TOWARDS FOOD SAFETY. POTENTIALLY HARMFUL ELEMENTS (PHEs) FLUXES FROM SOIL TO FOOD CROPS

LA SECURITE ALIMENTAIRE. FLUX D'ÉLEMENTS POTENTIELLEMENT NUISIBLES (EPN) DU SOL AUX CULTURES D'USAGE ALIMENTAIRE

VERSO LA SICUREZZA ALIMENTARE. FLUSSI DI ELEMENTI POTENZIALMENTE TOSSICI (EPT) DAL SUOLO ALLE COLTURE ALIMENTARI

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Abstract

Soil is the basis of the ecosystems and of our system of food production. Crops can uptake heavy metals and potentially toxic elements from the soil and store them in the roots or translocate them to the aerial parts. Excessive content of these elements in edible parts can produce toxic effects and, through the food chain and food consumption, result in a potential hazard for human health. In this study soils and plants (spring wheat, *Triticum aestivum* L. and maize, *Zea mays* L.) from a tannery district in North-East Italy were analyzed to determine the content of some major and micro-nutrients and potentially toxic elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, S, Zn, V). The soils of the area are moderately polluted; Cr is the most important inorganic contaminant, followed by Ni, Cu and V. Factor analysis evidenced that the contaminants are in part anthropogenic and in part geogenic. Major anthropogenic origin was detected for Cr, Ni (from industrial activities), Zn, Cu, Cd (from agriculture practices). Biological Absorption Coefficient (BAC) from soil to plant roots and Translocation factor (TF) within the plant were calculated; major nutrients (K, P, S) and some micronutrients (Cu, Zn, Mg, Mn) are easily absorbed and translocated, whilst other nutrients (Ca, Fe) and potentially toxic elements or micronutrients (Al, Cd, Cr, Ni, Pb, V) are not accumulated in the seeds of the two considered plants. However, the two edible species proved differently able to absorb and translocate elements, and this suggests to consider separately every species as potential PHEs transporter to the food chain and to humans. Cr concentrations in seeds and other aerial parts (stem and leaves) of the examined plants are higher than the values found for the same species and for other cereals grown on unpolluted soils. Comparing the Cr levels in edible parts with recommended dietary intake, besides other possible Cr sources (dust ingestion, water), there seems to be no health risk for animal breeding and population due to the consumption of wheat and maize grown in the area.

Key-words: *toxic elements; metal translocation; soil contamination; food chain*

DOI: 10.6092/issn.2281-4485/3930

Résumé

Le sol est la base des écosystèmes et de notre système de production alimentaire. Les cultures peuvent absorber métaux lourds et éléments potentiellement toxiques du sol et les stocker dans les racines ou les déplacer vers les parties aériennes. Un teneur excessive de ces éléments dans les parties comestibles peut produire des effets toxiques et, par la chaîne alimentaire, conduire à un danger potentiel pour la santé humaine. Dans cette étude, les sols et les végétaux (blé de printemps, *Triticum aestivum* L. et du maïs, *Zea mays* L.) d'un terroir agro-industriel dans le Nord-Est de l'Italie ont été analysés pour déterminer la teneur de certains éléments majeurs et micro-nutritives et potentiellement toxiques (Al , Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, S, Zn, V). Les sols de la région sont modérément polluées; Cr est le polluant le plus important, suivi par Ni, Cu et V. L'analyse factorielle a mis en évidence que les contaminants sont en partie d'origine anthropique et en partie géogénique. Origine anthropique a été détectée pour Cr, Ni (activités industrielles), Zn, Cu, Cd (à partir de pratiques agricoles). Le coefficient d'absorption biologique (BAC) du sol aux racines et le facteur de translocation (TF) des racines à la partie arienne ont été calculés. Les principaux nutritives (K, P, S) et certains oligo-éléments (Cu, Zn, Mg, Mn) sont facilement absorbés et transloqués, tandis que d'autres nutritives (Ca, Fe) et des éléments potentiellement toxiques (Al, Cd, Cr, Ni, Pb, V) ne sont pas accumulés dans les graines des deux plantes considérées. Toutefois, les deux espèces comestibles sont différemment capable d'absorber et déplacer ces éléments. Cela suggère d'examiner séparément chaque espèce comme potentiel transporteur des métaux à la chaîne alimentaire et à l'homme. Cr concentrations dans les graines et autres parties aériennes (tiges et feuilles) des plantes examinées sont plus élevés que les valeurs trouvées pour les mêmes espèces et pour les autres céréales cultivées sur des sols non pollués. En comparant les teneurs en Cr dans les parties comestibles des plantes étudiées avec les apports du Cr conseillés, en plus d'autres possibles sources du Cr (ingestion de poussières et d'eau), il semble que il n'y a aucun risque sanitaire pour l'élevage et la population en raison de la consommation de blé et de maïs cultivés dans la région.
Mots clés: *éléments toxiques; translocation sol-plant; sols pollués; chaîne alimentaire.*

