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Title: Pathways of inorganic and organic pollutants from land to deep sea: the case study of the Gulf of Cagliari (W Tyrrhenian Sea)

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Abstract: Dynamics of pollutants from land to deep sea have been investigated in a pilot area of the central Mediterranean basin (Gulf of Cagliari, S Sardinia) where important industrial plants are sited since beginning of the last century. The deep-sea (>200 m) has long been considered a pristine environment due to its remoteness from anthropogenic pollution sources. Nonetheless, in continental margins, canyons appear to act as natural conduits of sediments and organic matter from the shelf to deep basins, providing an efficient physical pathway for transport and accumulation of particles with their associated land-produced contaminants. The continental slope of the south Sardinia has been used as a natural laboratory for investigating mechanisms and times of transfer dynamics of contaminants from land to sea and from shelf and deep sea through an articulated system of submarine canyons. Five sediment cores dated by 210Pb and 137Cs reveal: i) a complex dynamics of organic and inorganic pollutants from point source areas on land to the deep sea and ii) a crucial role played by canyons and bottom morphology as primary pathway conveying sediments and associated contaminants from sources to very far deep sea environments. This study unequivocally suggests that land and deep sea appear much more connected than previously assumed. This is challenging mostly in regions where coastal pollution could represent critical threats for larger areas of the Mediterranean Sea.

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To the kind attention of the

Editor of the Science of the Total Environment

Dear Editor,
here enclosed you find the manuscript entitled
"Pathways of inorganic and organic pollutants from land to deep sea: the case study of the Gulf of Cagliari (W Tyrrhenian Sea)"

By *Stella Tamburrino*, Salvatore Passaro, Mattia Barsanti, Antonio Schirone, Ivana Delbono, Fabio Conte, Roberta Delfanti, Maria Bonsignore, Marianna Del Core, Serena Gherardi and Mario Sprovieri

that we would like to submit to the Science of the Total Environment.

The results presented in the manuscript have not been published elsewhere and they have been not submitted to other journals. An abstract ("*Contaminants transfer from land to the deep sea: processes and dynamics from the case study of the Gulf of Cagliari (W Tyrrhenian Sea)*") has been presented to the EGU 2018 Congress, where we reported only preliminary results from this study.

All authors are aware of and accept responsibility for the manuscript.

The geochemical and geophysical data were obtained through advanced analytical methods and they aim to provide a high-quality database useful to investigate dynamics of contaminants from land to sea. Furthermore we retain that this paper may represent a pilot study suitable for researchers interested both on coastal management of the Tyrrhenian region, and on exploring mechanisms and timing of transfer dynamics of contaminants from land to sea and from shelf to deep-sea through articulated system of submarine canyons.

We hope that the topic is interesting and suitable for the journal. I thank you in advance and hoping to hear from you soon I give you my best regards.

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*Title Page

Pathways of inorganic and organic pollutants from land to deep sea: the case study of the Gulf of Cagliari (W Tyrrhenian Sea)

