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Original Citation:

The trace element distribution in peat soils affected by natural burning events: A proxy of the original composition and metals mobility assessment / Natali, Claudio; Ferrari, Mattia; Bragagni, Alessandro; Bianchini, Gianluca; Salani, Gian Marco; Avanzinelli, Riccardo; Ghiotto, Matthias. - In: SCIENCE OF THE TOTAL ENVIRONMENT. - ISSN 0048-9697. - ELETTRONICO. - 905:(2023), pp. 167826.1-167826.13.

Availability:

The webpage <https://hdl.handle.net/2158/1335591> of the repository was last updated on 2023-10-19T08:15:50Z

Published version:

DOI: 10.1016/j.scitotenv.2023.167826

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Journal Pre-proof

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PII: S0048-9697(23)06453-7

DOI: <https://doi.org/10.1016/j.scitotenv.2023.167826>

Reference: STOTEN 167826

To appear in: *Science of the Total Environment*

Received date: 13 April 2023

Revised date: 11 October 2023

Accepted date: 11 October 2023

Please cite this article as: C. Natali, M. Ferrari, A. Bragagni, et al., The trace element distribution in peat soils affected by natural burning events: A proxy of the original composition and metals mobility assessment, *Science of the Total Environment* (2023), <https://doi.org/10.1016/j.scitotenv.2023.167826>

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The trace element distribution in peat soils affected by natural burning events: a proxy of the original composition and metals mobility assessment

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Abstract

This work evaluates for the first time the effects on the trace element composition of peat soils affected by natural burning events, a recurrent phenomenon in the reclaimed wetland of the Mezzano Lowland (Padanian plain, NE Italy). The trace element distribution of two neighboring soil profiles, one pristine and one deeply affected by burning events, were compared to identify the original geochemical fingerprint of saltmarsh peat environment. The pre-combustion composition of the fired profile was reconstructed to infer the physico-chemical changes occurred as a consequence of the burning event, with a special attention to the mobility of elements of environmental concern, such as potentially toxic trace metals. The increase in concentration of potentially toxic elements (PTE) was particularly evident in two layers of the fired profile. V, Cr, Cu, Zn, Pb, and As contents progressively increase toward intermediate depths (30-75 cm) together with Th, Sr, Ba, U. On the contrary, Tl, Bi and Cd show a concentration peak in a thin, shallower (14-17 cm depth) horizon. The trace element composition of the unfired profile allowed the identification of specific ratios between immobile elements that can be used as geochemical

fingerprint of the soils horizons with different soil organic matter (SOM) content. On the basis of Sr/Rb, Th/U and Ba/Sr it was possible to classify three types of sedimentary deposits characterizing both the unfired and fired profile, as well as to delineate the fire severity trends occurred in the different soil horizons of the fired profile. The distribution of immobile trace element, representative of the organic (U) and mineral (silicate, Th, Ba, REE and non-silicate, Sr) soil fractions with organic matter and bulk density in the non-fired profile, allowed the reconstruction of the original physico-chemical composition of the fired/burned profile and the accurate determination of the relative CO₂ lost during the burning event. Moreover, the distribution of PTE with respect to immobile trace elements, used to estimate the element redistribution and mobility after burning in the fired profile, suggested that elements such as Cr, Ni, Zn, V were mainly immobile, whereas Pb, Mo and in particular Tl and Bi suffered a significant redistribution along the burned profile. Nonetheless, results of the gain/loss calculation for the whole soil profile suggested that no significant entry or leak of these elements occurred, limiting their redistribution inside the investigated soil system.

Keywords: trace element, saltmarsh peat, natural burning, PTE mobility

1. Introduction

Peat soils are organic-rich sedimentary deposits that formed by the accumulation of biomass in waterlogging conditions (IPS, 2021). Although a uniform compositional criterion for peat definition is lacking, a recent review (Lourenco et al., 2022) suggests that peat soils are characterized by a minimum content of 12 wt% of organic carbon (SOC), representing the most important terrestrial carbon reservoir on Earth (Baylea et al., 2004, Smith et al., 2004, Rein, 2015, Natali et al., 2018). Globally, peat soils contain one-third of the world's soil carbon (Joosten and Clarke, 2002). Peat and organic-rich soils deposits originate from wetland characterized by low-energy environments both

in freshwater continental (bog) and coastal lagoon (saltmarsh) geomorphological settings (Cott et al., 2012). Wetland can act as carbon sink (the so-called blue carbon in coastal wetlands, Mcleod et al., 2011) and storage in peat deposits when water-saturated, but also as a source of greenhouses gases (GHG) when drained by reclamation (Wüst et al., 2003, Barthelmes et al., 2018).

In Italy, peats (and associated soils) were generated in alluvial basins from the late Würm (late Pleistocene) to the Holocene and are mainly distributed in the north (Martinelli et al., 2015). One of the biggest peat deposits from northern Italy is represented by the Mezzano Lowland, settled in the easternmost Padanian Plain facing the Adriatic Sea (Di Giuseppe et al., 2014a, 2014b). The Mezzano Lowland is an ancient coastal lagoon developed during Holocene within the Po river delta freshwater environment, which from the Roman times underwent tectonic subsidence accompanied by marine transgression thus evolving into a saltmarsh (Bordesan et al., 1995, Simeoni and Corbau, 2009). The area was almost totally drained in the 1960's (the remnant is represented by the Comacchio Lagoon) through a big reclamation program that originated the largest Italian peatland (area $168 \times 10^6 \text{ m}^2$ – volume $336 \times 10^6 \text{ m}^3$, Martinelli et al., 2013). The subsequent land use conversion of the Mezzano Lowland from wetland to cropland caused a notable depletion of the peat soil organic matter (SOM) content (Salani et al., in press), but also favored the occurrence of peat self-ignition phenomena of various extents (Moreno et al., 2011, Martinelli et al., 2013, 2015, Natali et al., 2021). These burning events started in buried horizons and developed as smoldering combustion due to the low oxygen conditions, causing a dramatic and sudden decrease of the peat SOM and a significant GHG emissions in atmosphere (Moreno et al., 2011, Rein et al., 2015, Natali et al., 2021). These events have a strong environmental and social impact since they induce loss of soil fertility associated to higher GHG emissions than vegetation fires and they occur more frequently under the growing drought periods due to the ongoing climate change (Langmann et al., 2004, Marchina et al., 2017, 2019). While the above cited detrimental effects caused by burned peat soils have been widely evaluated through the study of the SOM and physico-chemical parameters (e.g., Zaccone et al., 2014, Natali et al., 2021, Dymov et al., 2022), other environmental concerns,

such as the trace element variation and the mobility of Potentially Toxic Elements (PTE) in relation to peat burning, received much less attention, being mainly limited to experimental ex-situ peat firing (e.g., Summa and Tateo, 1999, Kalaitzidis et al., 2002).

The analysis of trace element distribution of soils is very important because it reflects the nature and composition of the mineral and organic soil fractions, as well as the geochemical features of the depositional environment. On the other hand, the mobility of trace elements during combustion (i.e., partitioning, volatilization, and condensation) depends on their geochemical affinity and on the chemical and mineralogical reactions during combustion, including those involving organic compounds, which are in turn related to fire severity and combustion kinetics (e.g., Kalaitzidis et al., 2002). In particular, fires may have negative effects on soil properties and fertility as well as on PTEs, either stabilizing or mobilizing them and/or transforming PTEs into more or less accessible and toxic forms for plants and microorganisms (Taczano et al., 2021, Rascio et al., 2023). In the present study we report the mineralogical and trace element composition of two neighboring saltmarsh peat soil profiles from the Mezzano Lowland one affected and one not affected by natural burning events. The comparison of the trace element distribution in the two soil profiles, and their relationships with other physicochemical parameters reported in a previous study (Natali et al., 2021), will be evaluated with the aim of 1) identifying the geochemical fingerprint of the different deposits along the peat profile 2) reconstructing the original geochemical composition of the burned profile including SOM content, 3) estimating the mobility of the trace elements in relation to the combustion event and 4) establishing the relative fire severity suffered by the fired profile by the evaluation of the reduction of the local carbon stock.

2. Materials and Methods

2.1. Samples description and preparation

The soil samples analyzed in this work belong to two peaty profiles, which are subset of five soil profiles that were collected in July 2018 (Natali et al., 2021) from a small area in the Mezzano Lowland (NE Italy, Fig. 1) characterized by natural firing events. Each peat fire occurrence was confined to a sub-circular area of approximately 3–4 m in diameter, characterized by the absence of vegetation. The profile TOR1 is representative of the soil sectors affected by burning phenomenon (Fired profile – F), whereas profile TOR4 of those unaffected by fire events (Non Fired profile – NF, see Natali et al., 2021 for additional details).

A total of 16 samples, representative of eight soil horizons for each F (TOR1) and NF (TOR4) profiles were selected for the analysis of their trace element content. These samples were previously classified from a pedogenic point of view according to Schimeneberger et al. (2012). In this light, both F and NF profiles share a top (0-15 cm depth) organic horizon (Opov in TOR1 and Op1 in TOR4), and a bottom (75-95 cm depth) clayey horizon (4Cg in TOR1 and 2Cg in TOR4) both not affected by combustion (Fig. 1).

The other horizons of the F profile TOR1 are characterized by AB1ov (14-17 cm depth), BCov (17-30 cm depth), 2BCcl (30-43 cm depth), 3Oecl (65-73 cm depth), and 3Oipy (73-84 cm depth), whereas those of the NF profile TOR4 by Op2 (12-25 cm depth), Op3 (25-38 cm depth), Oi (38-47 cm depth), 2Oi (54-63 cm depth), and 2AC (63-75 cm depth, (Natali et al., 2021)). A previous study dealing with the characterization of the carbon pools in the investigated profiles, showed that the NF profile (TOR4) was characterized by a large variability of soil organic carbon (SOC), which decreased from 22.3-33.1 wt% in the Op and Oi type, through 16.1 wt% in the Ac type down to 2.0-3.2 wt% in the Cg type horizons. In the F profile (TOR1) the SOC varied from 24.4 wt% in the upper Op type horizon to zero in the intermediate Ccl type horizons in relationship to the smoldering intensity along the profile (see Natali et al., 2021). On this basis, the maximum smoldering intensity of the F profile was estimated at depths of 30-65 cm, with decreasing effects upward and downward of this intermediate layer, and with no or negligible effects on the topmost (Opov, 0-14 cm depth) and the bottom horizons (4Cg, 84-96+ cm depth).

The available data indicate that the NF profile (TOR4) is characterized by a wide spectrum of sedimentary deposits with very high (Op and Oi horizons), intermediate (2Ac horizon) and very low (Cg horizons) organic/mineral fraction ratios. The heterogeneity of this profile can thus be used to fully constrain its trace element variability, which can in turn be compared with that of the F profile that lost most of its original features, and can be then used as a reference for the reconstruction of the pre-burning conditions of the latter. For this work, the investigated soil horizons of the NF and F profiles were subdivided in three categories: high (SOM >30 wt%), intermediate (SOM 10-30 wt%) and low (SOM < 10 wt%) organic/mineral ratio (SOM obtained multiplying the measured SOC value by the van Bemmelen factor of 1.724).

The collected samples were manually cleaned from plant remains, then dried at 65°C for 24h and sieved through a 2 mm mesh and finally powdered using a LAARMANN LMMG-100 at the Department of Physics and Earth Sciences of the University of Ferrara.

The obtained powders were dissolved by acid digestion at the laboratories of the University of Florence prior to the analysis of the trace elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Digestion of powdered samples (0.01 g for sample) was performed using ultrapure (sub-boiled distilled or Ronil-UpA grade) nitric acid (HNO₃, 14M), hydrofluoric acid (HF, 24M), hydrogen peroxide (H₂O₂, 30% v/v) and reverse Aqua Regia (3:1 – HNO₃ 14M:HCl 6M) in different proportions and steps. Sample digestion was achieved with sequential addition of different acids. First, to dissolve silicates, 14M HNO₃ and 24M HF were added to the sample powder (in a 1:4 proportions), before placing the closed beakers on hotplate for one day at 120 °C. After evaporating the solutions, 14M HNO₃ and 30% v/v H₂O₂ were added in equal proportions to destroy organic matter and residual fluorides. The solutions were then gently evaporated and the HNO₃-H₂O₂ step was repeated two more times. These steps were followed by the addition of reverse Aqua Regia to ensure of a complete destruction of organic matter. After evaporation, samples were then redissolved in 6M HCl, evaporated, treated with 14M HNO₃ to remove residual chlorides and re-dissolved in 2% HNO₃ for ICP-MS analysis.

2.2. Analytical Techniques

Samples were analyzed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) using an Agilent 7800 (Agilent Technologies, Tokyo, Japan) device at the Department of Earth Sciences of University of Florence using Rh and Re as internal standard and a multi-elemental standard solution for external calibration (specifically prepared from single elemental solutions provided by Inorganic Ventures, VA, USA).

In order to ensure the quality and accuracy of the analytical results, reagent blanks and reference materials (AGV-1 and SGR-1b from USGS and K1C-CRM008 from Sigma-Aldrich) were analyzed within the same analytical run. Repeated analyses of references materials yielded biases from the certified values smaller than 10 % for all the analyzed elements.