Riassunto

Il suolo è la base degli ecosistemi e del nostro sistema di produzione alimentare. Le colture possono assorbire metalli pesanti ed elementi potenzialmente tossici dal suolo e accumularli nelle radici o traslocarli nelle parti epigee. Un contenuto eccessivo di questi elementi nelle parti commestibili può produrre effetti tossici e, attraverso la catena alimentare e il consumo di cibo, si traducono in un potenziale pericolo per la salute umana. In questo studio i suoli e piante (grano primaverile, *Triticum aestivum* L. e mais, *Zea mays* L.) provenienti da un distretto conciario nel Nord-Est d'Italia sono stati analizzati per determinare il contenuto di alcuni macro e micro-nutrienti e di altri elementi potenzialmente tossici (Al , Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, S, Zn, V). I suoli della zona sono moderatamente inquinati ed il Cr costituisce il più importante dei contaminanti inorganici, seguito da Ni, Cu V e l'analisi fattoriali ha evidenziato come tali contaminanti siano in parte di origine antropica e in parte geogenica. Sono di origine antropica Cr e Ni derivanti da attività industriali e Zn, Cu, Cd da pratiche agricole. Sono stati calcolati il Coefficiente Biologica di Adsorbimento (CBA) dal suolo alle radici e Fattore di Traslocazione (FT) all'interno della pianta. I principali macro nutrienti (K, P, S) e alcuni micronutrienti (Cu, Zn, Mg, Mn) sono facilmente adsorbiti e traslocati, mentre altri nutrienti (Ca, Fe) o elementi potenzialmente tossici o micronutrienti (Al, Cd, Cr, Ni, Pb, V) non hanno evidenziato accumulo nei semi delle due piante considerate. Tuttavia, le due specie commestibili hanno evidenziato un diverso in grado di assorbimento e di traslocazione degli elementi, e questo suggerisce di considerare separatamente le varie specie vegetali in funzione della possibilità di traslocazione di elementi potenzialmente tossici nella catena alimentare e per l'uomo. Concentrazioni di Cr nei semi e altre parti aeree (fusto e foglie) delle piante esaminate sono risultati superiori ai valori trovati per le stesse specie e per altri cereali coltivati su suoli non inquinati. Tuttavia se si confrontano i livelli di Cr presenti nelle parti commestibili dei vegetali indagati con i valori di assunzione giornaliera raccomandata, a cui si possono aggiungere eventuali contributi da altre fonti (es.: ingestione di polvere, acqua), non sembra esserci nella zona indagata rischio per la salute degli animali e della popolazione in funzione del consumo del grano e del mais coltivati.

Parole chiave: *elementi tossici; traslocazione metalli; suoli contaminati; catena alimentare.*

Introduction

According to the definition given in the World Food Summit hold in Rome in 1996, *food security* is running when all people, in every time, may accede, both physically and economically, to a sufficient food quantity, in order to attain safe and active life (FAO, 2006). Although soil is not the only factor to consider, it is a fundamental component for food security in view of the global challenge posed by the more and more increasing population of the world (Abrahams, 2002). In this perspective, it is noteworthy to consider not only the food security, but also the *food safety*, i.e. the sanitary quality of food, including food contamination by bacteria, parasites, organic and inorganic contaminants, and potentially toxic elements (PTEs). Besides the different food preparation phases, contaminants may enter in the food crops during the growing stage, mostly by uptake from the soil solution, up to toxic/excessive concentrations for plants, animals and even humans. The presence of excessive levels of heavy metals in soil may compromise food safety entering the food chain but also determining phytotoxic effects that affect plant productivity, and therefore decreasing the available food quantity (Kabata-Pendias, 2011). In plants growing on contaminated soils, moreover, counteracting effects related to microelements excess/deficiency may occur simultaneously, because of antagonistic interactions between essential and not essential elements (e.g.

DOI: 10.6092/issn.2281-4485/3930

Cu deficiency determined by Mo excess) (Steinnes, 2009). In the next future it is likely that the increase of world population will determine increasing food production; meanwhile, more land will be degraded or eroded or sealed (Chen, 2007). This will result in a general loss of soil functionality, crop productivity and food quality, particularly in the proximity of urban agglomerates and industrial areas (Peralta-Videa *et al.*, 2009). It is estimated that in China, 20M ha of agricultural land are contaminated by heavy metals, with a net loss of 10M tons of cereal yield (Chen, 2007). Moreover, metals from contaminated soils may enter the food chain, and therefore decrease food safety for humans and animals (Kabata-Pendias, 2011). On the other hand, a defence strategy ("root barrier effect") is generally applied by plants against non-essential or critical elements (e.g. Ag, As, Cd, Cr, Hg, Pb, Sn, Tl, Y, Zr; McLaughlin *et al.*, 1999).

Human exposition to contaminants occurs through different pathways, both direct and indirect (Abrahams *et al.*, 2002):

- Ingestion of soil particles, particularly relevant for children;
- Inhalation of suspended soil particles;
- Dermal absorption by direct contact with contaminated particles.
- Element transfer from soil to plants or water and to the food chain: food consumption and drinking contribute to 90% of the human exposition to heavy metals (Huang *et al.*, 2008; Zheng *et al.*, 2007; Cui *et al.*, 2004).

The main purpose of this study is to ascertain if there is a significant translocation of contaminants from agricultural land impacted by human activities to food crops potentially harmful to stakeholders. A second objective is to assess whether and how two food crops diffused all over the world, winter wheat (*Triticum aestivum* L.) and maize (*Zea mays* L.) are able to absorb and to translocate PHEs in their aerial parts and to the food chain.

Materials and Methods

The study area is located in the central part of the Veneto alluvial plain, and is heavily impacted by several anthropic activities; the most prominent is a big tannery district, with more than 400 factories. A relevant proportion of the territory, however, is agricultural land with intensive cultivation of food crops (namely wheat, maize and soybean); the Milan-Venice highway crosses the investigated area with heavy vehicular traffic.

Field sampling

22 agricultural soils (1/100ha) from five transects crossing the study area have been sampled for topsoil (0-30cm) and subsoil (40-70cm); each sample resulted from 5 subsamples collected over a square meter surface (Rodrigues *et al.*, 2010).

At every site, food crops (*Triticum aestivum* and *Zea mays*) have been sampled with the following criteria :

- wheat: whole plant (20 specimens) during June, before harvesting;
- maize: young leaves (6 specimens) during June; the whole plant (3 specimens, including roots and seeds) during September, before harvesting.

Soil samples have been transferred to the lab in plastic bags, air dried, sieved (2mm) and then analysed for routine analyses (MIPAF, 2000) to characterise soil properties (pH, organic carbon, nitrogen, carbonate, cation exchange capacity, texture). Plant samples, once recovered to the lab, have been gently washed with tap water and rinsed with distilled water prior to subdivide roots, shoots and leaves. Subsequently, the different parts have been oven dried at 80°C for 48 hours (Unterbrunner *et al.*, 2007).