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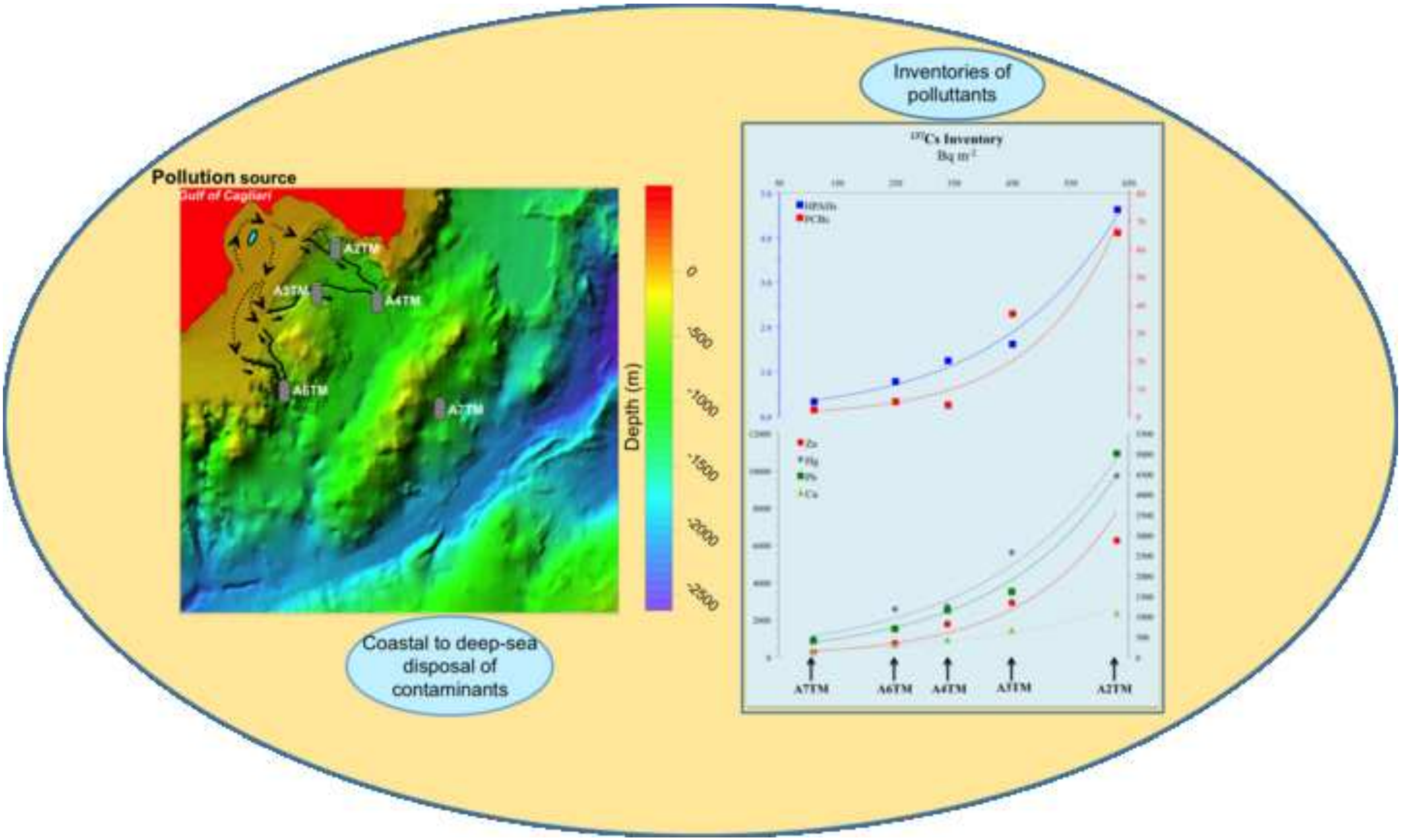
Abstract

Dynamics of pollutants from land to deep sea have been investigated in a pilot area of the central Mediterranean basin (Gulf of Cagliari, S Sardinia) where important industrial plants are sited since beginning of the last century. The deep-sea (>200 m) has long been considered a pristine environment due to its remoteness from anthropogenic pollution sources. Nonetheless, in continental margins, canyons appear to act as natural conduits of sediments and organic matter from the shelf to deep basins, providing an efficient physical pathway for transport and accumulation of particles with their associated land-produced contaminants. The continental slope of the south Sardinia has been used as a natural laboratory for investigating mechanisms and times of transfer dynamics of contaminants from land to sea and from shelf and deep sea through an articulated system of submarine canyons. Five sediment cores dated by ^{210}Pb and ^{137}Cs reveal: i) a complex dynamics of organic and inorganic pollutants from point source areas on land to the deep sea and ii) a crucial role played by canyons and bottom morphology as primary pathway conveying sediments and associated contaminants from sources to very far deep sea environments. This study unequivocally suggests that land and deep sea appear much more connected than previously assumed. This is challenging mostly in regions where coastal pollution could represent critical threats for larger areas of the Mediterranean Sea.

Key words
Tyrrhenian Sea, submarine canyons, deep sea, pollution focusing

*Graphical Abstract



*Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)

Highlights

- Five sedimentary records from the Gulf of Cagliari (W Tyrrhenian Sea) document anthropogenic impacts in the deep sea
- Bottom morphology reveals a complex and articulated system of submarine canyons
- Geochemical analyses: inorganic and organic compounds, radionuclide measurements
- Dynamics of contaminants from land to sea and from shelf to deep sea
- Pilot study to identify canyons as primary pathway conveying sediments and associated contaminants from sources to very far deep sea environments

