Th, U, REE BACKGROUNDS AND PHYTOAVAILABILITY IN SOILS OF THE PADANIAN PLAIN (NORTHERN ITALY)

Dario Di Giuseppe*, Gianluca Bianchini, Barbara Faccini, Massimo Coltorti, Alessandra Giurdanella

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara
* Corresponding author: E-mail dgsdra@unife.it

Abstract

In this contribution we present ICP-MS analyses carried out on agricultural soils from the eastern-most part of the Padanian plain (Ferrara Province) and on the related crop products. The aim is to provide, for the first time in this area, backgrounds for some trace elements such as rare earth elements (REE), thorium (Th), uranium (U) and to understand the related phytoavailability. In particular, detailed analyses have been done on *Sorghum Vulgare* plants, analyzing distinct plant parts in different vegetative periods. Results indicate that a) REE concentration in plant tissues is always lower than in the related soils, precluding the occurrence of bioaccumulation and b) no preferential elemental uptake and REE fractionation. In this light, the observed soil/plant relationships could be used in the definition of markers of territoriality (provenance fingerprint) for agricultural products.

Keywords: *REE, Th, U, backgrounds, soil-plant elements relationships.*

Introduction

The alluvial soils of the easternmost part of the Padanian Plain in Northern Italy have been extensively studied (Amorosi 2012; Di Giuseppe et al. 2014a). These studies (mainly based on X-ray fluorescence analyses) focused on the major element composition, and among trace elements emphasis was dedicated only to heavy metals. In this contribution, the investigation of agricultural soils from the same area have been implemented by ICP-MS taking into consideration further elements such as thorium (Th), uranium (U) and rare earth elements (REE), in order to define their backgrounds and their geochemical behavior in the soil-plant interactions. The aim is to discriminate between the natural (geogenic) geochemical fingerprint and potential anthropogenic contributions that could be related to the widespread agricultural practices. Relationships between soils and plants were also explored, analyzing plants (sorghum) grown on the same area; the analysis was performed on different underground (roots) and sub-aerial (stem and leaves) plant organs as well as on soil portions strictly associated with the plant roots, hereafter called rhizosphere. The approach has been repeated in distinct vegetative phases of plant development, allowing to define soil-plant partition coefficients and to evaluate possible bioaccumulation processes. Thanks to the coupled analysis of soils and plants it is also possible to evaluate if Th, U and REE

DOI: 10.6092/issn.2281-4485/4678

can be used as proxies (i. e. markers) of the provenance of agricultural products, thus representing a very useful tool to trace food origin.

Materials and methods

Geological and geomorphological outlines of the study area

The studied area is located in the delta of Po river (northern Italy; Fig. 1a) that is the terminal part of the Padanian plain, which is bordered to the north by the Alps and to the south by the Apennine chain, with structures reflecting a complex depositional and tectonic evolution (Bonini et al. 2014). The formation of this plain was due to the combination of geological (development of the surrounding mountain ranges) and climatic factors (Bondesan et al. 1995; Stefani and Vincenzi 2005). Coherently, during the late Holocene, the stratigraphy and geomorphology of the area recorded the evolution pattern of lowstand and highstand sea periods, due to eustatic changes. (Marchetti 2002; Amorosi et al. 2008; Ravazzi et al. 2013; Bitelli et al. 2014). In particular, the easternmost part of the Padanian Plain is the result of coastlines migration and the progradation of the Po River Delta (Simeoni and Corbau 2009).

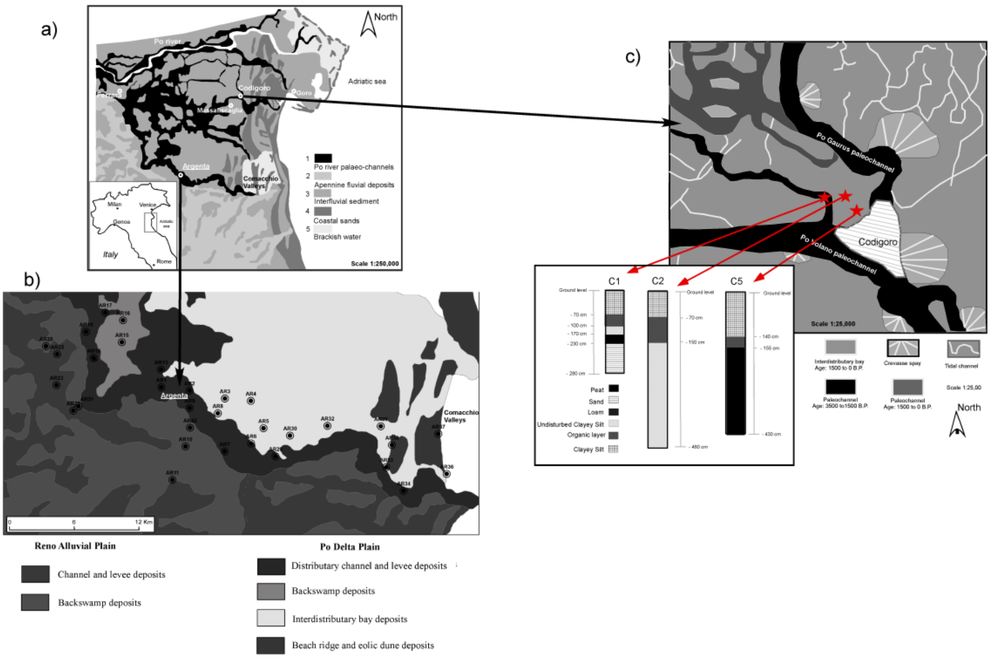

Figure 1. a) *Geographical and geological framework of the studied area;* b) *geologic sketch map of the area surrounding the town of Argenta;* c) *geologic sketch map of the area surrounding the town of Codigoro, also reporting the stratigraphy recorded in three distinct boreholes (C1, C2, C5).*

In particular, the investigated area is located in the Province of Ferrara; this specific sector of the plain resulted from the changes in the path of the Po River and the Reno, an Apennine river (Bianchini et al. 2012; 2014). The Reno River has been flowing from SW to NE, whereas the Po River flows from W to E (Fig. 1a). The geomorphology of the area has been also influenced by anthropogenic activities aimed at providing land for settlement and agriculture. These activities, mainly consisting in the reclaiming of swamps and lagoons in the delta zone of Po River, were developed at different times since Renaissance (Bianchini et al. 2004; Di Giuseppe et al. 2013; Di Giuseppe et al. 2014b). The most recent reclamation actions took place in the second half of XIX and in the first half of the XX centuries. Lands have been dried mechanically through the excavation of artificial channels as well as by the use of hydraulic pumps, which are still used to keep the area dry.