The mineralogical composition was determined at the Department of Earth Sciences of University of Florence through powder XRD using a Philips PW1050/37 diffractometer with Cu anode, graphite monochromator, operating at 40 kV-20 mA, with 2°/min goniometer speed, in the 5°–70° scanning range, utilizing a Philips X'Pert PRO (2007, Panalytical, Holland) data acquiring system).

3. Results

3.1. Distribution of trace elements along the NF and F soil profiles

The trace element contents of the investigated soil profiles are reported in Table S1, whereas their distribution with depth is shown in Fig. 2. The NF profile (TOR4) shows a nearly constant concentration in the topmost layer (from 0 to 38 cm depth: Op1, Op2, Op3 horizons) for most of the analyzed elements, with Th, Mo, U, Ga, Nb, Co, As and Ce, displaying the lowest (mainly < 10 mg/kg), Cr (and Rb) intermediate (around 90 mg/kg) and Sr the highest (250-350 mg/kg) values (Fig. 2a). The intermediate level (from 38 to 63 cm depth) of the soil profile is constituted by a

couple of Oi sandwiching a Cg horizon, the former (Oi) characterized by comparable (Oi 38-47 cm depth) or lower (2Oi 54-63 cm depth) values with respect to the topmost layer, and the latter (Cg 47-54 cm depth) by an abrupt increase in the concentrations of all elements (e.g., Co up to 18 mg/kg and Cr up to 245 mg/kg), with the exception of Mo, U, Sr and As that display instead a significant depletion (down to 3.30, 4.22, 114 and 7.10 mg/kg, respectively). Downward (from 63 to 85 cm depth) the concentration of most elements rapidly increases through an AC and Cg horizons to values significantly higher than the topmost layer (e.g., Th up to 11 mg/kg, Co up to 22 mg/kg, As up to 14 mg/kg and Cr up to 200 mg/kg). Even in this case, Sr, Mo and U show a distinct distribution remaining almost constant (Sr) or displaying a significant decrease in concentration (Mo down to 6.37 mg/kg, U down to 3.65 mg/kg). Other PTE such as Tl, Bi and Cd display very low concentrations (< 1 mg/kg) and a nearly constant distribution along the whole soil profile.

The F profile (TOR1) shows a different distribution of the investigated elements with depth. The topmost horizon (Opov 0-14 cm depth) is characterized by a trace element budget comparable with that of the topmost layer of the NF profile. Downward trace element contents display a gradual increase reaching the maximum values around 30-65 cm depth, in correspondence to 2BCcl, 2Ccl horizons (e.g., Mo up to 28.6 mg/kg, Th up to 15 mg/kg, U up to 20 mg/kg, Cr up to 245 mg/kg, Ba up to 505 mg/kg, Sr up to 605 mg/kg). Further downward (from 65 to 85 cm depth: 3Oecl, 3Oipy) a gradual decrease is observed for some elements (e.g., Ni, V, Cr, Cu, Zn, Pb) down to the deepest horizon (from 85 to +96cm depth, 4Cg) where a slight further increase in Co (21 mg/kg), Cr (203 mg/kg), Ni (127 mg/kg), As (22 mg/kg) and Zn (113 mg/kg) is observed.

Other PTE such as Tl, Bi and Cd display concentrations comparable to those recorded in the NF profile (<1 mg/kg) with the exception of an abrupt enrichment in the subsurface (14-30 cm depth) horizons (AB1ov, BCov), which is particularly marked in the 3 cm thick (14-17 cm depth) AB1ov horizon where they reach concentration of 7.0, 6.1, and 2.8 mg/kg, respectively.

The trace elements distribution of the investigated soil profiles shows interesting relationships. Element that are typically associated to the silicate mineral fraction (SMF, details in

subsection 3.2.) in alluvial sediments (e.g., Ba, Ti, Rb, Th, La, Cs) are positively correlated (Fig. 3). In particular, both the F and NF soil horizons are characterized by constant elemental ratios of Sc/Th (1.41 ± 0.06), Ti/Nb (295 ± 9), Rb/Cs (18.2 ± 0.8) and Ba/La (10.9 ± 1.51), Ga/Th (8.56 ± 1.30) indicating a similar nature of the SMF in the two soil profiles and suggesting that these elements suffered negligible mobility during the burning event. Although not shown in the figure, PTE such as Zn, V, Cr, Ni and Pb (and Bi) show significant positive correlations with the above cited SMF-related elements (e.g., Th) in samples from the NF profile (r^2 between 0.75 and 0.99) and a variably scattered distribution in those from the F profile. Other elements such as Cu, Co, As, Sb display instead weak or no positive correlations with the SMF-related elements in samples from the NF profile and a highly scattered distribution in those from the F profile (not shown). U and Mo show again a different behavior. Their contents are positively correlated both between them and with Sr (Fig. 3), but not with Th (not shown). This suggests that they are associated to a different soil fraction. The average REE content is remarkably lower in the NF profile (96.2 ± 35.9 mg/kg) than in the F profile (163 ± 32.2 mg/kg), whereas their North American Shales Composite (NASC, Gromet et al., 1984) normalized distribution is similar for most of the investigated soil horizons and characterized by a slight LREE enrichment ($La_N/Yb_N = 1.23 \pm 0.11$) and an upward convex pattern centered on Eu.

3.1. Mineralogical composition of NF and F soil profiles

The mineralogical composition of representative soil horizons that characterize investigated profiles is reported in Table S2. Quartz and albite are the ubiquitous mineral phases in investigated samples, whereas the presence of other minerals of the SMF is generally characteristic of the F and NF horizons. In particular, primary muscovite, kaolinite, chlorite and illite mainly occur in the NF profile and only in the deepest horizons of the F profile (3Oecl 65-73 cm, 4Cg 84-96+ cm), whereas in the others they are absent or in traces. Microcline is never recorded in the NF profile, whereas it is present in traces in the F profile. The distinct

mineralogical features of the investigated profiles is more evident in the NSMF, with the exclusive presence of gypsum and anhydrite+hematite in the NF and F horizons, respectively.

4. Discussion

4.1. Trace elements affinity with mineral and organic soil fractions

4.1.1. Evidence from the NF profile

The original geochemical affinity of the analyzed trace elements with the mineral and organic soil fractions is evaluated on samples from the NF profile, combining the new data with those reported in Natali et al. (2021). Overall, along this profile the lowest concentrations of most trace elements are recorded in the organic-rich (C_o and O_i type) horizons, whereas the highest concentrations characterize the mineral (C_m type) horizons (Fig. 2). In this light, trace elements representing the silicate minerals (e.g., Ba, Ti, Rb, Th, La, Cs), show significant negative relationships with the soil organic matter (SOM, $r^2=0.93-0.98$) indicating a strong affinity with the SMF. Few PTE, such as Mo and U, reveal an opposite behavior being characterized by a positive correlation with SOM (Mo $r^2=0.71$, U $r^2=0.88$) and among them ($r^2=0.81$), which indicate a link with the organic soil fraction (Fig. 4). A rummy distribution is shown by Sr, which correlates positively with the organic matter up to values of ca. 40 wt%, while its concentration decreases at higher SOM values (not shown). As depicted in Fig. S1, Sr is positively correlated with the total inorganic carbon content (TIC, wt%), showing a median Sr/TIC ratio >2000 , which is much higher than aragonite shells from the neighboring coastal lagoons (Sr/TIC = 115, author's unpublished data). This ratio is intermediate between that recorded in seep carbonates (Sr/TIC ca. 750, Ge et al., 2010) and that of marine gypsum (Sr up to 4000 mg/kg, e.g., Rosell et al., 1998, Playà and Rosell, 2005) where Sr replaces Ca the crystal lattice by isomorphic substitution, similar to carbonates. While the presence of gypsum in NF and anhydrite in F horizons was detected by mineralogical

analysis (Table S2), the presence of seep carbonates in peaty soils from the surrounding areas was reported by Martinelli et al. (2013). Therefore, the Sr content in the studied saltmarsh peats is considered as representative of a mixing of these two mineral components, defined as the non-silicate mineral fraction (NSMF).

4.1.2. Inferences on the original composition of the F profile

The F profile also generally displays the highest concentration of most trace elements in the horizons characterized by the lowest organic matter content (Fig. 2), but significant negative correlations with SOM are only displayed by Cr, Ga, Nb, Cs, Ba, LREE and Th (Fig. 4). These are all elements linked to the SMF and, as described in the previous section, show good correlations between each other (Fig. 3) in both F and NF profiles. Therefore we conclude that they were not affected by mobility due to burning.

A particular behavior is shown by elements, such as U and Mo, that display a strong affinity with the SOM in the NF profiles (Fig. 2). These elements lost their relationship with SOM in the F profile (Fig. 4), yet preserving a very good correlation between them ($r^2=0.80$, Fig. 3). The preservation of a constant U/Mo ratio in the F profile, despite the significant SOM loss, clearly indicates that the burning event did not mobilize these elements despite destroying/consuming the SOM. Therefore, U and Mo not only can be considered immobile during the burning event, but they can, in fact, be used as proxy for the reconstruction of the original organic soil fraction after burning. Indeed, it is well known that U (as well as Mo) accumulate in the peaty deposits under reducing conditions sourced by the circulating brackish/marine waters (Szalay, 1964, Zielinski et al., 2000, Swarzenski et al., 2003, McKee, 2008). Sr, which was previously interpreted as associated to the NSMF in the NF profile, displays a specific behavior also in the F profile, showing positive correlations with other trace elements and in particular with U ($r^2 =0.98$, Fig. 3), Sb ($r^2 =0.87$), Mo ($r^2 =0.86$), Mn ($r^2 =0.76$), Ni ($r^2 =0.71$), Cu ($r^2 =0.60$). According to the isotopic investigations of

Drexler et al. (2014) on analogous American saltmarsh peat, Sr and U mainly have a saltwater source in these deposits, thus reflecting a peculiar geochemical feature of the saltmarsh depositional environment. The Sr enrichment in the intermediate horizons of the F profile (i.e., those suffered the highest fire severity (Natali et al., 2021), together with the strong positive correlations with U and Mo (proxy of the soil organic matter in the saltmarsh peat, e.g., Drexler et al., 2014), confirm that Sr is intimately linked to the presence of organic matter in these environments. Indeed, Sr is the element that better represents the brackish/saltmarsh waterlogging condition responsible for organic matter accumulation in this depositional environment. As indicated by mineralogical analyses (Table S2) and by the very high Sr/TIC ratio (ca. 2000, Fig. S1), Sr is plausibly trapped in the NSMF, mainly in sulphates and secondarily in authigenic scap carbonates, and was not mobilized during the burning event. The paucity of inorganic carbon in the intermediate horizon of the F profile was interpreted by Natali et al. (2021) as due to carbonate decomposition at temperatures over 750°C, the maximum fire severity suffered by the Mezzano Lowland peat. Therefore, the Sr enrichment in these horizons is mainly due to the persistence of sulphates that underwent phase transition from gypsum (mainly recorded in the NF profile) to anhydrite (mainly recorded in the F profile) during the burning event.

According to the above considerations, trace elements can therefore be used to define the geochemical features of a soil, which are not only dependent on the composition of the parent material, but are also affected by the depositional environment (e.g., the saltwater derived elements). The use of immobile trace elements ratios allows defining the geochemical fingerprint of the Mezzano Lowland saltmarsh deposits, which was not modified by the burning event and therefore represented a tool to reconstruct the whole original composition of the F profile. This is consistent with the results of Summa & Tateo (1999), which did not report any variation among immobile trace element ratios of a saltmarsh peat (from Massaciuccoli coastal lake, Italy) and the related ash. In summary, the geochemical composition of a soil reflects the relative proportion and the nature of its mineral (silicate and non-silicate) and organic fractions. On the basis of the correlations

described above, the most representative and immobile element of the SOM is certainly U, whereas Sr certainly represent the NSMF (carbonate, gypsum) and Ba (or Th, Ti, Rb) the SMF (mainly clay minerals). As depicted in Figure 5 the ratio of these elements are useful geochemical proxies both to define the nature of the NF horizons and to infer the original nature of the F horizons.

The Sr/Rb ratios (Fig. 5a) of the NF profile show a distinct bimodality with the clayey (Cg, 2AC, 2Cg) horizons characterized by significantly lower (0.57-0.98) Sr/Rb ratios with respect to the organic matter-rich (Op1, Op2, Op3, 2Oi) horizons (Sr/Rb 2.65-4.30). Low Sr/Rb ratios are typical of silicate-rich mineral sediments, whose lithological end-member can be represented by the North American Shales Composite (NASC, Sr/Rb = 1.1, Gromet et al., 1984). On the other hand, high Sr/Rb ratios are typical of organic-rich saltmarsh deposits, whose compositional end-members can be represented by analogous Italian and Spanish Mediterranean occurrences (Massaciucoli, Sr/Rb = 35.5, Summa & Tateo (1999), Valencia Sr/Rb = 25.1, Lopez-Buendia et al., 1999). Samples from the F profile exhibit a bimodal distribution, irrespective of the post-fire SOM content, with the upper layer (0-65 cm depth) that shows high Sr/Rb ratios (2.5-3.2) and the bottom layer (65-96+ cm depth) characterized by a constant low Sr/Rb value of 0.7. The four upper horizons of the F profile (Opov, AB1ov, BCov, 2BCcl, 2Ccl) have Sr/Rb ratio compatible with organic-matter-rich horizons from the NF profile (Op1, Op2, Op3, 2Oi), thus confirming that Sr, and in turn the NSMF, enrichment is a key feature of saltmarsh peat deposits. On the other hand, the three bottom horizons (3Oecl, 3Oipy, 4Cg) of the F profile show a Sr/Rb ratio in the range of clayey horizons (Cg, 2AC, 2Cg) that are mostly settled in its lower part.