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Abstract

Dynamics of pollutants from land to deep sea have been investigated in a pilot area of the central Mediterranean basin (Gulf of Cagliari, S Sardinia) where important industrial plants are sited since beginning of the last century. The deep-sea (>200 m) has long been considered a pristine environment due to its remoteness from anthropogenic pollution sources. Nonetheless, in continental margins, canyons appear to act as natural conduits of sediments and organic matter from the shelf to deep basins, providing an efficient physical pathway for transport and accumulation of particles with their associated land-produced contaminants. The continental slope of the south Sardinia has been used as a natural laboratory for investigating mechanisms and times of transfer dynamics of contaminants from land to sea and from shelf and deep sea through an articulated system of submarine canyons. Five sediment cores dated by ^{210}Pb and ^{137}Cs reveal: i) a complex dynamics of organic and inorganic pollutants from point source areas on land to the deep sea and ii) a crucial role played by canyons and bottom morphology as primary pathway conveying sediments and associated contaminants from sources to very far deep sea environments. This study unequivocally suggests that land and deep sea appear much more connected than previously assumed. This is challenging mostly in regions where coastal pollution could represent critical threats for larger areas of the Mediterranean Sea.

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1 Introduction

Coastal marine areas are under increasing pressure due to various anthropogenic activities with their relevant input of pollutants to the sea and consequent concerns for the fragile marine ecosystems. The complex biogeochemistry of inorganic and organic contaminants in the marine environment combined to their persistence and limited potential for degradation, produces long-term residence time, long-range potential transport and relevant effects of bioaccumulation and biomagnification in the trophic web (e.g., Lohmann et al., 2007; Scheringer et al., 2009). Pollutants in the marine sediments undergo a combination of chemical (e.g., adsorption/desorption, water/particle exchanges, etc.), early diagenetic and sedimentological processes (e.g., re-suspension and re-deposition), which make difficult to track, in terms of chemical and physical dynamics, their evolution in the marine environment.

Recent investigations demonstrated that many chemical pollutants reach the deep-sea (e.g. Storelli et al., 2009; Jamieson et al., 2017) representing, with the reduced physical and chemical dynamics of this environment, a long-term risk with unpredictable effects for the deep ecosystem (Froescheis et al., 2000; Covaci et al., 2008). The deep-sea (>200 m) has long been considered a pristine environment due to its remoteness from anthropogenic sources. Nevertheless, in continental margins, canyons act as natural conduits of sediments and organic matter from the shelf to the deep basins, providing an efficient physical pathway for transport and accumulation of particles with associated land-produced pollutants. Several recent multidisciplinary projects have focused on the study of canyons, and have considerably increased our understanding of their ecological role, the goods and services they provide to humans, and the impacts that anthropogenic activities have on their ecological condition (Fernandez-Arcaya et al., 2017). Being a link between coastal areas and deep oceans, they serve as conduits for the transport of sedimentary material from the surface to the bottom of the sea (Fabres et al., 2008). Also, the role played by canyons in transporting pollutants to the deep sea is enormously reinforced when they are the locations of highly dynamic shelf to basin export processes (i.e. Dense Shelf Water Cascading-DSWC in the NW Mediterranean Sea; Canals et al., 2006). In this context, the continental slope of the south Sardinia is an interesting natural laboratory for exploring mechanisms and timing of transfer dynamics of contaminants from land to sea and from shelf to deep-sea through an articulated system of submarine canyons and specific source areas. An ensemble of chemical analyses of radionuclides, inorganic and organic compounds from sediment cores sampled from coastal to deep-sea areas provide a unprecedented opportunity to investigate dynamics of contaminants from the land sources to the marine sinks.

2 Site description

The Gulf of Cagliari (CG) is placed in the SE sector of Sardinia (Figure 1A), where fluvial sedimentation since Pleistocene caused favourable conditions for the development of coastal lagoons separated by the rhodalgal limestones Miocenic hills of Cagliari (Cossellu et al., 2006;

Kalb et al., 2008). Holocenic sandbars complete the evolution of the coastal margin. Clayey, sand and siliciclastic carbonate sediments characterize the latest Pleistocene-Holocene stratigraphy of Cagliari Basin. Because of sediment supply, sea-level changes and tectonics, CG has a pronounced shelf that extends about 15-20 km south-eastward (Lecca et al., 1998). The shelf abruptly interrupts with a marked break in slope located at 60/80 m below sea level (bsl). Extensive canyons (and several tributary incisions) dissect the offshore-continental slope margin of CG, named Pula (PC), Sarroch (SC), S. Elia-Foxi (SEC) and Carbonara (CC), respectively (Figure 1B). In this area, also two major seafloor relative highs are present: the Carbonara Ridge (CR) and the Banghittu Knoll (BK; Figure 1B and 1C). CR is a 85 km long, 25 km wide NE-SW striking seamount rising more than 1000 m from the surrounding seafloor (Figure 1C). The deeper flanks of CR slopes are located at 1250 m bsl, while its apical sector reaches 156 m bsl. BK is located in the SW sector of CG, on the uppermost portion of the slope, where it acts as a physiographic boundary between SC and PC. BK shows an almost flat, SW gently dipping top (ca 0.5°) on its apical part, which is located between 110/140 m bsl.