Laboratory analyses
All the chemicals utilised for determining major and trace elements are of analytical grade and produced by Sigma-Aldrich.

Sample preparation
Soil fine earth has been grinded to fine powder (<100μm) with agate mill; one soil aliquot (0.2g) has been digested in Teflon containers with acidic solution (5mL aqua regia + 1mL HF) in microwave (Ethos 1600-Milestone), accordingly with Abollino *et al.*, (2009). Digested samples have been made up to 50mL with milli-Q water, filtered with cellulose filters (Whatman, 0.2 μm) and stocked in poliethylen containers. As reference sample, two replicates of certified SOIL 5 (*International Atomic Energy Agency*) were analysed. A portion of dried plant samples (0.1 g) has been grinded with stainless steel mill (A 10 basic yellowline IKA), digested with acidic solution (8 mL HNO_3 + 2 mL H_2O_2) in microwave (Ethos 1600-Milestone), as proposed by Bi *et al.* (2009) e Zhu *et al.* (2007), made up to 25 ml and filtered as soils above. The certified sample BCR 62 (olive leaves; *Commission of European Communities*) was retained as reference sample.

Elemental analyses
Total (pseudo-total) concentrations of elements Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, S, Zn, V have been determined by ICP-OES, *Inductively Coupled Plasma – Optical Emission Spectroscopy* (Optima 5300 DV, Perkin Elmer), by AAS – *Atomic Absorption Spectroscopy* (Spectra 250 Plus Varian equipped with graphite furnace GTA-96, Varian), or by ICP-MS, *Inductively Coupled Plasma-Mass Spectrometry*(Elan 6100, Perkin Elmer), depending on the element concentration.

Results and Discussion

Soil Routine analyses
Soil characters are rather uniform in the whole studied area . The pH, in particular, has a *range* between 7.3 and 8.2 both at surface and at depth, consistent with the parent material which is primarily limestone and secondarily basalt alluvium. Differences in parent material are reflected also in the carbonate content (range 0-38%). Sites showing the highest carbonate contents are located in the south-eastern part of the studied area, while the less abundant are located in the western part, where basaltic sediments are widespread. Organic carbon ranges between 8 mg kg^{-1} and 24 mg kg^{-1} in the topsoil, with a little decrease with depth. Soil texture is clay-

DOI: 10.6092/issn.2281-4485/3930

loam to silty-clay, with sand percentage less than 30%, and clay up to 49% in top-soil at site 5. Cation exchange capacity is >20 cmol kg^{-1} for each sample, consistently with the high clay content

Soil elemental analyses (Tables 1, 2)
Macronutrients in soils (Ca, K, Mg, P, S) present concentrations consistent with those reported in current literature (Kabata-Pendias, 2011; Kabata-Pendias e Mukherjee, 2007), and with Italian legislation (D.L. 152/2006) and background levels recorded in local alluvial deposits (ARPAV, 2011).

Table 1– *Total (aqua regia) metal concentrations (mg kg^{-1} d.w.) in surface soils (0-30cm)*

	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	V	Zn
A1 s	60488	26554	0.219	284.1	99.99	137234	6369	18838	1550	180.88	4131	10.44	822	258.0	128.6
A2 s	41370	73232	0.272	195.5	43.15	75202	5481	41393	903	143.92	3020	6.65	1898	168.9	79.7
A3 s	49595	53568	0.355	239.5	124.5	91516	5877	37094	1154	172.94	3183	8.12	1461	192.3	112.1
A4 s	48160	58934	0.450	126.6	40.33	59050	11910	35264	1012	77.92	1696	16.76	1587	136.1	92.3
A5 s	61890	11489	0.731	115.7	95.93	67152	23824	8924	1439	64.24	1790	20.00	593	169.5	110.6
A6 s	48601	79546	0.290	159.6	111.7	70065	9557	43071	954	99.16	1931	15.00	2024	161.0	96.9
A7 s	46611	33465	0.396	261.7	89.46	99118	5917	26670	1245	191.24	3597	8.59	1074	224.1	108.2
A8 s	47944	47758	0.350	252.3	58.33	93157	6098	34743	1185	175.04	3585	8.27	1453	206.9	106.3
A9 s	32471	37641	0.369	213.1	118.0	92153	5134	28137	1110	181.65	3328	9.25	1109	202.0	100.8
A10 s	50680	41533	0.373	242.7	108.9	106795	5969	31810	1220	180.32	3377	9.95	1197	210.6	108.1
A11 s	57700	54763	0.305	572.7	117.2	109909	7761	25000	1148	147.79	4139	17.99	1522	204.8	148.8
A12 s	58847	27460	0.223	178.4	95.38	138010	7481	19123	1734	211.39	4869	8.99	798	250.1	139.5
A13 s	53662	29491	0.220	326.4	87.38	134131	6703	17073	1597	187.99	4280	30.18	871	247.6	134.7
A14s	63754	75390	0.404	215.5	59.34	81285	9450	51733	1087	94.49	2612	17.16	1888	193.4	103.4
A15s	60962	62054	0.393	164.2	63.14	90814	10580	41105	1300	100.84	2485	31.16	1579	216.6	96.8
A16s	61496	87456	0.454	143.1	159.5	81792	11844	51902	1134	92.15	2603	13.74	2399	191.1	114.9
A17s	62587	62335	1.373	155.1	66.92	82281	12666	42002	1205	89.60	2367	12.72	1571	194.5	95.9
A18s	59392	36576	0.381	95.5	78.05	67750	23682	33515	1289	51.36	1681	17.39	1061	172.2	90.0
A19 s	52988	34443	0.467	105.4	46.84	59815	13905	21707	1126	58.93	1644	18.51	1162	144.0	101.1
A20s	47891	87292	0.341	112.3	58.31	72188	11861	42878	1032	79.70	2128	14.03	2116	165.8	87.9
A21s	47039	106250	0.438	329.4	41.73	79948	9853	42670	1096	90.65	3223	16.99	2667	178.2	109.3
A22s	46943	93425	0.543	121.0	79.59	69648	10325	55128	1035	83.73	2299	16.65	2295	170.6	98.3
Mean	52976	55609	0.424	209.5	83.84	89086	10106	34146	1209	125.32	2913	15.06	1509	193.6	107.6
St.Dev	8287	25248	0.242	107.3	31.65	23771	5145	12245	213	51.71	951	6.43	562	32.7	17.5
Median	51834	54166	0.377	186.9	83.48	82036	9503	35003	1151	100.00	2816	14.52	1492	192.9	104.8
Max	64886	106250	1.373	572.7	159.5	138119	23824	55128	1734	211.39	4869	31.16	2667	258.2	148.8
Min	32471	11489	0.195	95.5	40.33	59050	5134	8924	903	51.36	1644	6.65	593	136.1	79.7