More detailed information on the geochemical fingerprint of the silicate mineral fraction and the organic matter of the NF and F samples are obtained by the use of the Th/U ratio (Fig. 5b). The organic-rich horizons of the NF profile invariably show Th/U ratios < 0.6 (down to 0.3), and trend toward the ratio of the saltmarsh peat of the Massaciucoli lake and the Valencia coastal lagoon (Th/U = 0.2). The low Th/U ratio of the bulk Massaciucoli lake saltmarsh peat was maintained in the relative ash, confirming the immobile behavior of these elements in consequence to burning.

Among the organic horizons of the NF profile a further distinction can be made, with Op type that shows higher Th/U ratios (0.5-0.6) with respect to Oi type (0.3) horizons. On the other hand, the clayey horizons (Cg type) show comparatively distinct higher Th/U ratio (around 3.0), similar to that of the NASC (Th/U = 4.6), whereas the 2AC horizon, characterized by an intermediate SOM content, has Th/U around 1.5. In this framework, all samples from the upper layer of the F profile (0-65 cm depth), irrespective of their measured SOM content, show Th/U ranging from 0.6-0.7, thus comparable with that of Op type horizons of the NF profile, suggesting a similar original composition before the burning event. On the other hand, the lower part of the F profile is characterized by comparatively high Th/U, with the 3Oecl and 3Oipy (65-84 cm depth) showing a uniform Th/U = 1.5, in spite of their very different SOM content, comparable to the 2AC horizon of the NF profile. Accordingly, the bottom horizon of the F profile (i.e., 4Cg, 84-96+ cm depth) displays the highest Th/U (2.7) similar to the Cg type horizon of the NF profile.

A positive relationship defined by samples of the NF and F profiles can be obtained by the use of Th/U and Ba/Sr elemental ratios (Fig. 5c), confirming the distinct geochemical fingerprint of different soil classes: i) SMF-rich (Ba/Sr > 2.7, Th/U > 2), iii) SOM- and NSMF-rich (Ba/Sr and Th/U < 1) and ii) intermediate soil samples (Ba/Sr ca. 2, Th/U between 1 and 2). Samples belonging to the class i) soils are the Cg horizons that generally settled at the bottom of the NF and F profiles and conform with the high Ba/Sr and Th/U values of the NASC. The class iii) includes the Op and Oi horizons of the NF profile and the Opov, AB1ov, BCov, 2BCcl, 2Ccl horizons of the F profile, that generally characterizes the upper layer (0-65 cm depth). Their low Ba/Sr and Th/U ratios are very similar to those of Massaciuccoli saltmarsh peat and its ash, in particular those of the Oi horizons characterized by comparatively lower Th/U (inset of Fig. 5c). The class ii) soils includes the 2AC horizon of the NF profile and the 3Oecl, 3Oipy of the F profile, generally settled in the intermediate/lower layer (from 65 to 75-85 cm depth). In this framework, the absolute contents of U and Th in the F profile are simply modified by passive parallel enrichment due to the loss of SOM and volatiles during the burning event. Therefore, the bivariate Th vs. U diagram can be used to

estimate the magnitude of fire severity, which increases along the direction of each constant Th/U at progressively higher Th and U contents departing from those of the NF horizons.

4.2. Trace element-based reconstruction of the pre-burning SOM content of the F profile

The trace element composition of the NF and F profiles of the Mezzano Lowland saltmarsh deposits allowed us to infer their original geochemical fingerprint irrespective of the physico-chemical modifications occurred in the F profile in relation to the burning phenomena. On this basis it was possible to identify some similarities existing between the NF and F horizons and to group them into three distinct geochemical classes representative of the wide compositional heterogeneity both in terms of mineral and organic soil fractions. This was possible after the careful evaluation of the trace element mobility reported in section 4.1., followed by the detection of the most immobile elements representative of the distinct soil mineral and organic fractions. The same approach can be further extended to the reconstruction of the original SOM endowment of the F profile, and in particular, of its distinct horizons. To verify the possible existence of a relationship between the SOM and trace element contents in saltmarsh deposits from the Mezzano Lowland, we tested some key trace element ratios in the NF horizon. In this light, the Ba/U, Zr/U and Th/U ratios showed a strong polynomial (Ba/U) and logarithmic (Zr/U and Th/U) relationships with the SOM content (r^2 0.99, 0.98 and 0.96, respectively, Fig. 6). These ratios further characterize the three classes of soil horizons defined in Fig. 5c: class i) horizons have $Ba/U > 72$, $Zr/U > 14.3$ (and $Th/U > 2.7$) trending toward the values of the NASC ($Ba/U = 250$, $Zr/U = 75$, $Th/U = 4.6$), class iii) horizons are characterized by $Ba/U < 23$, $Zr/U < 3.4$ (and $Th/U < 0.6$) similar to the Massaciucoli bulk and ash ($Ba/U = 6$, $Zr/U = 1.3$ and $Th/U = 0.2$) saltmarsh peat, class ii) horizons show intermediate ratios with $34 < Ba/U < 39$, $6.9 < Zr/U < 17$ (and $1.2 < Th/U < 1.7$). These immobile trace element ratios can thus be used to constrain the original SOM composition of the investigated profiles, and in turn to reconstruct the SOM endowment of the F horizons. The polynomial

relationship between Ba/U vs SOM (Fig. 6) is able to reproduce with very good accuracy (Root Mean Squared Error - RMSE of 0.46 wt%), the organic matter content of the NF horizons, whereas the use of the logarithmic relationship between Zr/U and SOM yield a less precise reconstruction (RMSE of 0.63 wt%). The trace element modelling indicates a SOM threshold of ca. 3 wt% for Ba/U and 4 wt% for Zr/U under which the gain/loss of SOM has not to be considered significant. The comparison between the measured SOM contents along the F profile and those pre-burning reconstructed using the Ba/U ratio (Table S3) allows calculating the SOM loss in response to the burning event, which reveal a variable depletion of the original soil organic matter content with depth. According to this calculation, a maximum SOM loss (-25 wt%) occurred in the 17-65 cm depth (BCov, 2BCcl, 2Ccl), an intermediate loss in the 14-17 cm (AB1ov) and 65-73 cm (3Oecl) (ca. -25 and -20 wt%, respectively), and a minimum loss (ca. 5 wt%) in the 73-84 cm depth (3Oipty). The use of the Zr/U ratio gives slightly different results (Table S3), with a maximum SOM loss (-41 wt%) occurring in the intermediate (2BCcl, 30-43 cm depth), followed by a symmetric lower depletion in the neighboring upper and lower horizons (38-40 wt%) and by a decidedly asymmetric loss in the AB1ov (14-17 cm depth, -28 wt%) and 3Oecl (65-73 cm depth, -18 wt%) horizons. In this case, in the 3Oipty (73-84 cm depth) does not show any SOM loss, as well as the topmost and the bottom horizons (Opov, 0-14 cm depth and 4Cg 84-96+ cm depth respectively). A schematic representation of the pre-burning SOM content of the F profile is provided in Figure 7, which also reports the changes occurred after burning for comparison. The reconstruction allowed to identify a rough distribution of the fire severity along the F profile, which caused the maximum SOM depletion in the 30-65 cm depth interval progressively vanishing upward and downward with the deepest and superficial horizons unaffected by SOM loss. This is in agreement with the results of Natali et al. (2021), that described a paucity of carbonates at the same depth range due to a local burning temperature above 700-750°C.

The environmental and social implications related to the peat burning events were not only related to the loss of fertility of these soils, but also to the emissions of pollutant GHG such as CO₂

in the atmosphere. Previous evaluations of the potential environmental impact of the Mezzano Lowland peat burning were based on the indirect comparison of the NF with F profiles, assuming a SOM loss and dry bulk density (Bd) value by the differences between NF and F soil horizons for the calculation of equivalent CO₂ (CO₂eq). In this work, a direct comparison of F and NF profiles can be done using the trace element distribution, thus allowing a well constrained reconstruction of the SOM content of the F horizons prior to the burning event. A tentative reconstruction of the dry bulk density can be also carried out using the same approach. Following the rationale reported in section 4.2., we used the very good relationship between the Bd and Sr/Y ($r^2 = 0.95$, Fig. S2) along the NF profile to infer the Bd of the F profile.

Sr and Y are indeed two elements controlled by (and thus representing) the different fractions of saltmarsh peat deposits: Sr is proxy of the NSMF (and the SOM), whilst Y represents the SMF. Our reconstruction of the Bd values represents the first use of trace elements in a pedotransfer function. As classical pedotransfer functions, based on SOM and/or grain size data, (e.g., Huntington et al., 1989, Tomasella and Holden, 1998), its applicability is limited to the local scale (Nanko et al., 2014). The results of the calculation of the loss of SOC for the F profile indicates that ca. 950 tonn/hect of SOC (equally to the 75% of the original SOC Stock of the F profile) were lost in consequence of the burning event. Calculations of CO₂eq emissions for the investigated F profile yield values of 350 kg/m³, slightly lower than those reported by Natali et al. (2021) who estimated a CO₂ flux of 397 kg/m³ from the Mezzano Lowland peat deposits in consequence to the burning event.

4.3. Trace element-based reconstruction of the geochemical composition of the F profile

The reconstruction of the original trace elements composition of the F profile reported in the previous section can also be used for the evaluation of their enrichment factors (EF) related to the burning event. Enrichments of elements of possible environmental concern could be related either

to a passive concentration inside the burned soil horizon, as a consequence of SOM and volatile (e.g., water, CO₂) compounds loss, or to their selective mobility and accumulation in other soil horizons. The most immobile trace elements were passively concentrated during burning, due to SOM loss and release of water and CO₂ from the breakdown of the crystal lattice of hydrated silicates and/or carbonate mineral, respectively. Our data indicated that in saltmarsh peat these elements were mostly those representatives of the SMF (Th, Ba, Cs, Rb, Zr). However, elements linked to the NSMF (Sr) and to the SOM (U) also behaved as immobile during the burning event (Figs 2 and 3). Other elements, mostly PTE, suffered instead a selective depletion/enrichment in response to the burning event. We recalculated the original contents of immobile elements related to the SMF, NSMF and SOM, fractions, simply by “diluting” the concentration measured in the F horizons by a specific “factor” obtained by adding the reconstructed SOM and the contribution of the volatiles lost during burning. This factor depends on the composition of the soil mineral fraction and by the fire severity suffered by the different horizons. In fact, accounting for the SOM the recalculated original immobile trace elements contents of the F profile do not reproduce the strong relationship between these elements and SOM contents observed in the NF profile. The addition of a further component to the “dilution factor” was then needed to reconstruct the original composition of the immobile element of the F profile. Although this additional dilution component could not be calculated, we derived it empirically fitting the relationship showed by the concentration of the same immobile element and the SOM content in the NF profile. The total “dilution factor” was then compared with the LOI experimentally determined at different temperatures (100-600°C) on some of the NF horizons by Natali et al. (2021). This comparison highlighted that different soil classes, identified by the geochemical fingerprint, were characterized by distinct LOI, deriving both from the different SOM content and the nature of the mineral fraction. In particular, experimental burning of class i) soils produced associated LOI values from 8-9 wt% at 200 °C to ca. 20 wt.% at the temperature of 600 °C. The “dilution factor” empirically derived for the related F horizon (4Cg, 14 wt%), suggest that it underwent a burning temperature around or lower than 400°C. On the other

hand, experimental burning of class iii) soils returned relatively higher LOI values (from 20 wt.% at 200°C, 63 wt.% at 400°C, up to 68 wt.% at 600°C) and the related F horizons show data compatible with a range of burning temperatures from ca. 400°C (54 and 55 wt% for O_{po}v, and AB1_{ov}, set at 0-14 and 14-17, respectively) to 600°C and higher (66-69 wt% for BC_{ov}, 2BC_{cl}, 2C_{cl}, set at 17-30, 30-43, 43-65 cm depth, respectively).

Among the non-immobile elements, we devoted a particular attention to PTE's such as V, Cr, Ni, Zn, Mo, Sn, Tl, Pb, Bi that showed a different distribution against the immobile elements (e.g., Th) along the F profile with respect to the NF profile. In response to the burning events, the concentration of most elements of environmental concern reached values often higher than the contamination thresholds (namely CSC) reported in the Italian legislation, even considering that these limits are referred to as pseudo total, and not bulk, content (DM 46/2019). In particular, the measured concentration of siderophile elements such as Cr (up to 247 mg/kg), Ni (up to 197 mg/kg) and V (up to 195 mg/kg) are well above the CSC reported in the DM 46/2019 for agricultural soils (150, 120 and 90, respectively), whereas those of chalcophile elements such as Cu, Zn, Pb do not exceed these limits. The measured concentration of other elements characterized by a less constrained geochemical affinity, such as As (up to 28 mg/kg) and Tl (up to 7.0 mg/kg) are close to, or slightly decidedly above, the relative CSC (30, 3, and 1 mg/kg, respectively). While siderophile elements are naturally enriched in soils from the Padanian plain in relation to the ophiolite legacy from their mother rocks (Amorosi et al., 2002, Bianchini et al., 2002, 2012, 2013) their mobility was proven to be very low and their pseudototal content always below the legislative CSC (Di Giuseppe et al., 2014a, 2014b), the mobility of other relatively volatile elements such as As and Tl deserve further investigation.