Soils

The studied soil samples are related to unconsolidated alluvial deposits characterized by a limited pedogenesis, in which the lack of soil maturity is related to the young depositional age (Holocene) and fluvial reworking.

In particular, the samples considered in this study have been collected in two distinct zones close to the towns of Argenta and Codigoro, respectively. They represent soils developed in different depositional facies. In the locality of Argenta (Fig. 1b), 29 soil samples (collected at depth between 100 and 120 cm) have been selected, starting from a more representative sample population previously investigated by Di Giuseppe et al. (2014c). According to previous XRF analyses (major elements and heavy metals content) 20 samples have been ascribed to Po river sediments, whereas 8 samples have been related to the Reno river deposits.

In the locality of Codigoro (Fig. 1c) soil samples developed from sediments deposited in wetlands fed by Po river deltaic branches, reclaimed at the end of the XIX century. In this area, 28 samples have been selected from a wider sample population previously studied by Di Giuseppe et al. (2013) in the framework of ZEOLIFE project (LIFE+10/ENV/IT/00321). It has to be noted that in this locality, samples have been taken at increasing depths along three distinct (0-300 cm) soil profiles (C1, C2, C5; Fig. 1c).

Plants

As delineated in Fig. 2, plants (*Sorghum vulgare*) have been sampled in the ZEOLIFE experimental field (locality of Codigoro), in two distinct vegetative phases of plant development (13/06/2013; 16/07/2013).

During the sampling, complete pants were uprooted, and then sectioned dividing underground (roots) and sub-aerial (stem and leaves) plant organs; soil rhizosphere has been also collected shaking the roots and recovering the soil particles that were intimately associated. Roots have been washed with distilled water to remove any trace of soil, before the analysis. All samples have been dried at 30 °C for 2 days.

DOI: 10.6092/issn.2281-4485/4678

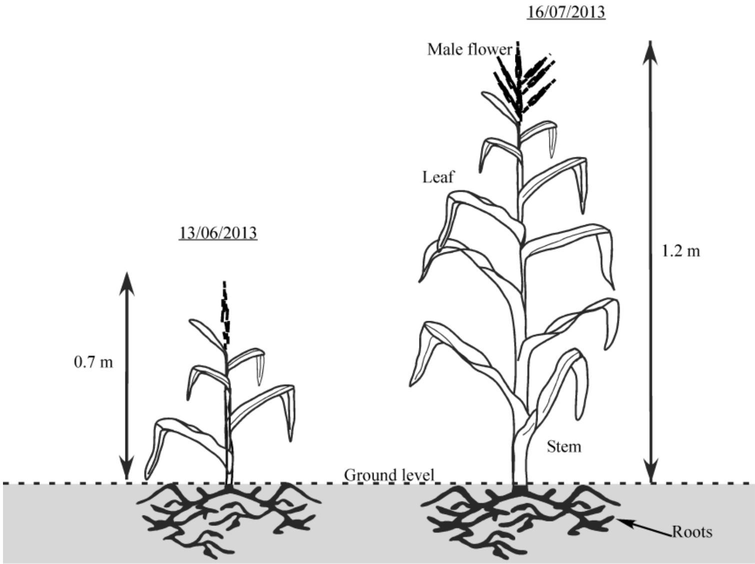

Figure 2
Sketch draw showing the studied sorghum plants.

Soil and plant analysis

Bulk soil Th, U, REE analyses were investigated by inductively coupled plasma mass spectrometry (ICP-MS); for these analyses powders (0.15 g) were totally digested with suprapure grade HF and HNO_3 (Merck, Darmstadt, Germany) on a hot plate. Plant samples were dissolved starting from 1 g of sample with H_2O_2 and HNO_3 (proportion 2:1). Dissolved samples were dried out and then re-dissolved in ultrapure water obtained from a Milli-Q purifier system (Millipore Corp., Bedford, MA, USA). Details of sample dissolution are reported by Bianchini et al. (2012).
The analyses were carried out using an X Series Thermo-Scientific spectrometer at the Department of Physics and Earth Sciences of the University of Ferrara. Specific amounts of Rh, In and Re were added to the analysed solutions as an internal standard, in order to correct for instrument drift. Accuracy and precision, based on replicated analyses of samples and standards are better than 10% for all elements, well above the detection limit. As reference standards, the NIST SRM1567a (wheat flour powder), NIST SRM1547 (peach leaves powder), NIST SRM1573a (Tomato leaves powder), E.P.A. Reference Standard SS-1 (a type B naturally contaminated soil) and the E.P.A. Reference Standard SS-2 (a type C naturally contaminated soil) were also analysed to cross-check and validate the results. One of the investigated elements, i.e. thorium has been analysed also by XRF, showing a remarkable coherence between the two distinct analytical techniques.