Table 2- *Total (aqua regia) metal concentrations (mg kg^{-1} d.w.) in subsurface soils (40-70cm). n.d.=not available*

	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	V	Zn
A1 p	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A2 p	50400	62716	0.233	232.1	47.69	92031	5829	40278	1084	177.60	3270	4.36	1495	200.2	90.9
A3 p	53866	49625	0.261	270.2	67.48	110234	6111	35029	1250	194.47	3293	5.06	1226	218.7	102.0
A4 p	38048	93456	0.457	116.6	52.30	51102	11164	48469	815	78.40	1817	17.66	2345	128.6	84.1
A5 p	57854	16147	0.524	116.0	64.29	66175	21065	8348	1485	66.20	1891	17.43	661	173.7	102.5
A6 p	37820	83275	0.255	153.3	97.35	69512	9215	39543	923	96.39	1922	11.57	2056	154.4	107.3
A7 p	49877	40148	0.346	256.1	66.27	100245	6480	29729	1268	192.78	3662	8.09	1198	215.4	115.2
A8 p	51369	62707	0.392	223.5	100.02	91643	6820	39539	1134	166.46	3577	11.37	1664	206.1	109.4
A9 p	48573	66638	0.290	231.4	64.60	91121	5605	40678	1087	172.17	3303	5.96	1645	200.8	98.31
A10 p	50112	45940	0.321	255.3	110.89	110014	6023	30929	1274	192.44	3356	7.73	1218	211.1	105.2
A11 p	63768	42478	0.165	248.8	120.84	121685	6941	25371	1304	165.72	4286	8.34	1085	215.6	116.5
A12 p	67322	32278	0.165	307.6	82.40	138036	7358	18830	1688	197.62	3950	8.54	900	255.8	131.7
A13 p	66585	31042	0.171	303.2	75.35	137907	7674	22684	1691	192.36	4522	7.64	847	252.2	131.3
A14 p	66803	59059	0.388	181.7	64.40	98560	10492	38346	1348	103.51	2927	9.36	1525	227.5	104.3
A15 p	63893	72544	0.396	144.4	57.30	80046	11039	51430	1400	88.61	2420	13.41	2095	192.2	93.8
A16 p	64623	68679	0.437	146.4	132.77	82266	11101	50174	1115	92.60	2581	13.32	1767	189.7	108.9
A17 p	62463	64095	0.432	131.8	62.19	82153	14387	40374	1214	81.76	2213	11.88	1586	191.7	95.2
A18 p	56223	37253	0.357	92.2	83.26	68614	24289	19003	1252	47.73	1545	16.83	1053	170.7	88.1
A19 p	53800	35165	0.367	103.4	42.24	60348	17577	22922	1104	57.65	1515	27.59	1053	140.7	91.4
A20 p	65410	82301	0.315	156.0	32.53	84495	9963	49370	1174	95.80	2394	8.82	1818	210.5	95.8
A21 p	47961	103623	0.428	369.4	43.64	75090	9563	44324	998	98.34	2913	22.64	2594	170.7	106.9
A22 p	46553	88213	0.414	123.8	56.15	70724	9577	53385	1018	82.53	1975	12.49	2054	173.4	83.4
Mean	55389	58838	0.337	198.2	72.52	89602	10394	35677	1220	125.56	2824	11.86	1517	195.1	103.0
St. Dev.	9159	23305	0.102	78.3	26.65	23734	5083	12457	222	53.19	896	5.89	521	32.6	13.3
Median	53866	62707	0.357	181.7	64.60	84495	9563	39539	1214	98.34	2913	11.37	1525	200.2	102.5
Max	67322	103623	0.524	369.4	132.77	138036	24289	53385	1691	197.62	4522	27.59	2594	255.8	131.7
Min	37820	16147	0.165	92.2	32.53	51102	5605	8348	815	47.73	1515	4.36	661	128.6	83.35

Micronutrients and PHEs (Al, Fe, Mn, Cd, Pb, Zn) present mean levels consistent or slightly higher than those in literature, and below the Italian regulatory guidelines (D.L. 152/2006). The levels of Cr, Ni, and V at several sites, instead, are higher than the regulatory threshold and ARPAV background levels. An anthropic contribution is likely, considering the high density of industrial activities in the area. However, data are partially consistent with the basaltic parent material, suggesting a partial geogenic origin.

DOI: 10.6092/issn.2281-4485/3930

Copper concentration overcomes the legislation threshold in four samples, and the recorded background (66 mg kg^{-1}; ARPAV 2011) in more that half of the samples examined.
The calculation of the Top Enrichment Factor (TEF = $metal_{topsoil}$ /$metal_{subsoil}$) of the studied soils allows to identify sites with anthropogenic contamination (TEF>1) in comparison to not contaminated sites (TEF<1) (Ungaro et al., 2008). The results obtained (data not shown) point to slight contamination at surface (TEF>1) with Cr, Cu and Zn in nearly 50% of the investigated sites, while Cd, Ni and Pb have generally TEF<1, excluding anthropogenic contamination.