The relative enrichment/depletion along the F profile can be evaluated using the ratio of the mobile/immobile element in the measured and reconstructed F profile composition obtained by the application of the "dilution factor" to the measured concentration followed by the application of the linear regression defined by the PTE and the immobile element (Th or U) in the NF profile. The

reconstructed PTE concentrations of the F horizons thus represents the expected concentrations before the burning event and allows us to identify where these elements were removed or accumulated. The parameter used for this investigation is the burning enrichment factor (BEF) expressed as: $BEF_{PTE} = \text{measured (PTE/immobile element)}/\text{expected (PTE/immobile element)}$, calculated for each horizon of the F profile. On the basis of the observed relationships between PTE and immobile element in the NF profile, Th was used to as immobile element for V, Cr, Ni, Zn, Pb, Tl and Bi, whereas U as immobile element for Mo. Values of $BEF_{PTE} < 1$ indicate PTE depletion whereas $BEF_{PTE} > 1$ PTE enrichment as a consequence of the burning phenomenon. The BEF variation along the F profile is showed in Figure 8.

Among siderophile elements only V shows an enrichment in almost every burning horizon, whereas Cr and Ni do not highlight any significant and/or systematic variation, showing BEF values mainly varying between 0.9 and 1.1. Zinc presents a bimodal distribution with the upper (0-43 cm depth) and bottom (43-84 cm depth) layers characterized by enrichment and depletion, respectively, showing similar negligible BEF values. A similar distribution is observed for Pb and Mo, but with more extreme BEF values that reach the highest value in the class (ii) 2BCcl horizon (30-43 cm depth, BEF 1.93 for Pb and 1.19 for Mo) and the lowest values in the class (iii) 3Oipy horizon (63-74 cm depth, BEF 0.75 for Pb and 0.47 for Mo). Metal redistribution along the soil profile is especially evident for elements that are considered highly volatile such as Tl and Bi (e.g., Ruppert et al., 1975), they show a parallel exceptional enrichment in the subsurface layer in the class (ii) AB1ov (14-17 cm depth) and BCov (17-30 cm depth) horizons where the BEF value is 8 for Tl and 12 for Bi. In order to evaluate if this effect was related to a mobility inside the soil profile or if gain or losses of these elements occurred in relation to the burning event, we compared the pre and post combustion PTE Stock (PTES) of the whole F profile. The PTE Stock, as well as the SOC Stock reported in section 4.2., represents the grams of PTE in ca. 1 m^3 (960 cm^3 , a surface of 1 m^2 of the F profile having a depth of 96 cm) and the calculation of this parameter using the measured (PTES_{burn}) and expected (PTES_{exp}) PTE concentrations allow us to verify the possible income or

leak of PTE in the profile occurred after the burning event. The expected PTE concentration is retrieved by the very good linear relationship with immobile elements (Th and U) in the NF profile. The comparison of the PTE_{Sburn} and PTE_{Sexp} values calculated for Cr (163 and 177 g, respectively), Ni (116 and 108 g, respectively), V (130 and 120 g, respectively) and Zn (85 and 85 g, respectively) confirms the negligible mobility for these elements already shown by the low BEF values. Surprisingly, even Tl and Bi show comparable PTE_{Sburn} (0.77 and 0.49 g, respectively) and PTE_{Sexp} (0.77 and 0.42 g, respectively), although having the most extreme BEF values. This important result indicates that the observed element variations along the F profile are related to a mobility within the soil column and that no significant exchange (income or leak) from the system of these PTE occurred in relation to the burning event. The most significant discrepancies between the PTE_{Sburn} and PTE_{Sexp} are shown by Pb and Mo (25 and 19, 1.3 and 1.1 g, respectively) but they can be due to the lower correlation coefficient with immobile elements (Th and U) that in turn may have affected their calculated PTE_{Sexp} values.

5. Conclusions

The trace element composition of soils and sediments represent a powerful tool for understanding the nature of their mineral and organic components even after the deep modification suffered by these matrices, such as those related to soil burning. Through a careful evaluation of the trace element distribution in NF and F soil profiles we identified the elements that did not suffer any selective mobility and can thus be used as a proxy for the reconstruction of the pre-burning original composition. Additional data (e.g., SOM) can help constraining the geochemical affinity of the relatively immobile elements for the mineral (silicate or non-silicate) and organic soil fractions. In particular, this work demonstrates that the ratio of some trace elements does not change even after natural burning processes that impart unpredictable modification to the soil matrices. This allows their use for many purposes, including: identification of the pre-burning soil lithology,

quantification of the carbon loss, evaluation of the mobility of potentially toxic element along the profile and between the soil and the atmosphere and hydrosphere. However, since recent studies demonstrated that soil burning modify the PTE uptake by plant-microorganism system, multidisciplinary and integrated approaches are necessary to unravel the actual consequences of a fire on agroecosystems and related crop productions.

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Funding:

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors thanks Dr. Elena Pecchioni for X-ray diffraction analysis and Dr. Chiara Maccelli for technical assistance during ICP-MS analysis.

Data availability

Data will be made available on request.

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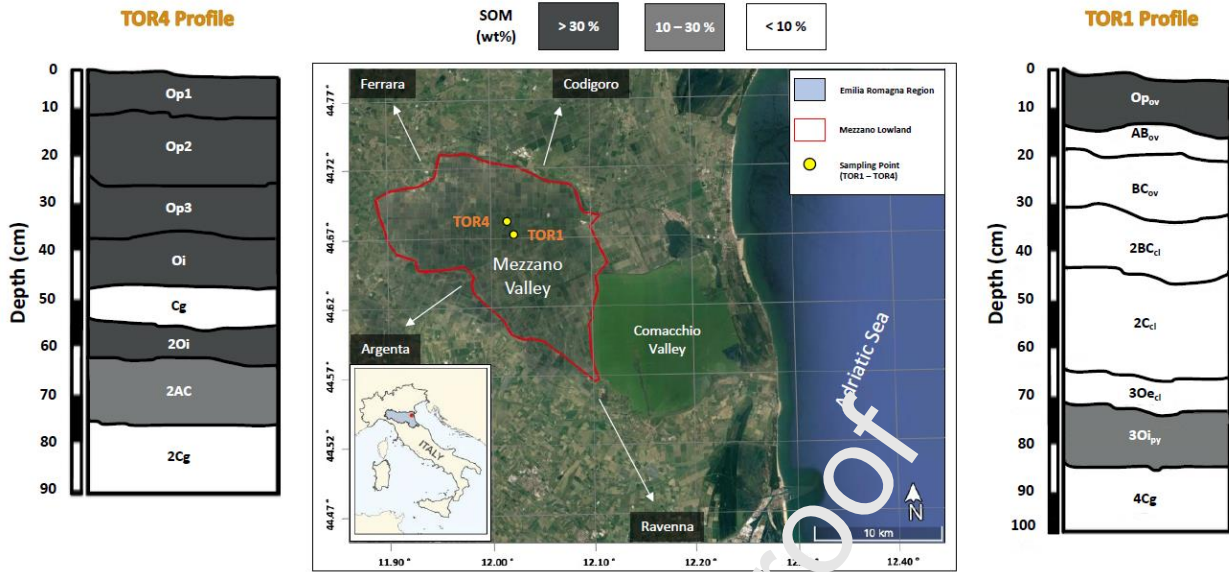


Fig. 1 - Geographic setting of the Mezzano Lowland reclaimed saltmarsh, including the locations of the Non-Fired (TOR4) and Fired (TOR1) peaty soil profiles. A schematic representation of the soil horizons with depth, on the basis of the pedological classification and of their SOM contents, is also reported (data from Natali et al., 2021).

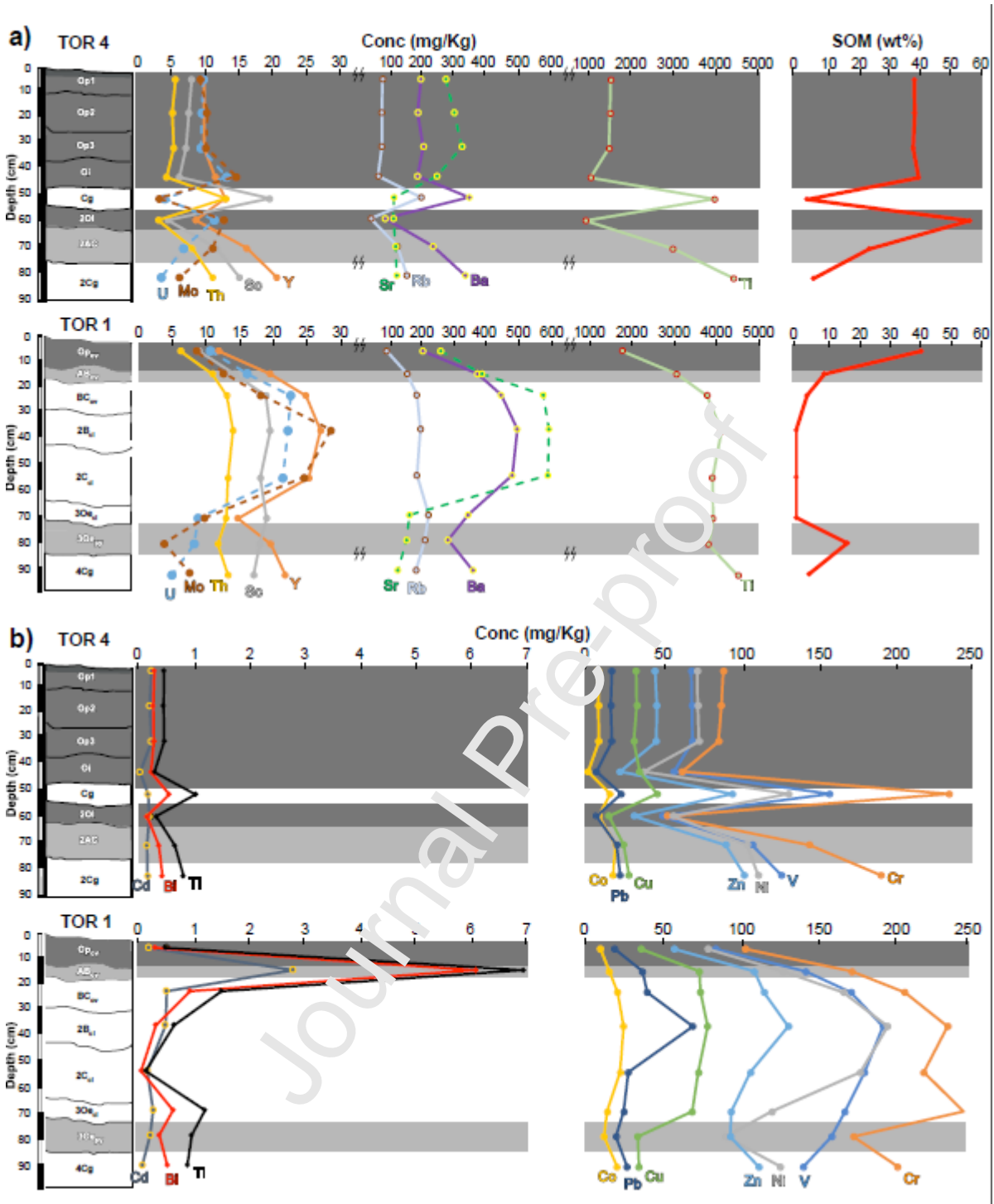


Fig. 2 - Distribution of Ti, Sr, Rb, Ba, Y, Sc, Th, U, Mo, SOM (a) and Cr, V, Ni, Zn, Cu, Pb, Co (b) contents along the two investigated soil profiles.