Results

Soils

The result of soil analyses have reported in Tables 1 and 2. As commonly observed in the literature (Rollinson 1993), to visualize all REE elements together the data

Po River sediments																							
	AR 1	AR 2	AR 3	AR 4	AR 5	AR 6	AR 7	AR 9	AR 13	AR 15	AR 16	AR 17	AR 18	AR 19	AR 29	AR 30	AR 32	AR 33	AR 34	AR 37	AR 38	Average	Standard deviation
Th	8,94	8,47	8,87	7,90	9,29	8,28	9,22	7,67	9,75	9,62	9,22	9,63	8,58	9,16	7,68	7,89	7,29	9,86	7,28	6,23	4,07	8,33	1,37
U	2,05	1,85	1,94	1,78	2,29	2,25	2,09	1,59	1,84	3,28	2,32	2,03	1,99	2,10	1,96	2,22	2,14	1,94	1,77	1,56	3,00	2,09	0,41
La	28,1	26,9	27,0	24,0	27,8	24,3	28,7	25,1	26,2	27,1	25,7	28,5	26,4	28,1	19,9	22,0	20,1	25,4	21,8	19,1	13,5	24,6	3,90
Ce	52,1	49,4	51,3	47,1	50,0	47,2	53,0	46,5	51,5	49,9	53,8	55,7	52,2	55,8	41,4	40,7	39,0	49,5	40,1	39,1	32,5	47,5	6,35
Pr	6,0	5,9	6,0	5,4	6,1	5,2	6,4	5,5	6,0	6,0	5,8	6,4	6,0	6,3	4,5	4,8	4,4	5,6	4,8	4,4	3,3	5,46	0,83
Nd	23,6	23,7	24,0	21,8	24,1	20,6	25,5	22,1	24,1	24,4	23,2	25,2	23,7	25,1	17,5	19,0	17,2	21,8	18,4	17,3	13,5	21,7	3,32
Sm	4,46	4,68	4,78	4,38	5,07	3,96	5,07	4,36	4,87	4,94	4,63	5,14	4,82	5,06	3,49	3,74	3,41	4,24	3,57	3,55	2,97	4,34	0,66
Eu	0,89	0,95	0,97	0,90	1,03	0,79	0,96	0,88	1,00	1,03	0,95	1,07	1,01	1,04	0,72	0,79	0,71	0,87	0,74	0,74	0,71	0,89	0,12
Gd	4,06	4,26	4,39	4,02	4,56	3,63	4,58	3,98	4,46	4,54	4,23	4,71	4,40	4,66	3,16	3,39	3,10	3,83	3,32	3,23	2,87	3,97	0,59
Tb	0,59	0,65	0,67	0,62	0,72	0,55	0,71	0,62	0,70	0,72	0,67	0,74	0,73	0,74	0,50	0,53	0,49	0,60	0,52	0,53	0,50	0,62	0,09
Dy	2,67	3,02	3,09	2,89	3,34	2,49	3,19	2,90	3,30	3,40	3,10	3,51	3,24	3,46	2,30	2,40	2,27	2,75	2,41	2,48	2,44	2,89	0,42
Ho	0,51	0,59	0,60	0,56	0,65	0,49	0,62	0,56	0,65	0,67	0,61	0,69	0,67	0,67	0,46	0,48	0,45	0,55	0,49	0,49	0,50	0,57	0,08
Er	1,37	1,58	1,59	1,50	1,74	1,30	1,62	1,50	1,76	1,79	1,62	1,84	1,70	1,80	1,22	1,29	1,21	1,46	1,30	1,29	1,32	1,51	0,21
Tm	0,21	0,25	0,25	0,23	0,27	0,21	0,26	0,23	0,27	0,28	0,26	0,29	0,30	0,28	0,20	0,21	0,20	0,24	0,22	0,21	0,22	0,24	0,03
Yb	1,27	1,45	1,43	1,35	1,58	1,20	1,51	1,36	1,62	1,62	1,49	1,68	1,55	1,65	1,13	1,21	1,11	1,35	1,24	1,17	1,23	1,39	0,18
Lu	0,19	0,21	0,20	0,19	0,23	0,17	0,23	0,19	0,24	0,23	0,22	0,25	0,26	0,24	0,17	0,18	0,17	0,20	0,19	0,17	0,19	0,21	0,03

Reno River sediments										
	AR 10	AR 11	AR 21	AR 22	AR 23	AR 25	AR 28	AR 36	Average	Standard deviation
Th	7,01	8,06	4,46	6,68	7,22	5,52	8,54	7,70	6,90	1,35
U	2,10	1,98	1,17	1,51	1,82	1,34	2,16	2,28	1,79	0,41
La	19,9	24,8	13,2	19,0	21,2	15,6	23,5	21,8	19,9	3,88
Ce	47,7	46,5	26,8	38,8	45,3	31,6	53,2	41,4	41,4	8,75
Pr	4,4	5,6	3,0	4,3	4,7	3,5	5,4	4,7	4,43	0,87
Nd	16,9	22,2	12,0	17,0	18,6	14,1	21,2	17,6	17,4	3,37
Sm	3,14	4,41	2,52	3,46	3,68	2,98	4,03	3,47	3,46	0,60
Eu	0,63	0,91	0,57	0,70	0,72	0,64	0,82	0,70	0,71	0,11
Gd	2,84	4,02	2,41	3,18	3,38	2,87	3,65	3,05	3,17	0,50
Tb	0,41	0,63	0,38	0,49	0,50	0,45	0,53	0,48	0,48	0,07
Dy	1,85	2,92	1,79	2,24	2,22	2,11	2,37	2,12	2,20	0,35
Ho	0,36	0,57	0,34	0,43	0,42	0,41	0,45	0,43	0,43	0,07
Er	0,98	1,55	0,91	1,15	1,11	1,09	1,20	1,14	1,14	0,19
Tm	0,15	0,24	0,14	0,18	0,17	0,18	0,18	0,19	0,18	0,03
Yb	0,91	1,46	0,86	1,07	1,01	1,05	1,09	1,06	1,06	0,18
Lu	0,14	0,21	0,13	0,16	0,15	0,15	0,16	0,16	0,16	0,03

Table 1. *ICP-MS analyses carried out on soils derived by both Po and Reno sediments in the surrounding of Argenta town.*

DOI: 10.6092/issn.2281-4485/4678

Table 2. *ICP-MS analyses carried out on soils from the ZeoLife experimental field located close to the Codigoro town.*