Basic Statistical Analysis

Univariate statistical analysis (Pearson coefficients, not shown) indicates a strong linear correlation ($p<0.05$) between metal couples: Cr-Ni (0,972), Cr-Pb (-0,817), Ni-Pb (-0,825), as expected with metals having similar/counteracting geochemical behaviour. A less strong correlation is shown by the couple Cu-Zn (0,586), which are negatively correlated with sand content. The factor analysis and the cluster analysis on normalized variables allowed identification of five groups of variables, related to: 1) calcareous parent material (Ca, Cd, Mg, Mn); 2) organic components (P, Pb, S); 3) soil matrix (Al, Fe, K); 4) basaltic parent material (Ni, V); 5) anthropogenic origin (Cr, Cu, Ni, Zn). Chromium is the most threatening element in the whole area. By way of a GIS *software* (ArcGis 9, ArcMap 9.3) it was possible to report the Cr spatial distribution (Fig. 1).

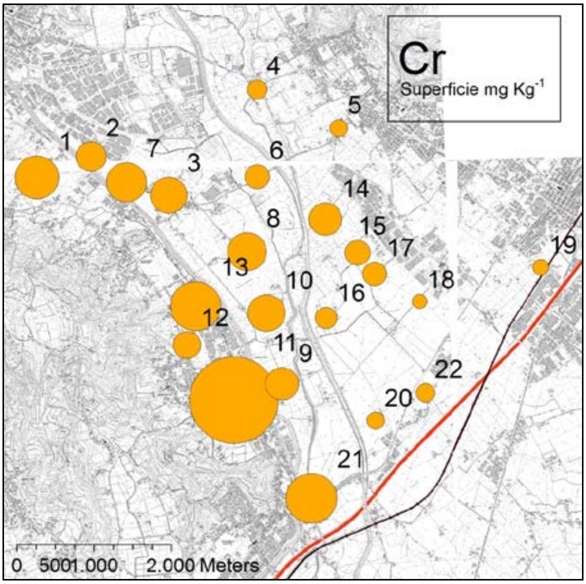

Figure 1
Spatial distribution of Cr concentration in topsoil of the investigated area. Circles size is proportional to metal concentration

The highest Cr concentrations in topsoil were recorded in the south-western part, where many tannery industries are located. A relevant anthropogenic contribution, therefore, is likely responsible for elevated Cr levels, besides the geogenic contribution from basaltic parent material

Elemental analyses in plants

A summary of results concerning food crops elemental analyses is shown in Tables 3 and 4. Full information is available in Fontana, 2013. Among macronutrients, the most prominent in both wheat and maize seeds is K, followed by P, Mg, S. Concerning other metals, the mean level in wheat seeds decreases in the following order:

$Ca(10^2)>Al \approx Fe(10^1)>Mn \approx Zn(10^1)>Cu(10^0)>Cr \approx Ni(10^{-1})>V \approx Pb(10^{-1})>Cd(10^{-2})$.

Similarly, in maize seeds the following trend was recorded:

$Ca(10^1)> Al \approx Fe(10^1)>Zn(10^1)>Mn(10^0)> Cr \approx Ni(10^{-1})> V \approx Pb(10^{-1})>Cd$.

Metal distribution in the different parts of the wheat plants is the following: Al, Ca, Cr, Fe, Ni, Pb, V are more abundant in roots than in shoots and seeds, while Cu, Mn and Zn are accumulated in the order roots>seeds>shoots.

Table 3 – *Elemental distribution (mg kg^{-1} d.w.) in different parts of wheat plants*

Wheat seeds	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	V
samples	18	21	15	21	21	21	21	21	21	16	21	13	21	21
Mean	67.06	368.0	0.026	0.562	3.94	68.40	4808	1373	36.25	0.543	3697	0.273	1342	0.302
St. Dev.	86.60	115.8	0.016	0.292	0.99	27.53	899	237	9.08	0.410	618	0.211	316	0.334
St. Dev. %	129	31	61	52	25	40	19	17	25	75	17	77	24	110
Median	52.30	334.0	0.023	0.563	3.98	62.70	4798	1378	33.74	0.373	3620	0.228	1334	0.135
Max	389.85	655.5	0.076	1.140	6.13	154.52	6492	1777	65.50	1.508	5205	0.840	2203	1.126
Min.	8.52	220.2	0.014	0.157	2.60	45.58	3534	968	25.63	0.105	2576	0.062	954	0.046
Wheat shoots	**Al**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Ni**	**P**	**Pb**	**S**	**V**
samples	19	21	21	21	21	21	21	21	21	21	21	14	21	15
Mean	113.9	3212	0.046	6.956	3.05	169.5	15038	1170	33.84	3.365	1120	0.466	1378	0.449
St. Dev.	112.0	2516	0.025	4.052	5.22	114.4	6315	977	22.71	1.223	751	0.300	1082	0.344
St. Dev. %	98	78	54	58	171	67	42	83	67	36	67	64	78	77
Median	94.8	2058	0.042	7.335	1.45	126.4	12857	681	29.38	3.392	1020	0.461	933	0.281
Max	523.5	10724	0.124	14.828	25.421	594.2	29840	3029	108.44	6.107	3074	1.101	4224	1.383
Min.	8.5	1046	0.015	1.272	0.98	53.1	7995	444	8.52	1.493	328	0.111	404	0.112
Wheat roots	**Al**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Ni**	**P**	**Pb**	**S**	**V**
samples	21	21	21	21	21	21	21	21	21	21	21	21	21	21
Mean	4383	5778	0.147	19.32	15.34	6308	4724	2813	80.63	11.53	1058	1.701	843	10.03
St. Dev.	1750	2776	0.055	11.58	8.53	2222	2737	1324	26.59	3.63	427	1.004	370	4.20
St. Dev. %	40	48	37	60	56	35	58	47	33	32	40	59	44	42
Median	4029	5042	0.127	16.37	14.39	6097	4498	2748	78.52	11.71	937	1.416	769	9.53
Max	8430	11961	0.303	47.73	36.07	12517	14018	5729	137.19	18.30	2384	4.218	2112	20.09
Min.	1349	2503	0.071	7.09	4.09	2814	1064	1207	24.66	5.32	613	0.369	364	3.44