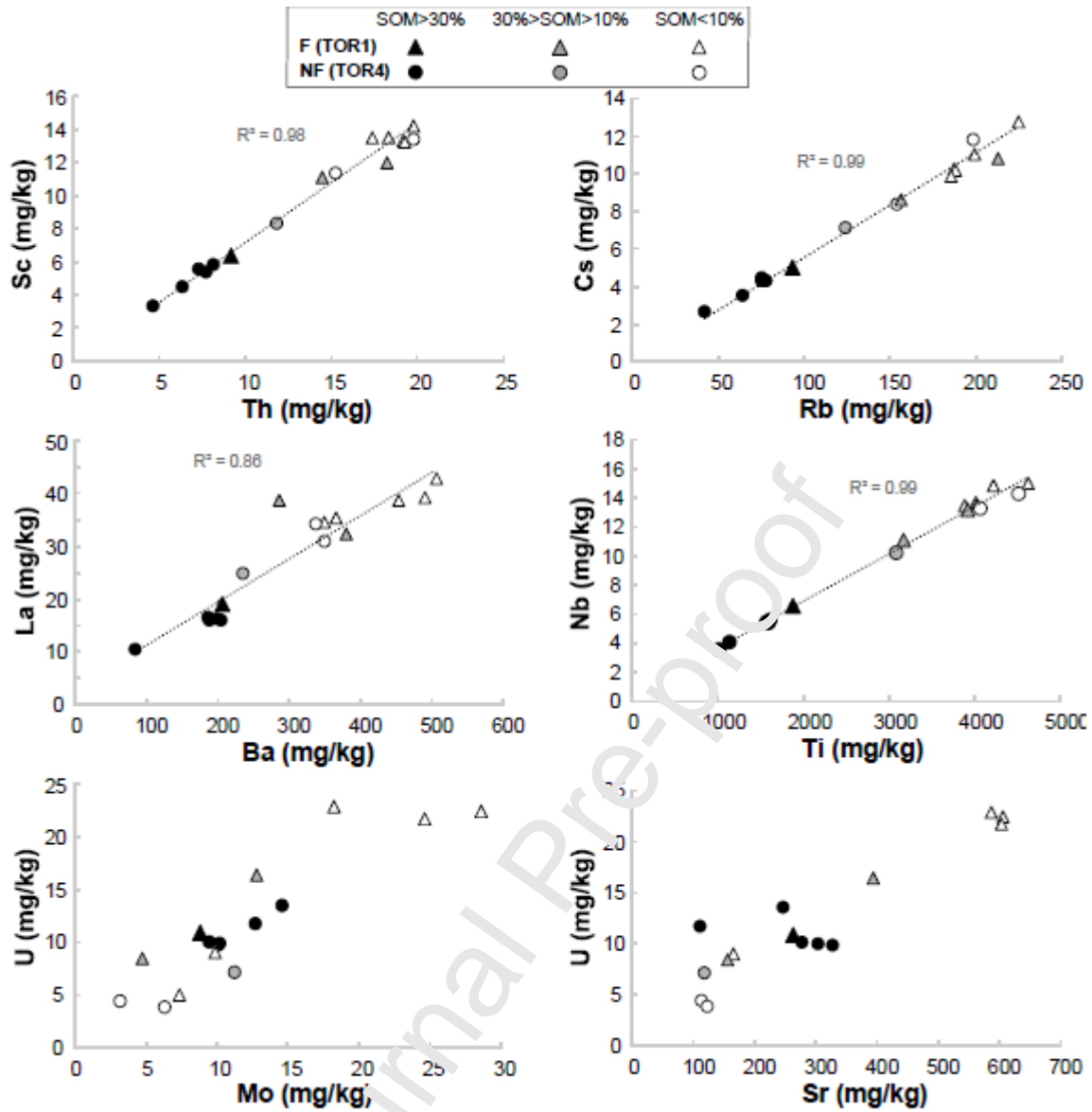


Fig. 3 - Distribution of trace element and of SOM contents along the the NF (TOR4) and F (TOR1) soil profiles.

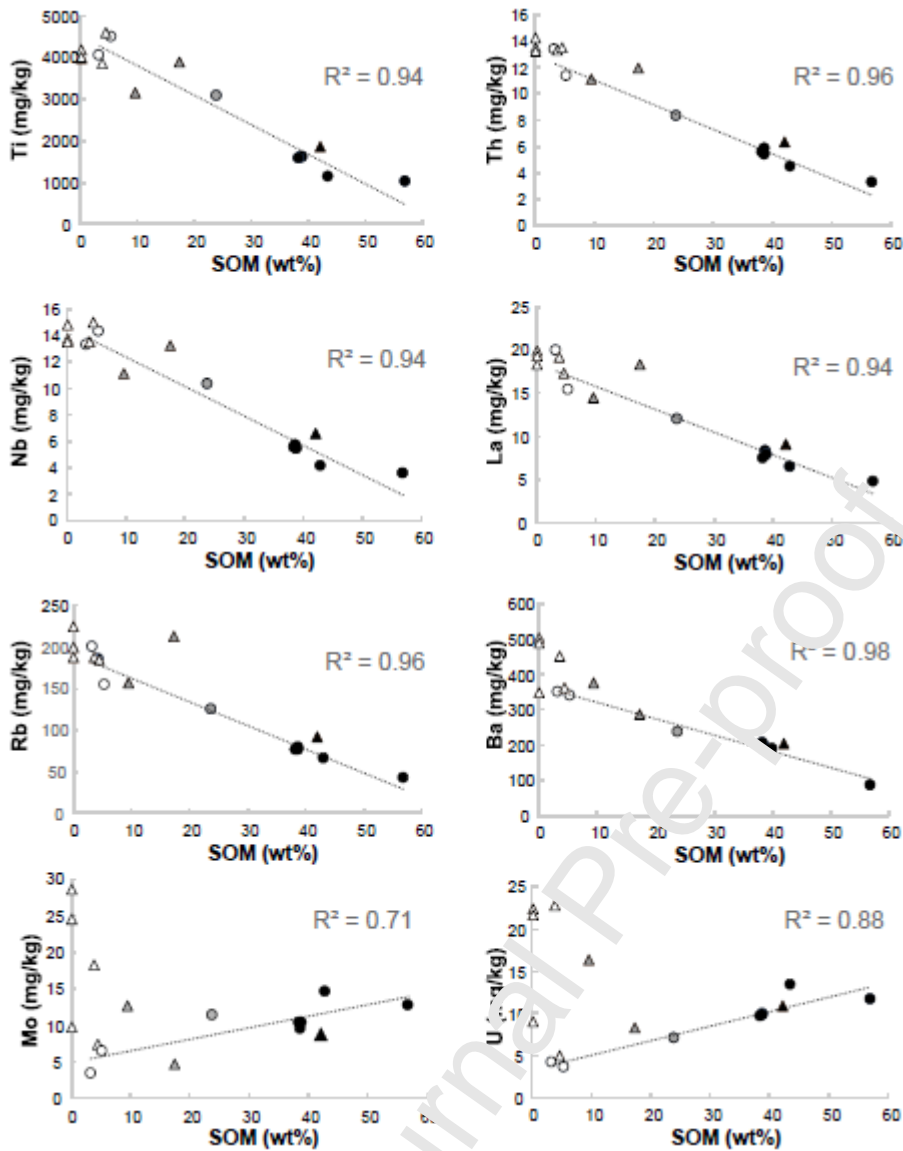


Fig. 4 - Distribution of trace elements (mg/kg) with respect to SOM (wt%) in samples from the NF (TOR4) and F (TOR1) soil profiles. The reported linear regression is calculated using the samples from the NF profile. Symbols as in Fig. 3.

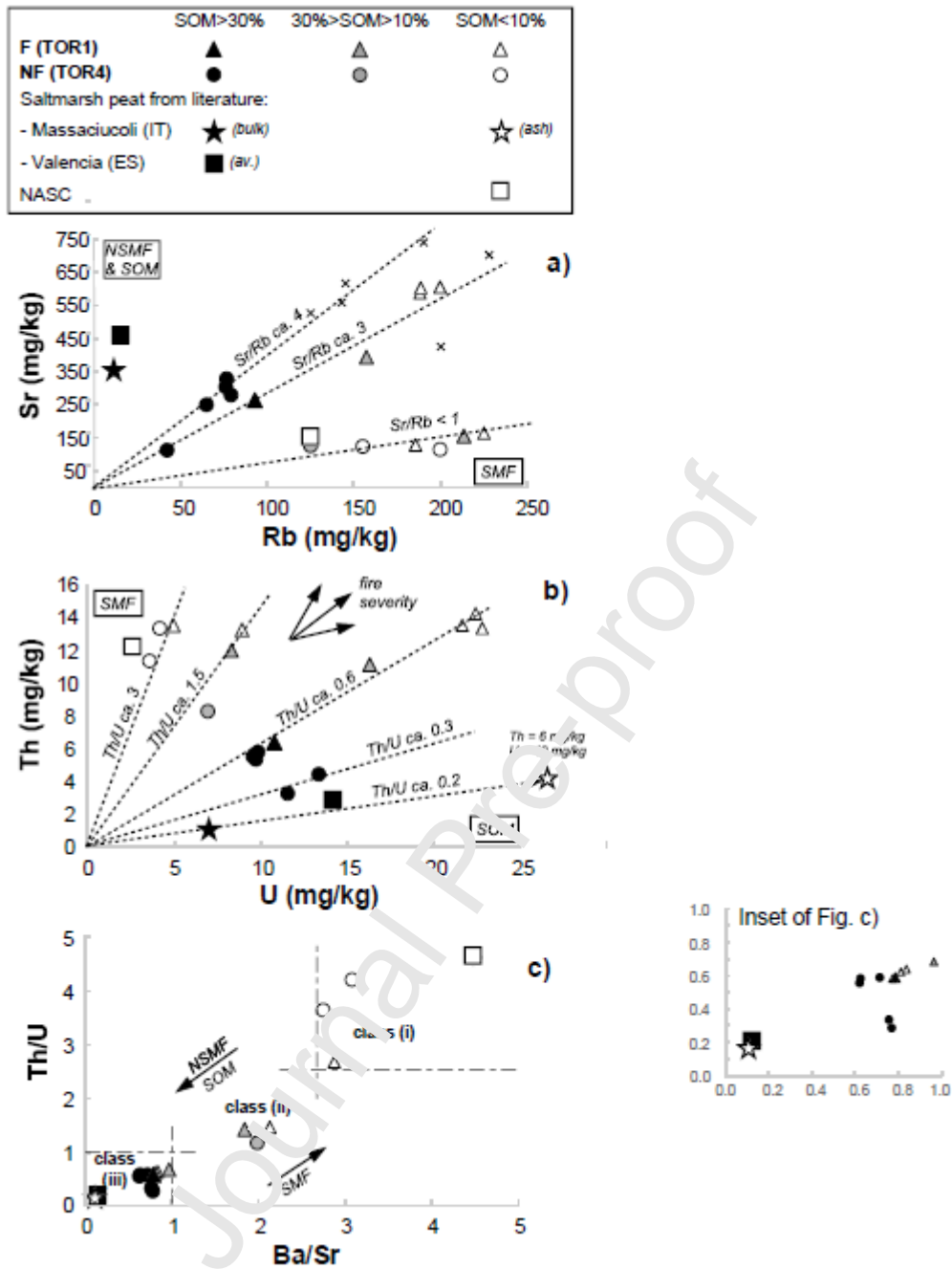


Fig. 5 - Distribution of Sr vs Rb (a), Th vs U (b) and Th/U vs Ba/Sr (c) in samples from the NF (TOR4) and F (TOR1) soil profiles. The composition of sediment samples from the neighboring Comacchio coastal lagoon (x, Migani et al., 2015) is reported for comparison. In (c) the classification of the three sediment classes on the basis of immobile trace element ratios is also shown.

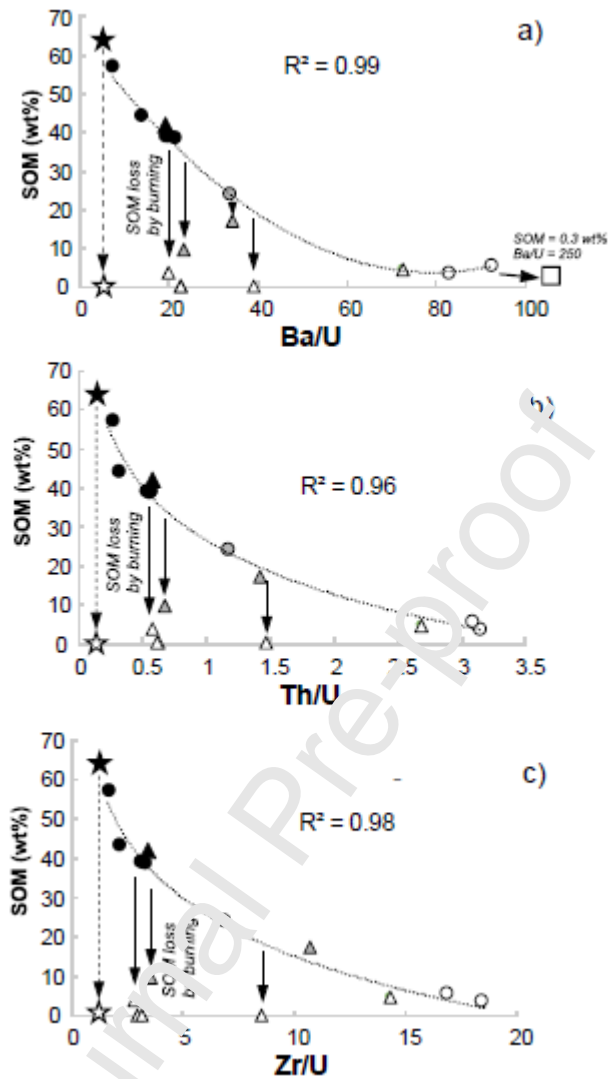


Fig. 6 - Relationship between the SOM content and immobile trace element ratios Ba/U (a), Th/U (b) and Zr/U (c) in the two investigated profiles. The regression is calculated using samples from the NF profile. Symbols as in Fig. 5.