C5	Th	U	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0 cm bgl*	7,51	2,55	28,2	55,6	6,42	25,8	5,09	1,07	5,49	0,73	3,55	0,69	1,97	0,30	1,87	0,26
30	6,23	2,38	21,7	39,3	5,27	21,7	4,39	0,93	4,70	0,64	3,06	0,59	1,70	0,25	1,55	0,22
60	7,01	2,31	25,9	50,3	6,14	25,0	4,99	1,05	5,41	0,72	3,44	0,66	1,87	0,28	1,73	0,24
80	7,44	2,48	27,6	55,0	6,49	26,5	5,28	1,12	5,84	0,77	3,68	0,72	2,04	0,31	1,88	0,26
100	7,38	2,33	25,0	48,8	5,83	23,7	4,67	1,01	5,10	0,67	3,20	0,62	1,80	0,27	1,68	0,23
115	7,86	1,81	25,8	50,5	6,06	24,0	4,87	1,04	5,30	0,68	3,18	0,61	1,77	0,26	1,63	0,22
160	3,71	11,5	12,9	24,8	3,18	13,0	2,57	0,58	2,99	0,37	1,74	0,34	1,00	0,15	0,93	0,13
180	7,17	5,08	26,6	54,6	6,18	24,3	4,67	0,98	5,30	0,66	3,07	0,60	1,75	0,26	1,64	0,23
250	7,58	2,68	32,1	64,4	7,14	27,7	5,05	1,01	5,68	0,67	2,96	0,57	1,73	0,26	1,64	0,23
300	6,04	4,28	22,9	48,1	5,86	24,9	5,39	1,12	5,79	0,81	4,01	0,77	2,15	0,32	1,98	0,27
350	6,55	5,40	24,3	49,8	5,96	24,6	5,13	1,05	5,50	0,75	3,62	0,70	1,97	0,29	1,85	0,26
Average	6,77	3,89	24,8	49,2	5,87	23,7	4,74	1,00	5,19	0,68	3,23	0,62	1,80	0,27	1,67	0,23
SD**	1,17	2,81	4,83	10,2	1,01	3,87	0,77	0,15	0,80	0,11	0,59	0,11	0,30	0,05	0,28	0,04
C1																
0 cm bgl*	7,30	2,50	23,4	42,5	5,61	22,9	4,56	0,95	4,93	0,65	3,15	0,61	1,74	0,26	1,60	0,22
25	7,19	2,68	26,4	52,6	6,07	24,4	4,77	1,01	5,25	0,68	3,21	0,63	1,81	0,27	1,68	0,24
50	7,45	3,06	27,4	54,3	6,22	24,8	4,77	1,00	5,32	0,68	3,23	0,63	1,85	0,28	1,76	0,25
75	7,71	3,25	28,2	55,4	6,37	25,2	4,81	0,99	5,18	0,67	3,21	0,63	1,82	0,28	1,74	0,24
100	7,97	4,94	26,9	40,1	6,60	27,4	5,59	1,18	6,08	0,84	4,10	0,81	2,31	0,35	2,15	0,30
150	5,95	1,67	22,5	42,1	5,53	22,6	4,59	0,92	4,83	0,65	3,08	0,59	1,67	0,25	1,55	0,22
170	5,42	1,52	21,1	43,4	4,96	20,3	4,10	0,83	4,29	0,59	2,82	0,54	1,53	0,23	1,41	0,20
200	4,92	1,27	20,7	41,8	4,93	20,2	4,13	0,86	4,35	0,60	2,88	0,55	1,53	0,23	1,41	0,20
240	4,42	1,25	20,7	41,7	4,90	20,2	4,14	0,85	4,38	0,62	3,02	0,58	1,63	0,25	1,52	0,21
Average	6,48	2,46	24,1	46,0	5,69	23,1	4,61	0,95	4,96	0,66	3,19	0,62	1,77	0,27	1,65	0,23
SD**	1,32	1,20	3,08	6,18	0,66	2,59	0,47	0,11	0,58	0,07	0,37	0,08	0,24	0,04	0,23	0,03
C2																
0 cm bgl*	7,28	2,27	27,1	54,2	6,34	25,8	5,13	1,05	5,57	0,72	3,47	0,67	1,92	0,29	1,78	0,25
50	7,71	2,73	28,3	56,2	6,54	26,3	5,18	1,09	5,65	0,73	3,48	0,67	1,95	0,29	1,83	0,26
80	7,53	3,58	27,5	54,0	6,40	26,0	5,14	1,08	5,86	0,74	3,49	0,68	1,99	0,29	1,88	0,26
110	7,72	5,17	28,7	54,9	6,58	26,2	5,18	1,10	6,00	0,75	3,57	0,69	1,98	0,30	1,84	0,25
150	7,03	1,98	27,4	55,7	6,49	26,2	5,19	1,07	5,95	0,74	3,40	0,66	1,91	0,28	1,77	0,25
170	5,12	1,57	23,0	47,1	5,38	21,7	4,18	0,86	4,64	0,58	2,65	0,51	1,48	0,22	1,34	0,19
230	6,88	1,46	28,4	56,8	6,54	26,4	5,06	1,03	5,63	0,71	3,27	0,62	1,80	0,26	1,63	0,23
300	6,69	1,48	26,4	53,0	6,24	25,3	5,05	1,03	5,51	0,72	3,36	0,65	1,86	0,28	1,72	0,24
Average	7,00	2,53	27,1	54,0	6,32	25,5	5,01	1,04	5,60	0,71	3,34	0,64	1,86	0,28	1,72	0,24
SD**	0,85	1,29	1,81	3,04	0,40	1,57	0,34	0,08	0,43	0,05	0,29	0,06	0,17	0,03	0,17	0,02

*cm below the ground level; ** Standard Deviation

are presented as "normalized" patterns taking into consideration a proper reference composition. For sediment and related soils the notional NASC (North American Shale Composition) values, which represents an average of several shales (Gromet et al. 1984), is generally employed. Normalized multi-element patterns are useful to highlight positive or negative anomalies of one element respect to the other.