DOI: 10.6092/issn.2281-4485/3930

Table 4 - *Elemental distribution (mg kg^{-1} d.w.) in different parts of maize plants*

Maize seeds	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	V	Zn
Samples	21	21	0	21	21	21	21	21	21	21	21	21	21	21	21
Mean	45.22	76.58	-	0.707	1.649	51.80	3989	1281	7.37	0.630	3092	0.170	1078	0.280	23.36
St. Dev.	12.56	46.20	-	0.197	0.390	12.15	692	245	2.33	0.312	543	0.080	281	0.114	4.61
St. Dev. %	28.00	60.00	-	28.00	24.00	23.00	17.00	19.00	32.00	49.00	18.00	47.00	26.00	41.00	20.00
Median	43.50	71.39	-	0.657	1.659	48.91	3967	1314	7.28	0.560	3107	0.142	1053	0.278	22.81
Max	79.46	254.0	-	1.192	2.404	83.01	6195	1743	11.47	1.722	4289	0.458	1632	0.566	33.51
Min.	22.78	29.82	-	0.477	1.087	32.80	3109	587	3.933	0.217	1936	0.089	549	0.092	17.38

Maize shoots	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	V	Zn
Samples	14	21	14	21	21	21	21	21	21	21	21	6	21	16	21
Mean	38.89	1915	0.020	1.535	1.508	38.53	18811	1659	5.264	0.731	1467	0.352	415.9	0.162	15.04
St. Dev.	20.05	620	0.016	0.812	0.463	27.48	9641	986	2.961	0.368	1177	0.117	140.7	0.135	6.56
St. Dev. %	51.55	32.00	79.09	52.90	30.68	71.33	51.00	59.00	56.25	50.37	80.00	33.28	33.80	83.66	43.61
Median	33.08	2031	0.016	1.394	1.353	32.92	19527	1422	4.502	0.615	1293	0.326	363.8	0.129	13.28
Max	76.08	3118	0.073	4.104	2.334	122.7	50622	3852	13.13	1.706	4712	0.493	772.3	0.514	30.86
Min.	14.59	911	0.012	0.580	0.715	8.46	3026	409	1.427	0.220	165	0.240	226.9	0.015	6.55

Maize leaves	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	V	Zn
Samples	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21
Mean	181.5	11539	0.058	6.862	9.179	314.9	14982	4880	68.49	3.402	2548	0.603	1715	0.812	28.12
St. Dev.	112.8	2341	0.043	2.074	3.829	180.2	7175	1808	30.79	0.883	1018	0.298	407	0.456	8.21
St. Dev. %	62.00	20.00	74.00	30.00	42.00	57.00	48.00	37.00	45.00	26.00	40.00	49.00	24.00	56.00	29.00
Median	145.9	11565	0.043	6.440	7.908	260.9	14692	4535	63.06	3.250	2078	0.553	1666	0.608	29.04
Max	560.6	16896	0.195	12.33	22.74	940.9	30256	9717	167.5	5.642	4327	1.429	2665	1.744	43.36
Min.	70.5	7562	0.018	3.464	4.755	148.1	2777	2816	34.33	1.935	1335	0.280	1045	0.204	14.63

Maize roots	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	V	Zn
Samples	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21
Mean	3047	6240	0.137	17.99	23.60	4329	7804	2404	52.89	14.89	1224	0.992	1144	6.405	42.11
St. Dev.	836	1764	0.047	16.02	8.28	1311	5396	670	16.18	7.05	570	0.417	213	1.559	35.24
St. Dev. %	27.00	28.00	34.50	89.03	35.10	30.00	69.00	28.00	30.60	47.38	47.00	42.00	19.00	24.34	83.69
Median	3039	6029	0.120	15.97	23.73	4026	6370	2462	52.98	13.76	1036	0.995	1204	6.196	34.13
Max	4631	10847	0.241	84.69	39.98	6692	22434	3350	98.84	41.13	2374	2.035	1551	9.477	152.6
Min.	1375	3545	0.062	6.49	11.22	2011	1555	1052	27.80	7.22	380	0.289	696	3.122	14.92

In maize plants, metal behave with a different pathway: Cr, Ni and Cd present concentrations in roots> leaves>shoots>seeds, while Al, Cu, Fe, Zn, V present higher concentrations in seeds, with the following trend: roots>leaves>seeds>shoots; Ca and Mn are more concentrated in leaves. Critical levels of Cr, Cu, Zn are recorded at nearly 50% of the investigated sites, and the consequent phytotoxicity could explain the decline of crop yield.

PHEs (Cd, Cu, Pb, Zn) contents in seeds of the two food crops are consistent with data from literature (Kabata-Pendias, 2011; Kabata-Pendias and Mukherjee, 2007). Chromium levels in seeds, instead, are higher than the reference values, and this is consistent with the presence of numerous tannery industries in the area.

Nickel and V present levels a little higher than the reference values (Kabata-Pendias, 2011; Lavado et al., 2001; Adriano, 2001), suggesting a contribution from parent material.

Metals (Cd, Cu, Ni, Pb, V, Zn) concentration in maize leaves is consistent with normal ranges reported in literature (Kabata-Pendias, 2011; Kabata-Pendias and Mukherjee, 2007), out of chromium, whose level is generally higher than tolerable concentration in crops (2 mg kg^{-1}), ranging between 5-30 mg kg^{-1}.