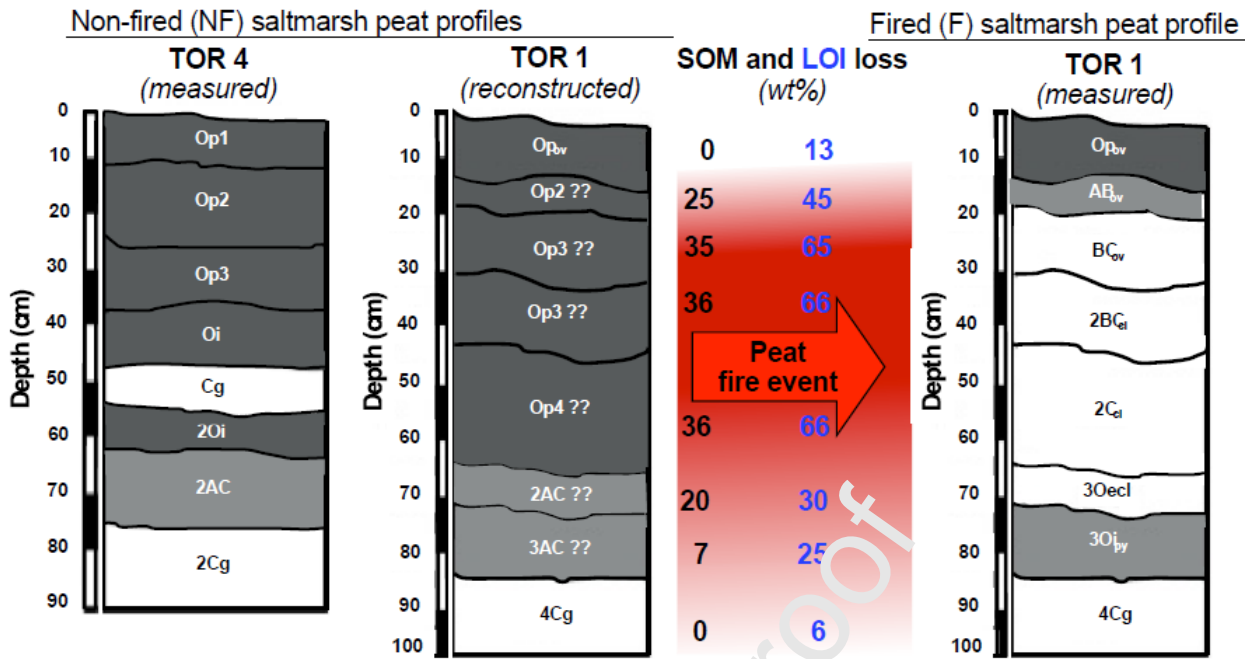


Fig. 7 - Schematic representation of the reconstruction of pre-burning SOM content of the F profile based on trace element distribution. The reconstructed total LOI (referred as “dilution factor” in the text) and the related fire severity estimate are also reported.

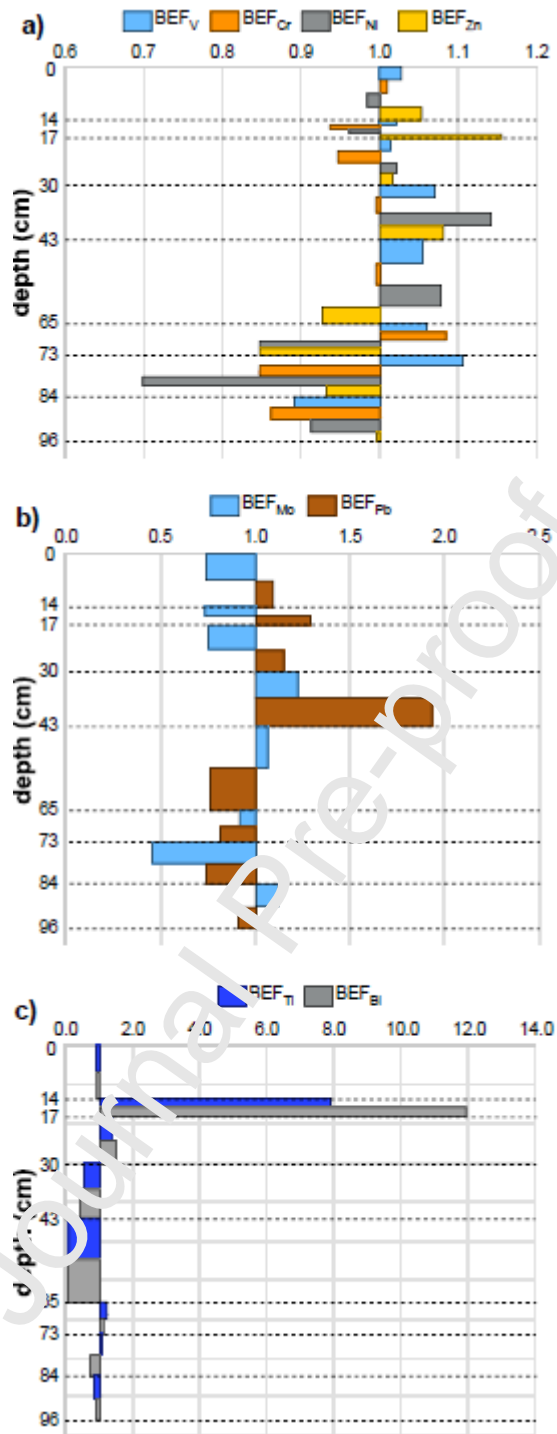


Fig. 8 – Burning enrichment factor (BEF) variation for relatively immobile (V, Cr, Ni, Zn) (a), mobile (Pb, Mo) (b), and highly mobile (Tl, Bi) (c) PTE along the F profile (TOR1).

CRedit author statement

Claudio Natali: conceptualization, methodology, data curation, writing—original draft preparation.

Gianluca Bianchini: conceptualization, writing—original draft preparation. **Mattia Ferrari:**

methodology, data curation, writing—original draft preparation. **Alessandro Bragagni:**

methodology, data curation, writing—original draft preparation. **Riccardo Avanzinelli:**

methodology, writing—original draft preparation. **Matthias Ghiotto:** methodology, writing—

original draft preparation. **Gian Marco Salani:** writing—original draft preparation.

Journal Pre-proof

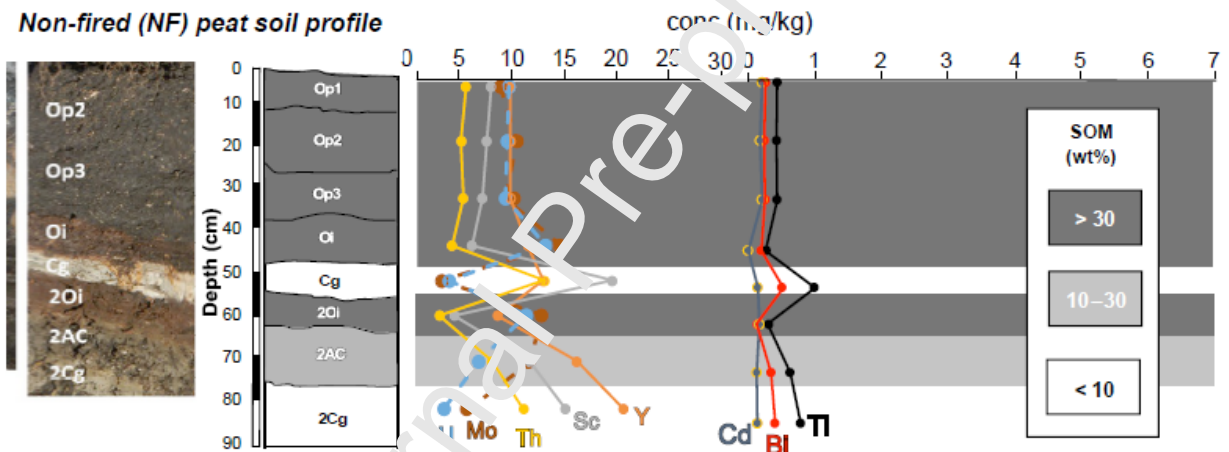
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

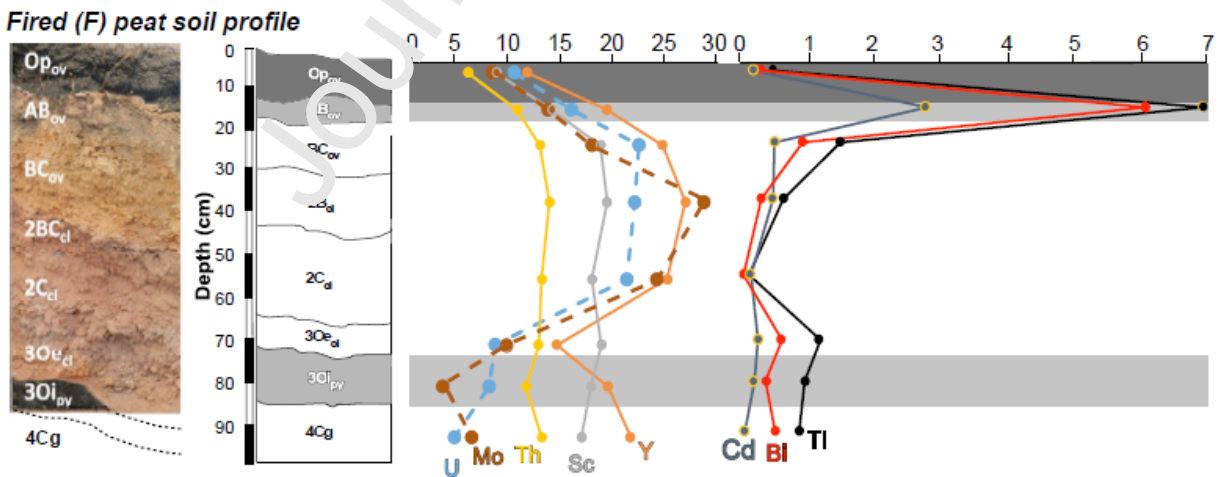
The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract

Non-fired (NF) peat soil profile



Fired (F) peat soil profile

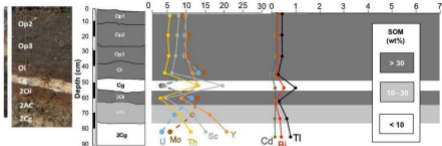


Highlights

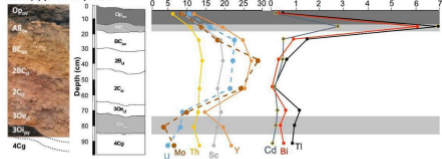
- Natural peat fire effectively changes the soil carbon and trace element contents
- Immobile trace element ratios allow reconstructing the original soil composition
- Potentially toxic elements show variable redistribution along the burned soil profile
- Peat fire caused a 75% loss of the original SOC stock and a release of 350 kg/m³ of CO₂eq

Journal Pre-proof

Non-fired (NF) peat soil profile

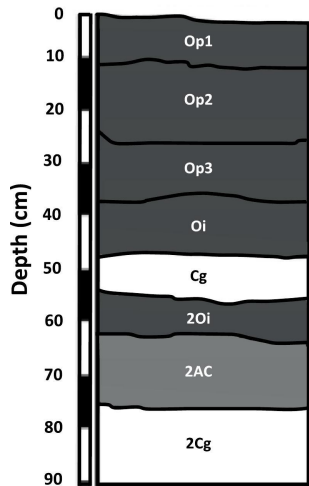


Fired (F) peat soil profile



Graphics Abstract

TOR4 Profile

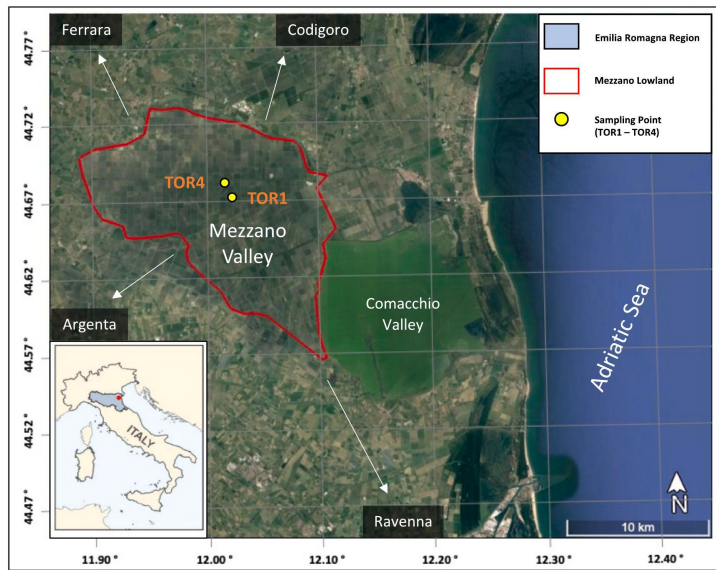


SOM
(wt%)