The presence of two major industrial complexes dominate potential inputs of contaminants at sea from the coastal area of the CG: the major and industrial area of the Cagliari town and, in the westernmost part of the gulf, the refinery industrial plant of Sarlux-Saras (Figure 1).

3 Data and methods

Seafloor bathymetry and sediment cores were acquired during the Anomcity_2014 oceanographic cruise on-board of the R/V Minerva Uno (National Research Council, CNR). Bathymetric data were used to deploy a Digital Terrain Model (DTM) covering an area of 17’000 km^2 in the 2670 m to 1 m bsl bathymetric range.

Five sediment cores were collected using a box-corer, at depths ranging from 475 and 1153 m (Figure 1A and 1B; Table 1). The A2TM and A3TM cores are located at a depth of about 600 m bsl in the SEC and SC canyon branches, respectively; these two sampling sites were selected where a slope decrease in the seafloor morphology has been observed. The A4TM sets at the confluence of SEC and SC active branches, at a depth of about 900 m bsl, while the A6TM was sampled at the confluence of the PC active branches (SW from A2TM and A3TM, at about 780 m bsl). Finally, the A7TM lies SE from the apical sector of the CR main axis, at about 1140 m bsl depth. Core sub-samples were prepared for grain size, geochemical and radiometric analyses. Cores analysis included: radionuclide measurements, grain-size fraction, concentrations of Al, Fe, Mn, Cd, Pb, Co, V, As, Cr, Cu, Ni, Zn, Hg, TOC, TN, PAHs (16 US-EPA priority congeners) and ΣPCBs. Results are reported in Supplementary Table S1. A full description of data and methods can be found in the additional materials (see text in Supplementary Material).

4 Results

4.1 Seafloor morphology

The morphology shows the existence of several abandoned canyon branches, partially filled by sediments and presently unlinked to the active sections of SC and SEC (Figure 1B). Contrary to the active canyon thalwegs, minor incisions tend to disappear toward deeper sectors of the slope. Since their intrinsic sediment dynamic, the CG active set of canyons and incisions rules the mechanism of sediment distribution from land to deep sea (e.g., Puig et al., 2014). The overall emplacement of uppermost branches of canyons is mainly controlled by the slope direction, i.e., ca NW-SE (Figure 1B and 1C). On the contrary, the presence of CR, located at the slope foot, constraints the pattern of deeper segments of canyons (Figure 1B).

4.2 Radionuclide tracers and chronology

The combined use of ^{210}Pb and ^{137}Cs profiles provides a solid based geochronology during the last century, since these elements have similar half-lives (22.23y and 30.05y, respectively) but quite different inputs in the environment: natural ^{210}Pb is continuously produced by its parents while artificial ^{137}Cs is time dependent (Hancock et al., 2000; Smith, 2001). In fact, ^{137}Cs has been diffused in the environment mainly during the nuclear tests in atmosphere in the 1945-1963 period and then reached an ubiquitous distribution. In the marine environment, a large fraction of radionuclides and pollutants is associated with particles and fine sediments (Baskaran et al., 1993; van Wijngaarden et al., 2002 and reference therein) settling through the water column and reaching the seafloor. Therefore, high deposition of ^{137}Cs marks sites with high accumulation of recent fine particles.