In order to evaluate the plant ability to uptake metals and translocate them from soil to roots, and from roots to the aerial parts, we have calculated two of the most applied indexes: the Biological Absorption Coefficient (Malik et al, 2010), and the Translocation Factor (Marchiol et al, 2008).

The Biological Absorption Coefficient (BAC= $Metal_{soil}/Metal_{roots}$) shows (Table 5) the following trend: Zn > Cu > Ni > Cr, consistent with the essential role of Zn and Cu as micronutrients.

Table 5a - *BAC in wheat plants. Results are expressed as %*

	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	Zn	V
Mean	**8.4**	**11**	**39**	**9.5**	**19**	**7.2**	**57**	**8.7**	**6.9**	**10**	**38**	**12**	**61**	**37**	**5.3**
St. Dev.	3.1	6.0	18	4.2	9.0	2.4	34	3.5	2.5	4.2	17	6.5	28	12	2.3
Median	8.0	9.7	34	8.9	17.3	6.9	50	7.7	6.9	9.6	36	10.8	53	34	5.3
Max	15	35	90	19	39	11	118	20	13	19	92	25	122	65	10
Min	2.8	5.2	22	2.8	7.0	3.0	10	3.5	2.1	3.0	16	3.9	21	19	1.7

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Table 5b - *BAC in maize plants. Results are expressed as %*

	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	S	Zn	V
Meam	**5.9**	**14**	**37**	**11**	**31**	**5.1**	**81**	**8.7**	**4.5**	**14**	**45**	**7.5**	**88**	**42**	**3.4**
St. Dev.	1.8	9.4	14	15	14	1.9	49	6.1	1.4	12	24	4.3	37	42	0.9
Median	5.8	11	34	8.5	29	4.9	72	6.8	4.4	12	42	6.5	79	34	3.5
Max	11	47	78	73	76	10	228	32	7.5	64	99	20	180	192	5.1
Min	2.3	6.0	8.3	2.9	11	1.5	26	2.9	1.6	5.0	15	2.3	46	13	1.2

The Translocation Factor (TF= $metal_{shoots}/metal_{root}$) indicates the ability of plants to transfer metals from roots to shoots; when TF<1, the plant is considered excluder; conversely, when TF>1, translocation occurs. Data (not shown) indicate that in wheat shoots most metals have TF <1, while in maize leaves TF> 1 for Pb and Zn, and TF<1 for Cr, Cu, Ni.

DOI: 10.6092/issn.2281-4485/3930

In summary, macronutrients and zinc are easily translocated from soil to aerial parts of wheat and maize; Cu is easily tanslocated in wheat but not in maize; not-essential metals (Al, Cd, Cr, Ni, Pb, V) are scarcely absorbed by roots, and translocated to aerial parts.
Metals such as Cd, Cr, Pb tend to accumulate in maize leaves, although not-essential, and even toxic; atmospheric deposition, however, could contribute to metal enrichment in leaves. Chromium, in particular, is considered nearly immobile in soils, or at least blocked by roots (Bini et al., 2001); however, several studies (Bini et al., 2008; Maleci et al., 2013) have demonstrated that with particular chemical-physical conditions it may be translocated to aerial parts of edible plants (e.g. dandelion, lettuce or spinach), and therefore constitute a potential threat for human health, if ingested.

Estimation of chromium intake with cereals

Our results showed that Cr, although less mobile than other metals, is translocated to leaves and seeds, and may enter the food chain. An estimation of the daily Cr intake from cereals consumption in the studied area, therefore, is due, in order to avoid toxic effects in resident population.
The Cr amount ingested with food in Italy is estimated 198 µg/day, consistent with data from other countries (132 µg in Netherland, 206 µg in Greece; Santoprete, 1997). The normal daily oral intake is indicated by Kabata-Pendias and Mukherjee (2007) as 50-200 µg Cr(III), a value recommended by U.S.A. *National Research Council* for adults. The European Commission (2003), however, highlights that at the moment it is not possible to define a maximum tolerable Cr intake, given the lack of specific data on Cr toxicity on humans. As an example, we have estimated a possible intake level for resident population consuming cereals in the investigated area. Consuming pasta (150 g/day) and bread (150 g/day) prepared from flower containing 1.14 mg kg^{-1} Cr, a daily intake of 270 µg Cr would occur, an amount higher than the Italian average (198 µg/day), but largely below the suggested USEPA threshold (1.5 mg kg^{-1} body weight).
Based on the above estimation, any particular health risk would occur for residents. However, differences could exist among various workers categories (e.g. tannery workers and farmers), among consumers of local vegetables, and especially children, that are more sensitive than adults.

Conclusions

Diffuse, although moderate, soil contamination by Cr, Cu, Ni, V was ascertained in the whole area, with metal concentration above the Italian legislation limits (D.L.152/2006) for green areas. Copper concentration is above the regulatory guidelines at few sites, and is related to agricultural practices. However, it is difficult to separate the anthropogenic and the geogenic contribution, since the parent material composition and the local environmental conditions may influence metal availability and mobility. Application of specific indexes, metal spatial distribution and statistical analyses allowed evidencing top enrichment with Cd, Cr, Cu, Pb, S of supposed anthropogenic origin.

Both wheat and maize showed higher metal concentrations in roots than in the aerial parts, suggesting to behave as excluder plants. A barrier effect is likely effective in the uptake process of critical and not-essential elements, while micronutrients have higher translocation capacity. However, significant differences were recorded between metal contents in different parts of the plants, and particularly in the large maize leaves. The calculation of specific indexes (BAC and TF) showed that root sorption and translocation to leaves occurred in the order Zn > Cu > Ni > Cr, thus confirming the barrier effect for not essential elements.

A comparison between wheat and maize evidenced the different behaviour of the two plants with regard to metal uptake and translocation, suggesting to consider separately every species for the possible response to metal contamination, with the aim of assessing risk for PHEs transfer to the food chain and ultimately for animal and human health.