> 30 %

10 – 30 %

< 10 %



TOR1 Profile

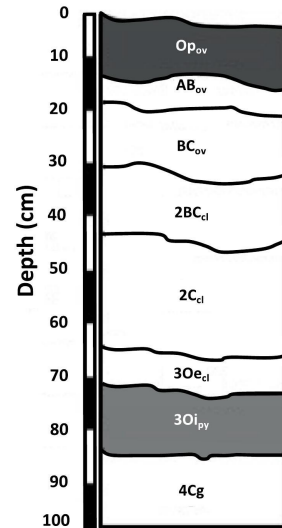


Figure 1

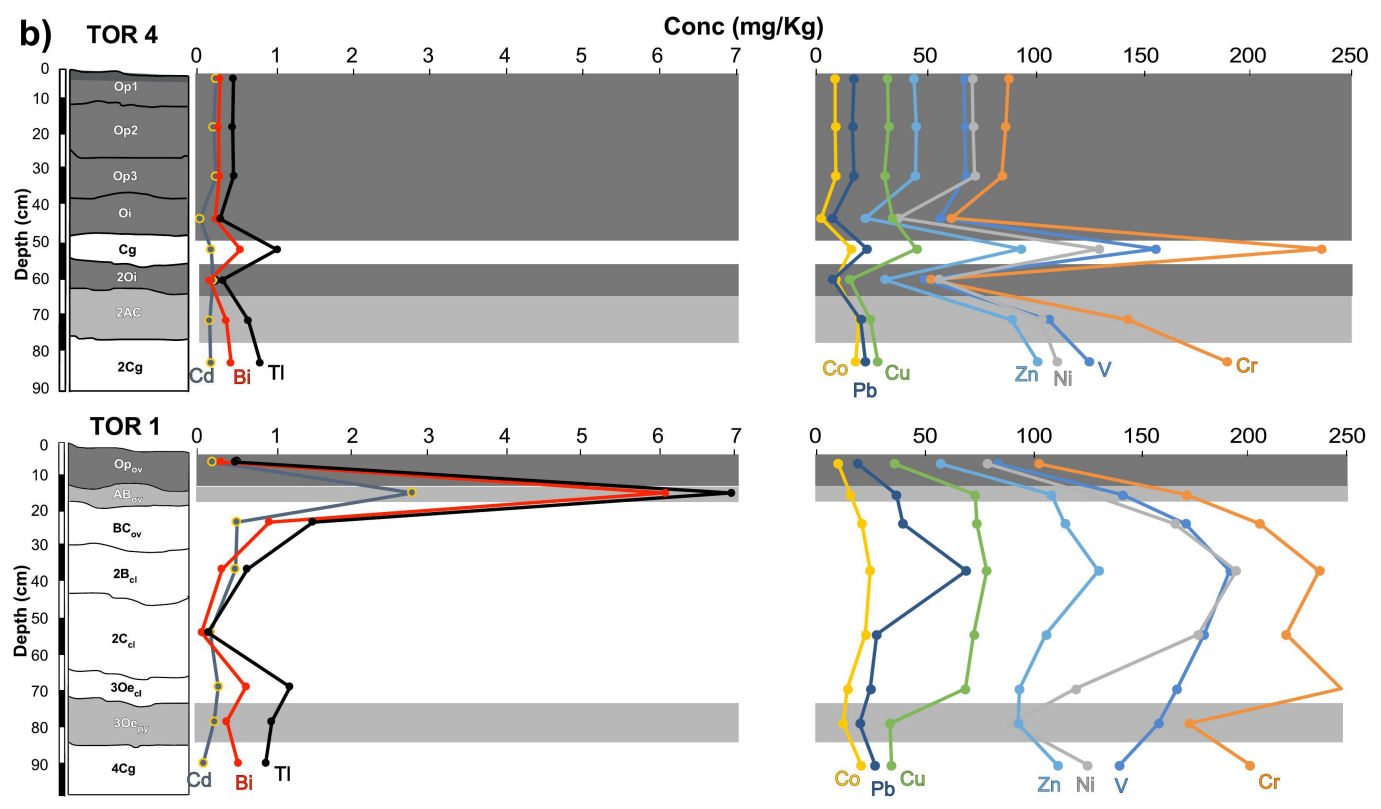
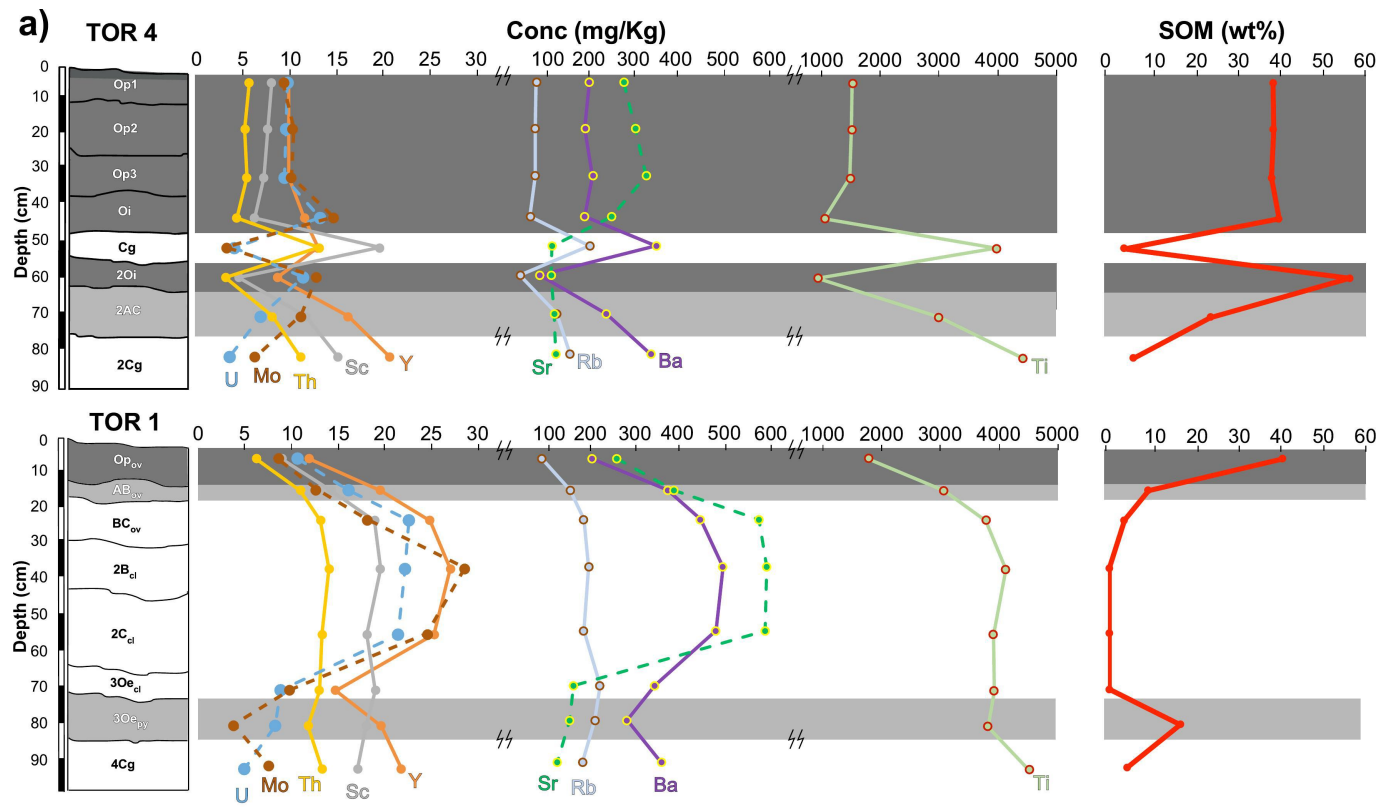


Figure 2

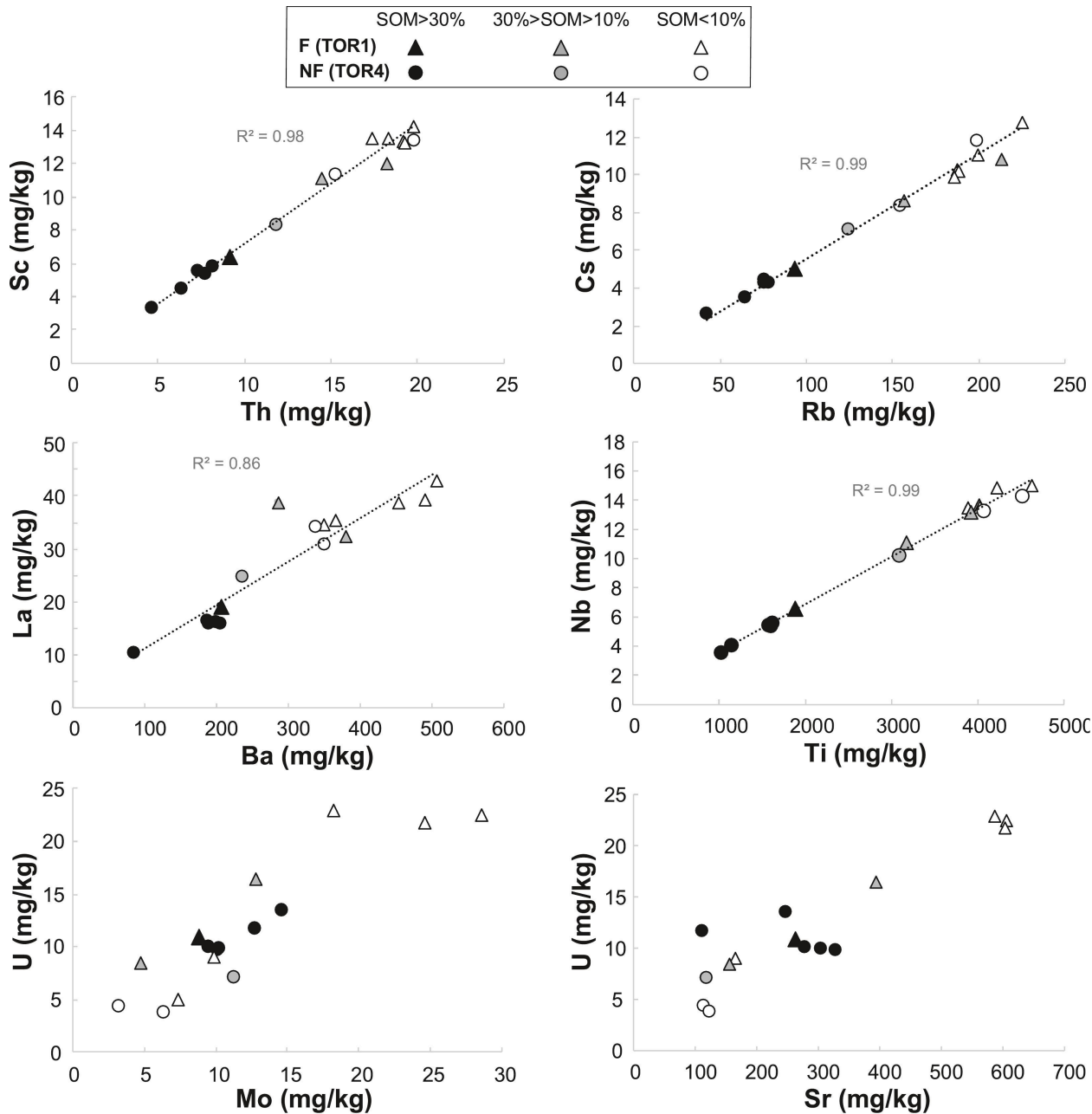


Figure 3

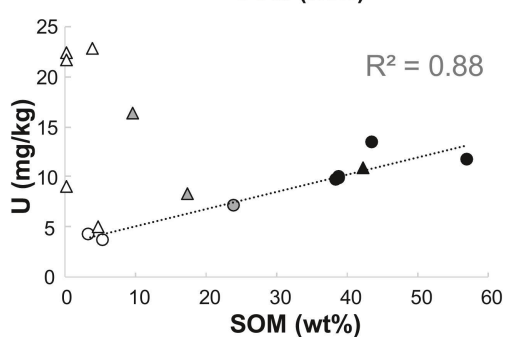
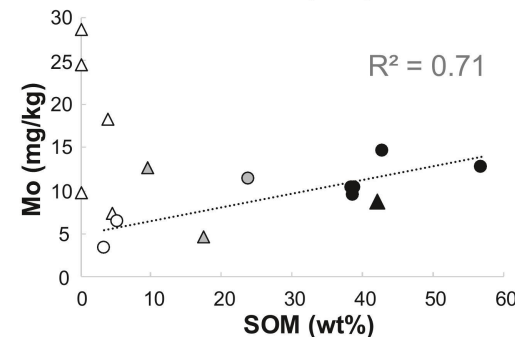
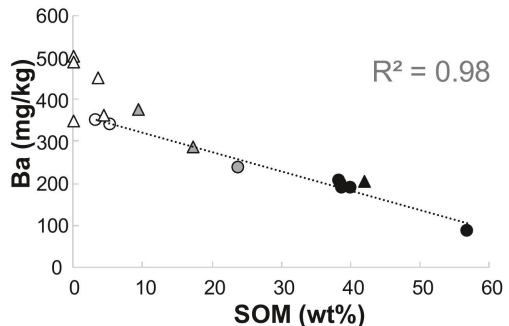
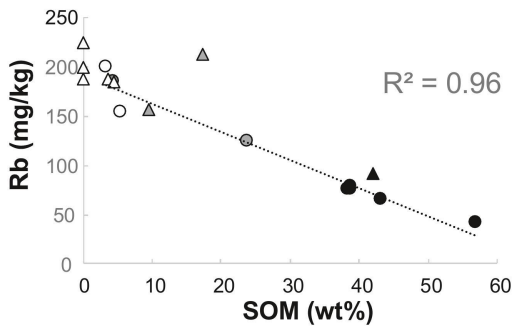
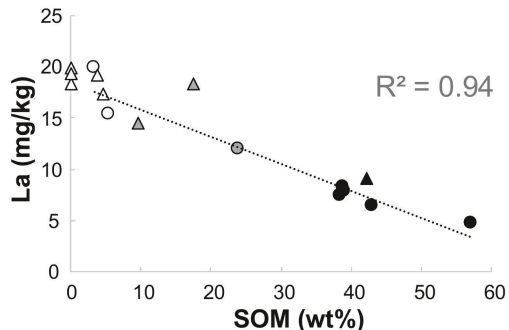
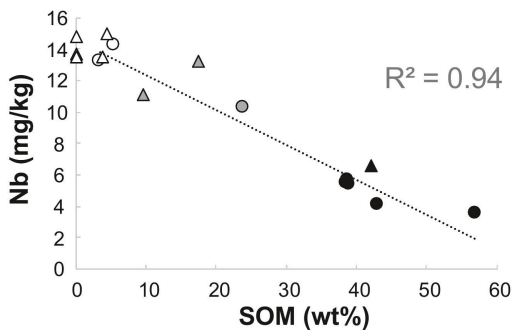
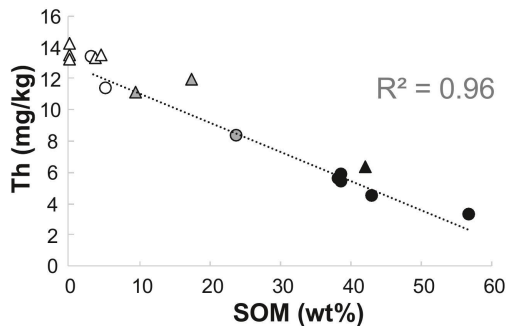
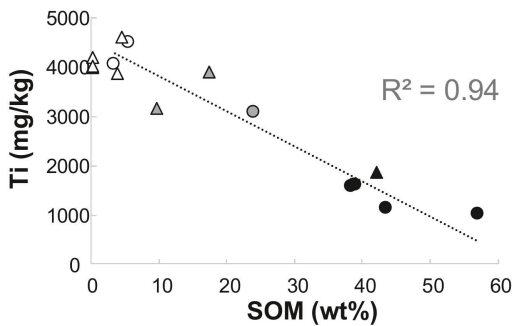