Accordingly, in figure 3, the new data presented in this contribution are reported as NASC-normalized multi-elementary patterns. Soil samples from Argenta are divided in two groups according to the distinct alluvial origin, namely to their sediment derivation from the Po and Reno rivers.

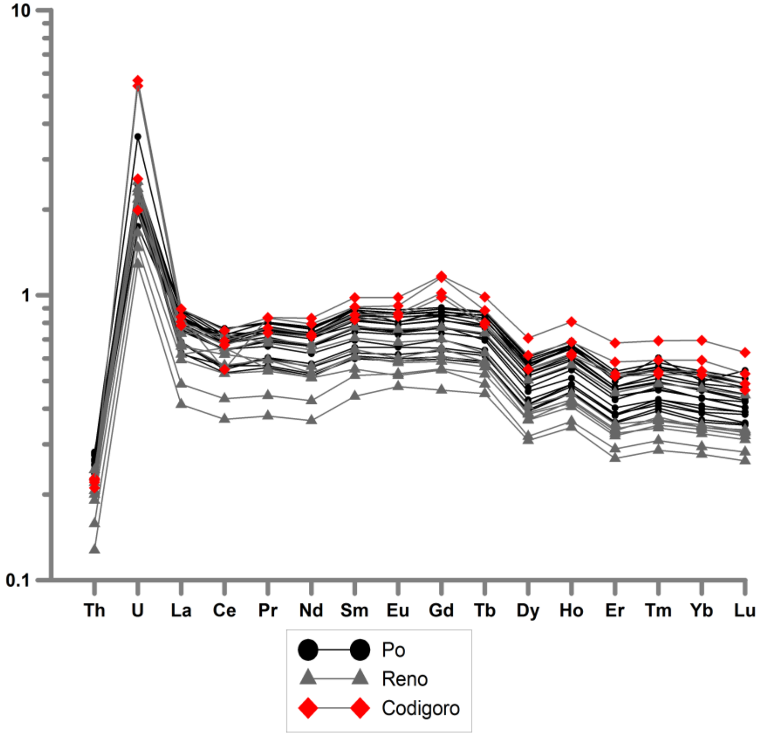

Figure 3
NASC-normalized trace element patterns of the outcropping soils. Normalization values from Gromet et al. (1984).

The NASC normalized patterns of all soils from Argenta are sub-parallel. Those related to the Reno river sediments have normalized values of Th varying between 0.13 and 0.24, of U between 1.28 and 2.51, of Light REE (LREE, i.e. La, Ce, Pr, Nd) between 0.36 and 0.77, of Middle REE (MREE, i.e. Sm, Eu, Gd, Tb) between 0.44 and 0.77 and of Heavy REE (HREE, i.e. Dy, Ho, Er, Tm, Yb, Lu) between 0.26 and 0.57. Those related to Po River sediments have Th spanning between 0.18 and 0.28, U between 1.17 and 3.21, LREE between 0.52 and 0.90, MREE between 0.58 and 0.91, HREE between 0.35 and 0.69. To evaluate possible differences between soil samples related to the Reno and Po rivers, normalized (N) elemental ratios have been also taken into account. The samples related to the Reno River have U_N/Th_N 8.67-11.5, Th_N/Yb_N 0.46-0.70, U_N/Yb_N 4.35-7.85, La_N/Yb_N 1.44-2.11, Gd_N/Yb_N 1.62-2.00. The samples related to the Po River have U_N/Th_N 7.26-13.1, Th_N/Yb_N 0.47-0.65, U_N/Yb_N 3.87-6.90, La_N/Yb_N 1.57-2.14, Gd_N/Yb_N 1.59-1.90. The trace element ratios confirm that in terms of U, Th, REE no significant differences are observed between soil samples related to the Reno and Po rivers, irrespective to their different origin. In both groups, the decoupling between U and

DOI: 10.6092/issn.2281-4485/4678

Th is remarkable. In this case, the U positive anomaly is plausibly related to its association with the organic fraction, which usually traps the reduced form (U^{+4}) of uranium (Kabata-Pendias 2011, Frazier et al. 2005). A comparison of the new trace element data with the major elements presented in the previous studies reveals that there is a remarkable positive correlation of Th with Al_2O_3 (Fig. 4a) suggesting its association to the fine-grained clay-rich fraction, whereas quartz and carbonate (which are prevalent in the coarser fraction) tend to dilute it. A similar relation, although less pronounced, is observed for LREE (e.g. Ce; Fig. 4b). This implies that REE are significantly included in the clay fraction but also in feldspars and accessory phases such heavy minerals which trap MREE (pyroxenes, amphiboles, epidotes, sphene, apatite/monazite) and sometimes also HREE (garnet, zircon).

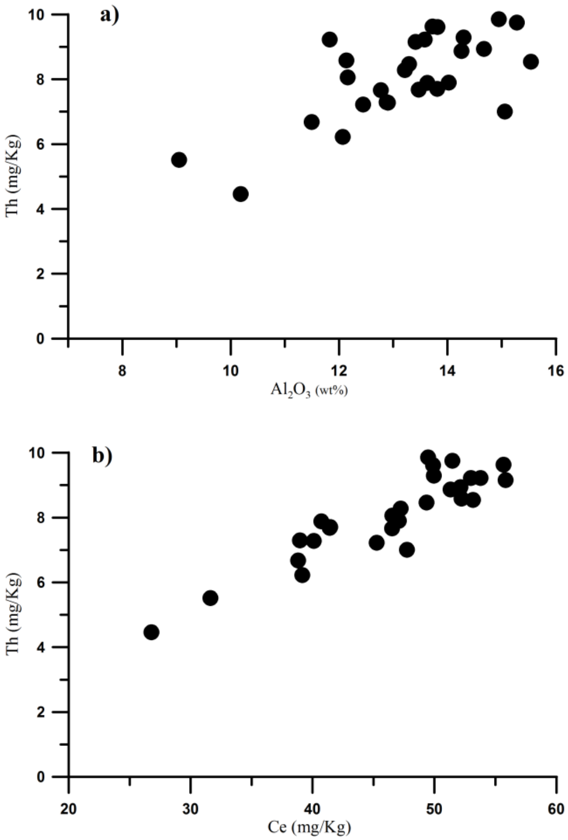

Figure 4
Scatter plots showing the correlation between a) Th and Al_2O_3 ($r = 0.693$; $p<0.01$), b) Th and Ce ($r =0.903$; $p<0.01$).

