019). *Hexavalent chromium quantification by isotope dilution mass spectrometry in potentially contaminated soils from south Italy.* Chemosphere 233, 92-100, https://doi.org/10.1016/j.chemosphere.2019.05.212

- ✓ Adamo P., Agrelli D., Caporale A.G., Rocco C. (2017). *Analisi della biodisponibilità di metalli potenzialmente tossici.* In: *Manuale Operativo per il Risanamento Ecocompatibile dei Suoli Degradati - Progetto LIFE 11 ENV/IT/275 EcoRemed.* Editor: Fagnano M., Ediguida

- ✓ Caporale A.G., Porfido C., Roggero P.P., Di Palma A. Adamo P., Pinna M.V., Garau G., Spagnuolo M., Castaldi P., Diquattro S. (2023). *Long-term effect of municipal solid waste compost on the recovery of a potentially toxic element (PTE)-contaminated soil: PTE mobility, distribution and bioaccessibility.* Environmental Science and Pollution Research, https://doi.org/10.1007/s11356-023-30831-y

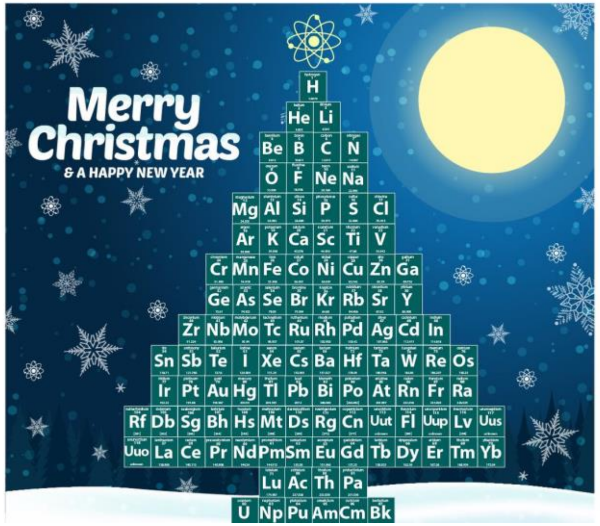
- ✓ Adamo P. and Caporale A.G. (2023). *Il suolo urbano.* In: *Agricoltura urbana. Tecnologie, sistemi e innovazione.* Editors: Orsini F., Pennisi G., Prosdocimi Gianquinto G. Edagricole, Milano, Italy, ISBN: 978-88-506-5627-1

- ✓ Duri L.G., Caporale A.G.*, Rouphael Y., Vingiani S., Palladino M., De Pascale S., Adamo P. (2022). *The potential for Lunar and Martian regolith simulants to sustain plant growth: a multidisciplinary overview.* Frontiers in Astronomy and Space Sciences 8, 747821, https://doi.org/10.3389/fspas.2021.747821

Take-home messages

- ✓ The mitigation of soil threats and the sustainable soil management are paramount to keep soils in a good health for both agriculture and environmental needs
- ✓ The cultivation systems would be resilient to climate change and oriented toward site-specific models, leading to a better use of resources and the enhancement of soil fertility, biodiversity and food quality/safety
- ✓ … … …

Acknowledgements



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- ✓ You all for your kind attention!