$^{210}Pb_{xs}$ and ^{137}Cs downcore profiles in the five sediment cores of this study are shown in Supplementary Figure S1. The A2TM and A3TM cores (SI Figure S1A and S1B) show a clearly visible ^{137}Cs sub-surface peak in the downcore activity profiles. At station A2TM, assuming a Constant Flux of ^{210}Pb and a Constant Sedimentation rate (CF:CS model) (Appleby, and Oldfield, 1992; Robbins, 1978) in the last century, a Mass Accumulation Rate (MAR) of 0.24 ± 0.01 g/cm^2 y, equivalent to a Sediment Accumulation Rate (SAR) of 0.33 ± 0.01 cm/y, is calculated. With this MAR value, the ^{137}Cs sub-surface peak (mass depth = 12.3 g/cm^2) corresponds to the year 1963 ± 2, in perfect agreement with the real maximum fallout deposition in 1963. Furthermore, ^{137}Cs disappears below 16,27 g/cm^2, dated back to 1946 ± 2, very close to the beginning of the nuclear weapons testing. Consequently, the ^{210}Pb dating for the A2TM core is considered to be totally reliable and accurate. Differently for station A3TM, MAR calculated by the CF:CS model from the $^{210}Pb_{xs}$ downcore profile is 0.18 ± 0.01 g/cm^2 y (equal to a SAR of 0.26 ± 0.02 cm/y). This dates the ^{137}Cs peak (mass depth = 6.5 g/cm^2) at 1978 ± 3, which is not consistent with the ^{137}Cs global fallout peak in 1963. If we assume a variable sedimentation rate and apply the Constant Rate of Supply (CRS) model (Appleby, and

Oldfield, 1978) to the $^{210}Pb_{xs}$ activity profile, the ^{137}Cs peak dating improves with the result of the year 1956 ± 5, closer to the 1963 peak. With the CRS calculation, the $^{210}Pb_{xs}$ dating of the A3TM core is more reliable although it shows a greater uncertainty than the A2TM core. The use of two different models highlights a different nature in terms of sedimentary dynamics of SEC and SC Canyons where the A2TM and A3TM cores are located, respectively.

For the other three sediment cores (A4TM, A6TM and A7TM), $^{210}Pb_{xs}$ and ^{137}Cs downcore activity profiles (SI Figure S1C, S1D and S1E) are more disturbed because of post-depositional processes such as bioturbation and sediment mixing. Furthermore, ^{137}Cs activity profile does not allow a validation of the ^{210}Pb-based dating models and no reliable dating is available for sediment cores A4TM, A6TM and A7TM.

4.3 Grain size, inorganic and organic geochemistry of sediments: trends and potential sources of pollution

Some relevant features emerge, particularly in the two cores A2TM and A3TM, which reveal in great detail some of the most important and historically documented anthropogenic impacts on the near coast during the last 110 years. In particular, in the A2TM core, ΣPAHs, Pb and Hg increase since 1930, testifying the first industrial activities already well documented for the Cagliari industrial area (Figure 2A). ΣPCBs have been detected since 1940, immediately after the industrial use of these chemicals in Italian chemical plants. Also, three time intervals 1900-1940, 1940-1980, 1980-recent well document (particularly in the A2TM core), in terms of gradually increasing silty fraction (see box plot at the bottom of the Figure 2A), the effects of anthropogenic damming on land which progressively reduced input of sediments fine fraction at sea. The ΣPCBs profile in the A3TM core shows a similar behaviour with As and Hg increasing only since 1960, thus reflecting the start-up of industrial activity in the Sarlux-Saras refinery (Figure 2B). Thus, these two sediment cores document with high accuracy the most important anthropogenic events on land with different spatial responses to the two diverse point sources.

The A4TM core clearly reflects, considering the last ~110 years, anthropogenic inputs from land of ΣPCB, ΣPAHs, Pb, Hg and As, thus documenting an efficient transport and accumulation in the sediments (Figure 2C). Although documented in a shorter sedimentary record, the input of anthropogenic contaminants (ΣPAHs, ΣPCBs, As and Pb) is identified in the last ~110 years of the A6TM core (Figure 2D). Noteworthy, significant amounts of ΣPCBs and minor of ΣPAHs, Co, Cr, Ni, V and Zn were also found in the upper part of the A7TM, characterised by extremely low sedimentation rate (Figure 2E).

4.4 Inventory of pollutants and patterns of distribution

The estimate of the inventories for the anthropogenic contribution of each single Trace Element (hereafter TE) in each sediment core layer was calculated firstly by subtracting the percentage related to the different mineralogical and background components from the total concentration of the TE and then by multiplying by the mass depth value estimated for each sample. More in detail, in order to minimize the contribution of grain size and mineralogy on the concentration of each TE in the sediments and thus estimate the anthropogenic component, we subtracted the percentage calculated as TE/Al ratio from each point with respect to the minimum TE/Al documented in each core. On the other hand, background values for ΣPAHs and ΣPCBs were calculated as the lowest concentration value documented in the lowermost part of the five cores. Then, for each TE, including ^{137}Cs, the inventory was calculated as cumulative sum of the concentrations in each sediment layer multiplied by its bulk dry density and divided by the core surface area (Table 2).