Samples from Codigoro give indications on the nature of soils developed from a distinctive depositional facies, as they evolved from sediment deposited in saline wetlands (recently reclaimed), where the Po river contribute was partially mixed with marine fluxes. Their REE normalized patterns (Fig. 3) tend to be slightly higher than those described above for the soil of Argenta, with Th varying between 0.23 and 0.11, U between 1.37 and 16.8, LREE, between 1.54 and 3.63, MREE between 1.95 and 4.12, HREE between 1.81 and 4.21. It has to be noted that the

Codigoro soils are typically characterized by a peculiar Gd positive anomaly, highlighted by the parameter $Gd_N^{*}= Gd_N/[(Eu_N+Tb_N)/2]$,which is always higher than 1.17. The Gd relative enrichment is a feature that could be related to anthropogenic contributions, as typically observed in rare earth element patterns of natural waters which drain densely populated and industrialised areas in Central Europe and North America (Bau and Dulski 1996; Ogata and Terakado 2006; Kulaksiz and Bau 2007).

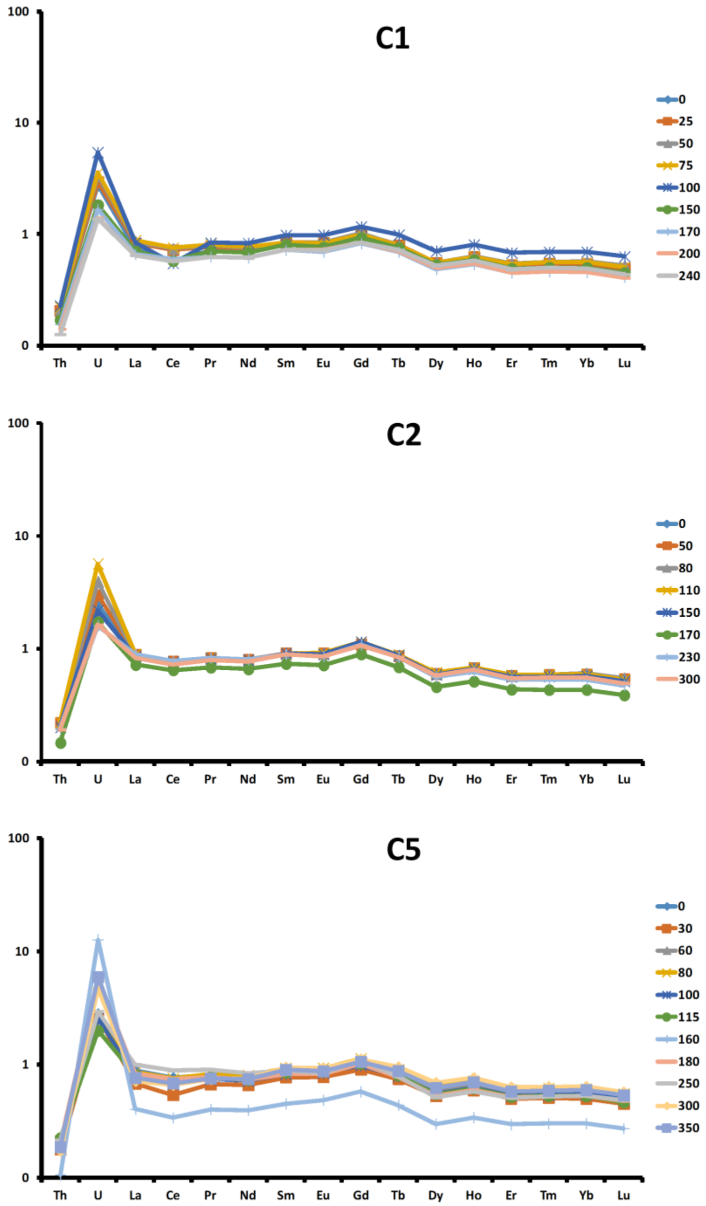

Figure 5
NASC-normalized trace element patterns of the soils collected at different depths in 3 distinct boreholes drilled in the ZeoLife experimental field. Normalization values from Gromet et al. (1984).

DOI: 10.6092/issn.2281-4485/4678

This anomaly is not confined in the more superficial horizons, but is maintained also at greater depths, as can be observed in figure 5, where the normalized elemental values down to depth of 3 m is shown.

Plants

The result plant analyses have reported in Table 3 and in Fig. 6, where the analyses have been normalized to the average soil composition of the considered locality. Coherently, the rhizosphere composition approaches that of the average soils having the following normalized values: Th 1.40, U 1.52, LREE 4.12, MREE 4.10, HREE 6.33.

Table 3. *Trace elements determined in the rhizosphere and plant (Sorghum Vulgare) organs cultivated in the ZeoLife experimental field.*