It is noteworthy to recall that the whole maize plant may be utilized to prepare animal feeding and, in case of high TF, biomagnification phenomena could occur along the food chain. Conversely, wheat seeds are largely used to prepare human food such as bread and pasta, and high TF could increase PHEs concentration in food, determining concrete risk for human health.

References

ABOLLINO O., MALANDRINO M., GIACOMINO A., MENTASTI E. (2009). Investigation of metal pollution in soils by single and sequential extraction procedures. In: Steinberg R.V. (Ed.) Contaminated soils: Environmental impact, disposal and treatment: 139-180. Nova Science, New York.

Abrahams P.W. (2002). Soils: their implications to human health. The Science of the Total Environment 291:1-32.

ADRIANO D.C. (2001) Trace Elements in Terrestrial Environments. Biogeochemistry, Bioavailability, and Risks of Metals. Springer, New York. 967 pp.

ARPAV (2011) Metalli e metalloidi nei suoli del Veneto – Determinazione dei valori di fondo. Regione del Veneto, 188 pp.

BI X., FENG X., YANG Y., LI X., SHIN G.P.Y., LI F., QIU G., LI G., LIU T., FU Z. (2009) Allocation and source attribution of lead and cadmium in maize (*Zea mays* L.) impacted by smelting emissions. Environmental Pollution 157: 834-839.

BINI C., MALECI L., ROMANIN A. (2008). The chromium issue in soils of the leather tannery district in Italy. Journal of Geochemical Exploration 96: 194-202.

BINI C., MALECI L., ZILOCCHI L. (2001) Chromium accumulation and mobility in soils and plants of a tanning industrial area in NE Italy. Proc. VI Int. Conf. Biogeoch. Trace Elements, 79, Guelph, Ontario, Canada.

CUI Y.J., ZHU Y.G., ZHAI R.H., CHEN D.Y., HUANG Y.Z., QIU Y., LIANG J.Z. (2004). Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. Environment International 30: 785-791.

DECRETO LEGISLATIVO 152/2006 Gazzetta Ufficiale n.88 del 14/04/2006 – S.O. n.96.

EC – European Commission, Scientific Committee on Food (2003). Opinion of the Scientific Committee on Food on the tolerable upper intake level of trivalent chromium.

DOI: 10.6092/issn.2281-4485/3930

HUANG M., ZHOU S., SUN B., ZHAO Q. (2008). Heavy metals in wheat grain: assessment of potential health risk for inhabitants in Kunshan, China. Science of the Total Environment 405: 54-61.

KABATA-PENDIAS A. (2011). Trace elements in soils and plants. 4th edition. CRC Press, Boca Raton, 505 pp.

KABATA-PENDIAS A., MUKHERJEE A.B. (2007). Trace elements from soil to humans. Springer, Berlin, 550 pp.

LAVADO R.S., PORCELLI C.A., ALVAREZ R. (2001). Nutrient and heavy metal concentration and distribution in corn, soybean and wheat as affected by different tillage systems in the Argentine Pampas. Soil & Tillage Research 62: 55-60.

MALIK R. N., HUSAIN S. Z., NAZIR I. (2010). Heavy metal contamination and accumulation in soil and wild plant species from industrial area of Islamabad, Pakistan. Journal of Botany 42:291-301.

MARCHIOL L., FELLET G., PEROSA D., ZACCHEO P., ZERBI G. (2008).Utilizzo di piante agrarie nel fitorisanamento di suoli contaminati da metalli pesanti e metalloidi: (II) primi risultati della sperimentazione in situ di Torviscosa (Udine). Rivista di Agronomia, 1:15-29.

MCLAUGHLIN M.J., PARKER D.R., CLARKE J.M. (1999). Metals and micronutrients – food safety issues. Field Crops Research 60:143-163.

MIPAF (2000). Metodi di analisi chimica del suolo. Franco Angeli, Milano.

PERALTA-VIDEA J.R., LOPEZ M.L., NARAYAN M., SAUPE G., GARDEA-TORRESDEY J. (2009). The biochemistry of environmental heavy metal uptake by plants: implications for the food chain. The International Journal of Biochemistry & Cell Biology 41:1665-1677.

RODRIGUES S.M., HENRIQUES B., FERREIRA DA SILVA E., PEREIRA M.E., DUARTE A.C., GROENENBERG J.E., RÖMKENS P.F.A.M. (2010). Evaluation of an approach for the characterization of reactive and available pools of 20 potentially toxic elements in soils: Part I – The role of key soil properties in the variation of contaminants' reactivity. Chemosphere 81:1549-1559.

SANTOPRETE G. (1997). Total chromium content in foodstuffs and evaluation of the average amount of chromium uptake. In: Canali S., Tittarelli F., Sequi P. (Ed.) Chromium environmental issues: 153-179. Franco Angeli Editore, Milano.

STEINNES E. (2009). Soils and geomedicine. Environmental Geochemistry and Health 31:523-535.

UNGARO F., RAGAZZI F., CAPPELLIN R., GIANDON P. (2008). Arsenic concentration in the soils of the Brenta Plain (Northern Italy): mapping the probability of exceeding contamination thresholds. Journal of Geochemical Exploration 96:117-131.

UNTERBRUNNER R., PUSCHENREITER M., SOMMER P., WIESHAMMER G., TLUSTOŠ P., ZUPAN M., WENZEL W.W. (2007). Heavy metal accumulation in trees growing on contaminated sites in Central Europe. Environmental Pollution 148:107-114.

ZHENG N., WANG Q., ZHANG X., ZHENG D., ZHANG Z., ZHANG S. (2007). Population health risk due to dietary intake of heavy metals in the industrial area of Huludao city, China. Science of the Total Environment 387:96-104.

ZHU Y., YU H., WANG J., FANG W., YUAN J., YANG Z. (2007). Heavy metal accumulation of 24 asparagus bean cultivars grown in soil contaminated with Cd alone and with multiple metals (Cd, Pb, and Zn). Journal of Agricultural and Food Chemistry 55:1045-1052.