Figure 4

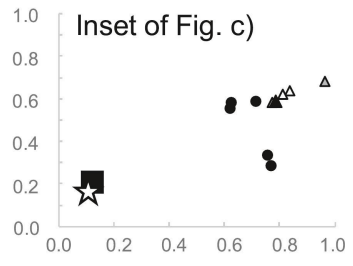
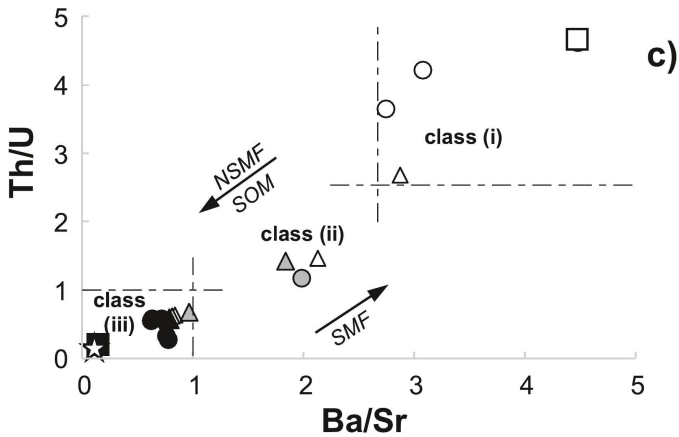
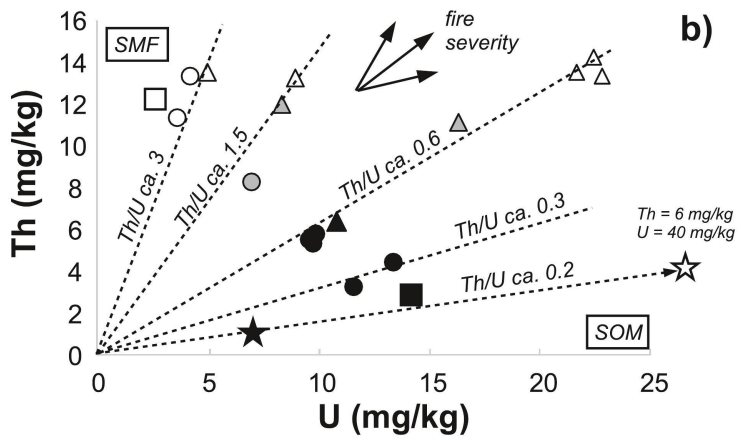
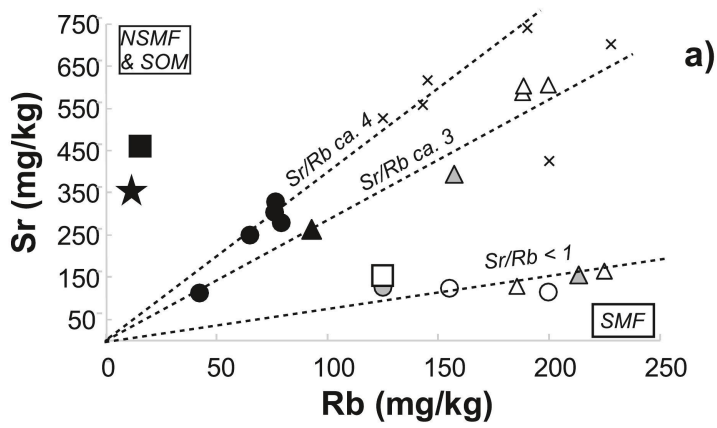
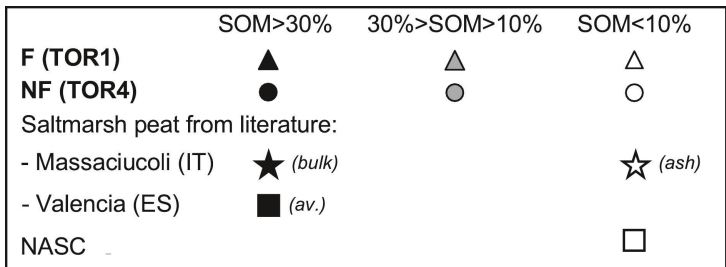


Figure 5

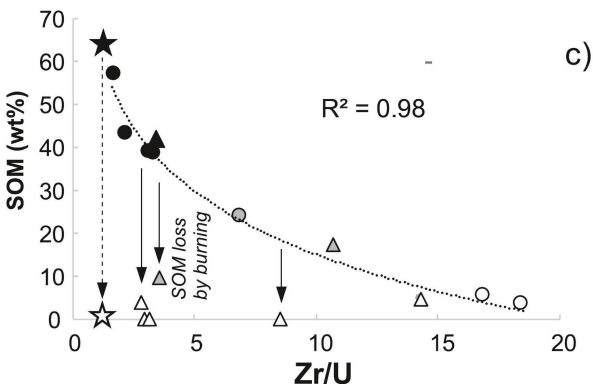
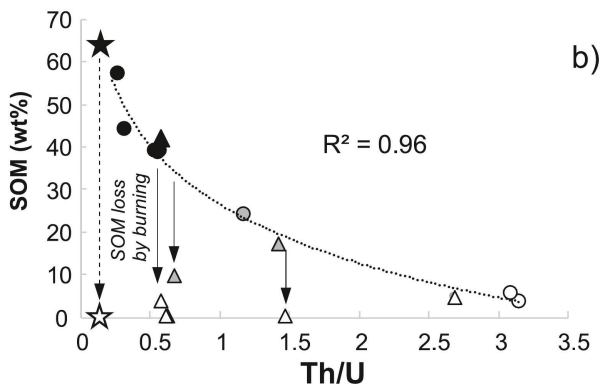
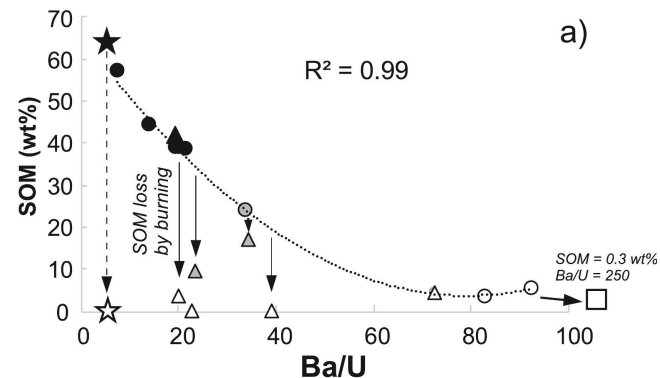


Figure 6

Non-fired (NF) saltmarsh peat profiles

Fired (F) saltmarsh peat profile

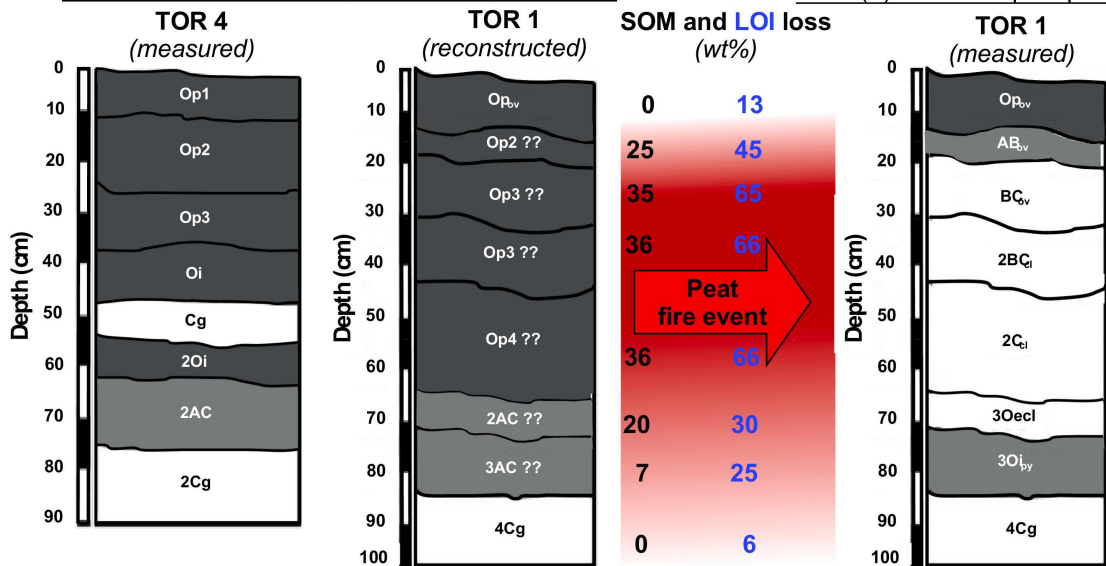


Figure 7

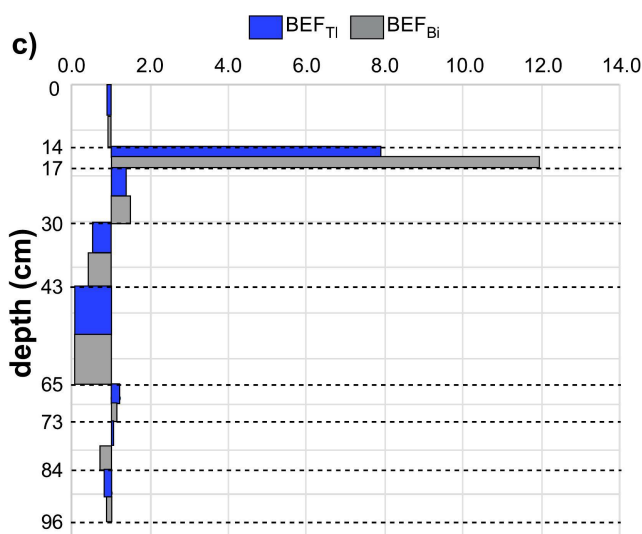
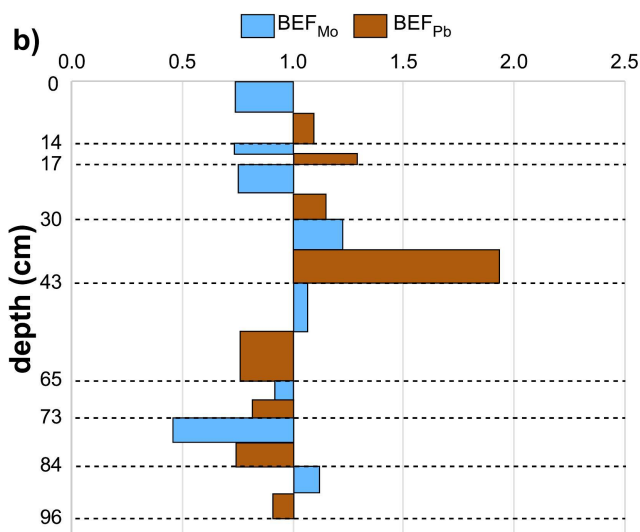
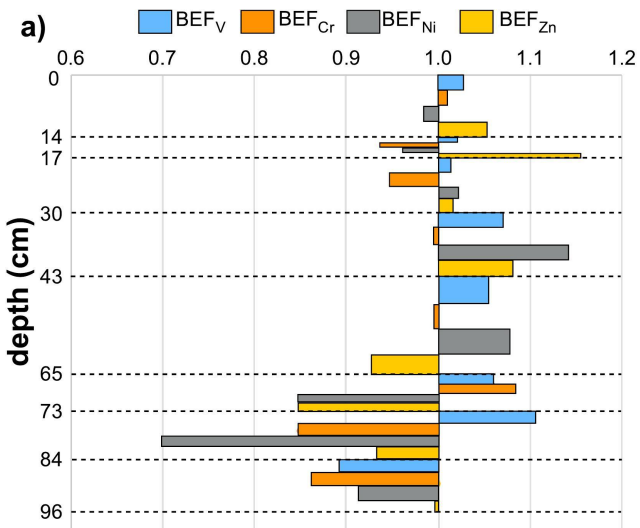


Figure 8