	Th	U	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Rhizosphere	10,5	3,94	29,5	47,0	6,49	26,3	5,19	1,10	4,90	0,76	3,65	0,72	1,96	0,29	1,83	0,26
13/06/2013																
Roots_1	1,66	0,69	2,55	5,39	0,66	2,95	0,72	0,16	0,76	0,13	0,64	0,12	0,31	0,05	0,27	0,04
Roots_2	1,28	0,50	2,11	4,49	0,55	2,46	0,60	0,13	0,61	0,11	0,51	0,10	0,25	0,04	0,22	0,03
Roots_3	2,50	0,88	3,61	7,10	0,89	3,80	0,93	0,21	0,96	0,17	0,80	0,16	0,40	0,07	0,35	0,05
Subaerial organs _1	0,12	0,04	0,16	0,35	0,04	0,19	0,05	0,01	0,05	0,01	0,04	0,01	0,02	0,00	0,02	0,00
Subaerial organs _2	0,12	0,07	0,20	0,41	0,05	0,22	0,05	0,01	0,06	0,01	0,05	0,01	0,02	0,00	0,02	0,00
Subaerial organs _3	0,11	0,06	0,20	0,39	0,05	0,22	0,05	0,01	0,05	0,01	0,04	0,01	0,02	0,00	0,02	0,00
16/07/2013																
Roots_1	0,07	0,03	1,44	3,06	0,37	1,55	0,37	0,07	0,34	0,06	0,27	0,05	0,13	0,02	0,11	0,02
Roots_2	0,03	0,01	1,79	3,72	0,45	1,91	0,46	0,09	0,43	0,07	0,34	0,07	0,16	0,03	0,13	0,02
Subaerial organs _1	0,74	0,24	0,22	0,43	0,05	0,21	0,05	0,01	0,05	0,01	0,04	0,01	0,02	0,00	0,01	0,00
Subaerial organs _2	0,94	0,32	0,03	0,06	0,01	0,03	0,01	0,00	0,01	0,00	0,01	0,00	0,00	0,00	0,00	0,00

Plants do not bioaccumulate, as the observed normalized composition are always lower that that the relative rhizosphere. Underground organs, i.e. roots, have normalized composition of Th between 0.004 and 0.333, U between 0.002 and 0.340, LREE between 0.236 and 0.569, MREE between 0.293 and 0.807, HREE between 0.421 and 1.335. Subaerial organs (stem + leaves) have normalized composition of Th between 0.014 and 0.125, U between 0.016 and 0.124, LREE between 0.005 and 0.034, MREE between 0.006 and 0.048, HREE between 0.008 and 0.075. This means that the plant parts that are in contact with the soil contain a higher REE concentration, whereas the behavior of Th, U is more complex. The analyses have been repeated in two distinct vegetative periods. The REE in the more mature stage of development appear less concentrated, suggesting that the REE are uptaken preferentially in the first vegetative period; subsequently they tend to be diluted within a higher plant volume/mass.

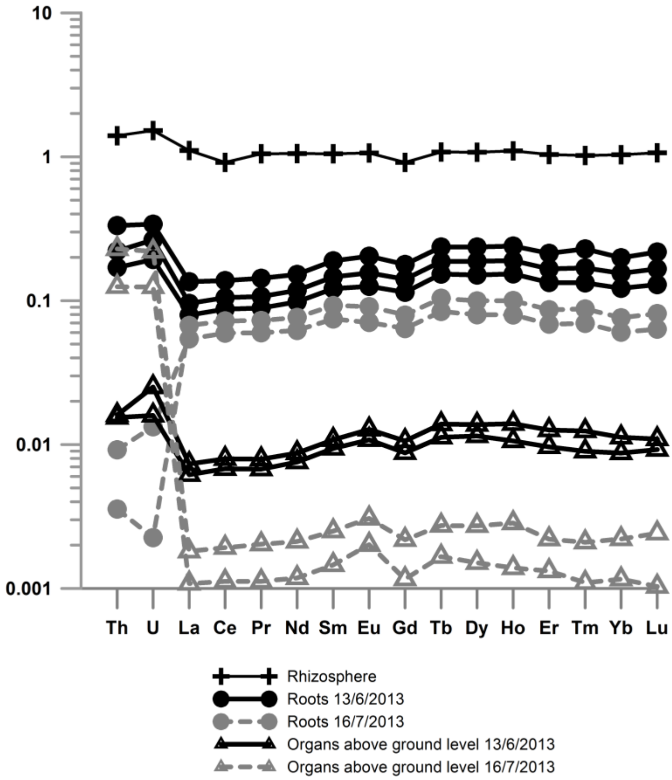

Figure 6
Trace elements patterns of rhizosphere (i.e. soil powder included between roots) and sorghum plant organs. Concentration are normalized to the average composition of the outcropping soils of the experimental field.

The above mentioned Gd positive anomaly typical of the soils of Codigoro is not replicated in the plants, which show a slight negative Gd peak in the REE profile, emphasized by Gd_N* lower than 0.21. In any case, the data show in both the vegetative periods higher values in the roots where the element are adsorbed, and limited re-distribution within the entire plant body. Th and U show higher concentration in the roots only in the first period of plant development, whereas in a more mature stage they are preferentially transferred and concentrated in the sub aerial parts.

Discussion and conclusions

REE (and Th-U) distribution appears to be unrelated to the provenance of the clastic particles of the studied soils, as soil related to Po River alluvial sediments are comparable to those related to Reno River sediments. A significant difference

DOI: 10.6092/issn.2281-4485/4678

is observed only for reclaimed soils developed from wetlands where a peculiar enrichment in gadolinium has been observed. This anomaly is probably anthropogenic, but further studies are necessary to constrain it and to identify its sources.
These elements, although not bioaccumulating in studied plants, can be detected by ICP-MS. The obtained results highlight that the uptake doesn't fractionate among different REE and that plants show normalized patterns miming (at lower concentration) those of the related soils.
Therefore, although absolute REE concentrations vary in the distinct plant organs (and also during the vegetative periods) the possible utilization of these elements as marker of territoriality (i.e provenance) for agricultural products is highly promising.

Acknowledgements
This work has been supported by EC LIFE+ funding to ZeoLIFE project (LIFE+10 ENV/IT/000321).

Reference

AMOROSI A., PAVESI M., RICCI LUCCHI M., SARTI G., PICCIN A. (2008) Climatic signature of cyclic fluvial architecture from the Quaternary of the central Po Plain, Italy. Sediment Geol, 209:58-68.
AMOROSI A. (2012) Chromium and nickel as indicators of source-to-sink sediment transfer in a Holocene alluvial and coastal system (Po Plain, Italy). Sedimentary Geology, 280: 260-269.
BAU M., DULSKI P. (1996) Anthropogenic origin of positive gadolinium anomalies in river waters Earth and Planetary Science Letters, 143:245-255.
BIANCHINI G., MARROCCHINO E., VACCARO C. (2004) Chemical and mineralogical characterisation of historic mortars in Ferrrara (NE Italy). Cement Concr Res, 34:1471-1475.
BIANCHINI G., NATALI C., DI GIUSEPPE D., BECCALUVA L. (2012) Heavy metals in soils and sedimentary deposits of the Padanian Plain (Ferrara, Northern Italy): characterisation and biomonitoring. J Soils Sediments, 12:1145-1153.
BIANCHINI G., CREMONINI S., DI GIUSEPPE D., VIANELLO G., VITTORI ANTISARI L. (2014) Multiproxy investigation of a Holocene sedimentary sequence near Ferrara (Italy): Clues on the physiographic evolution of the eastern Padanian Plain. J Soils Sediments, 14: 230- 242.
BITELLI G., CREMONINI S., GATTA G. (2014) Cartographic heritage: Toward unconventional methods for quantitative analysis of pre-geodetic maps. J Cult Herit, 15:183-195.
BONDESAN M., FAVERO V., VIÑALS M.J. (1995) New evidence on the evolution of the Po Delta coastal plain during the Holocene. Quat Int, 29/30: 105-110.
BONINI L., TOSCANI G., SENO S. (2014) Three-dimensional segmentation and different rupture behavior during the 2012 Emilia seismic sequence (Northern Italy). Tectonophysics, 630:33-42.
DI GIUSEPPE D., FACCINI B., MASTROCICCO M., COLOMBANI N. COLTORTI M., FERRETTI G. (2013). Geochemical assessment of the unconfined aquifer in a recently reclaimed wetland area: a case study from the Po River Delta. EQA, 10:37-49.

DI GIUSEPPE D., BIANCHINI G., FACCINI B., COLTORTI M. (2014a) Combination of wavelength dispersive x-ray fluorescence analysis and multivariate statistic for alluvial soils classification: a case study from the Padanian Plain (Northern Italy). X-Ray Spectrom., 43:165-174

DI GIUSEPPE D., BIANCHINI G., VITTORI ANTISARI L., MARTUCCI A., NATALI C., BECCALUVA L. (2014b). Geochemical characterization and biomonitoring of reclaimed soils in the Po River Delta (Northern Italy): implications for the agricultural activities. Environmental Monitoring Assessment, Environ Monit Assess., 186:2925-2940.

DI GIUSEPPE D., VITTORI ANTISARI L., FERRONATO C., BIANCHINI G. (2014c) New insights on mobility and bioavailability of heavy metals in soils of the Padanian alluvial plain (Ferrara Province, northern Italy). Chemie der Erde, Geochemistry, 74:615-623

FRAZIER S.W., KRETZSCHMAR R., KRAEMER S.M. (2005) Bacterial siderophores promote dissolution of UO2 under reducing conditions. Environ. Sci. Technol, 39:5709-5715.

GROMET L.P., DYMEK R.F., HASKIN L.A., KOROTEV R.L. (1984) The "North American shale composite": its compilation, major and trace element characteristics. Geochim. Cosmochim. Acta, 48:2469-2482.

KABATA-PENDIAS A. (2011) Trace elements in soil and plants, 3rd edn. CRC, Boca Raton, pp. 365.

KULAKSIZ S., BAU M. (2007) Contrasting behaviour of anthropogenic gadolinium and natural rare earth elements in estuaries and the gadolinium input into the North Sea. Earth and Planetary Science Letters, 260:361-371.

MARCHETTI M. (2002) Environmental changes in the central Po Plain (northern Italy) due to fluvial modifications and anthropogenic activities. Geomorphology, 44:361-373.

OGATA T., TERAKADO Y. (2006) Rare earth element bundances in some seawaters and related river waters from the Osaka Bay area, Japan: Significance of nthropogenic Gd. Geochemical Journal, 40: 463- 474.

RAVAZZI C., MARCHETTI M., ZANON M., PEREGO R., QUIRINO T., DEADDIS M., DE AMICIS M., MARGARITORA D. (2013) Lake evolution and landscape history in the lower Mincio River valley, unravelling drainage changes in the central Po Plain (N-Italy) since the Bronze Age. Quat. Int., 88:195-205

ROLLINSON H.R. (1993) Using Geochemical Data: Evaluation, Presentation, Interpretation. 352pp., New York (Longman).

SIMEONI U., CORBAU C. (2009) A review of the Delta Po evolution (Italy) related to climatic changes and human impacts. Geomorphology, 107:64-71.

STEFANI M., VINCENZI S. (2005) The interplay of eustasy, climate and human activity in the late Quaternary depositional evolution and sedimentary architecture of the Po Delta system. Mar Geol, 222-223:19-48.

DOI: 10.6092/issn.2281-4485/4678

TENORI DI FONDO E FITODISPONIBILITÀ DI Th, U, REE NEI SUOLI DELLA PIANURA PADANA (NORD ITALIA)

Riassunto
In questo contributo presentiamo analisi ICP-MS effettuate su suoli agricoli e piante coltivate nella parte orientale della pianura Padana (provincia di Ferrara). Lo scopo è determinare, per la prima volta, i tenori di fondo di alcuni elementi in tracce, quali le terre rare (REE) il torio (Th) e l'uranio (U), nonché comprendere la relativa fito-disponibilità. In particolare, dettagliate analisi sono state effettuate su distinte parti di piante di sorgo (*Sorghum Vulgare)* campionate in differenti stadi vegetativi. I risultati indicano che a) le concentrazioni di REE nei tessuti vegetali sono sempre inferiori a quelle dei suoli; b) non si riscontrano assorbimenti preferenziali e e frazionamenti delle REE. Per questo motivo le osservate relazioni suolo/pianta possono fornire utili informazioni relative alla territorialità (firma di provenienza) dei prodotti agricoli.
Parole chiave: *REE, Th, U, tenori di fondo, interazione elementare suolo-pianta.*