5 Discussion

5.1 Radionuclides as tracers for sediment transport

The levels and the downcore distribution of natural and anthropogenic radionuclides can be used to derive information about the sediment provenance and composition (Ra isotopes and ^{40}K) and to characterize depositional environments and sediment accumulation rates (^{210}Pb, ^{137}Cs).

The balance of ^{210}Pbxs fluxes (Bq m^{-2} y^{-1}) at the sediment-water interface is shown for each station in the Supplementary Figure S2. ^{210}Pbxs flux accumulated in sediments (F_s) exceeds the estimated flux from atmospheric deposition (F_a) and decay of ^{226}Ra in the water column (F_m), with the exception of A7TM. In detail, A2TM shows the strongest lateral transport of ^{210}Pbxs, and the ^{210}Pbxs profile of the A2TM station indicates a regular and constant sedimentation over a ~110 year time scale. These features are in agreement with (Meleddu et al., 2016) which identify hyperpycnal flows in the northern area of CG that, considering the limited extension of the continental shelf, influence the development of deposits in the head of the SEC (Figure 1B). ^{210}Pbxs data of A2TM core identify a sediment deposition transported by these hyperpycnal flows pointing out the constant SEC sediment transport activity.

Similarly to A2TM, A3TM station shows a significant lateral input of ^{210}Pbxs but displays a more disturbed trend of ^{210}Pbxs profile. These observations support the hypothesis made in the CRS model obtained by data (see previous chronology section), thus suggesting a variable sedimentation supply for A2TM and A3TM on the basis of the ^{210}Pbxs profiles. The obtained result is substantially in agreement with (Orrù et al., 2014), that mapped two significant marine slide deposits located in correspondence of Sarroch. These deposits extend from the edge of the continental shelf to a depth of about 400 m (until the head of SC). Moreover they are affected by erosion in the SC, causing a less regular deposition at A3TM than at A2TM. Although, A3TM is located at the same depth of A2TM, its ^{210}Pbxs surface activity is about half of A2TM, thus indicating that the A3TM station receives a relevant sediment input from these marine slide deposits.

A4TM and A6TM are quite similar and show a lower lateral supply of ^{210}Pbxs. However, ^{210}Pbxs fluxes are twice the expected ones by considering the atmospheric and the seawater contributions only, thus indicating a significant supply of sedimentation.

Differently, the A7TM core (the deepest one) shows a globally lower ^{210}Pbxs flux than the expected. Here the post-depositional are dominant compared to sedimentation rate values, very similar to those of the deep sea. Since the CR separate A7TM from the slope, this latter is poorly interested by sedimentation arising by the shelf and the slope, while is subjected to other marine sources of sediments as testified by ^{40}K, ^{234}Th and grain size data (SI Table S2 and Figure S4).

5.2 Inventories of contaminants and sediment patterns distribution

Despite ^{137}Cs in the oceanic water column behaves as a soluble nuclide and hence ^{137}Cs has properties that make it useful as a water mass tracer, a very little of ^{137}Cs delivered to the ocean reaches the seabed. At present, there is no global fallout of ^{137}Cs derived from nuclear weapons testing (Baskaran, 2011). The dominant source of ^{137}Cs in the air is a re-suspension (e.g. due to agricultural activities) of previously deposited ^{137}Cs in soil and its subsequent transport by winds (Pham et al., 2013 and references therein). Therefore, ^{137}Cs can be reliably applied as tracer of terrigenous inputs of fine sediment fraction in coastal areas.

The Cagliari urban area, with its harbour and lagoon, represents the major source point for sediment release in the CG. Taking into account that, we infer a potential relationship between the distance of each sampling station from Cagliari and ^{137}Cs inventories. Specifically, the inventory of ^{137}Cs has been reported in Figure 3: i) against the linear distance estimated from the main source area (Cagliari; Figure 3A and 3B) and ii) against the estimated morphological distance (following the thalweg of the canyon systems located in front of the two major industrial plants of Cagliari and Sarlux-Saras; Figure 3C and 3D) from land. The plot of ^{137}Cs inventories from each core vs the linear distances from the nearest coastline measured for each sample station shows a relatively low fit (Figure 3B). This plot testifies that ^{137}Cs "travels" from land-to-sea but does not follow the ideal linear connection from a point to the nearest emerged sectors. Conversely, if we calculate a "morphological distance" from land, assuming that sediments travel from the shelf to the station following the preferential way of the axis of canyons, we obtain values that are in very closer relation with the ^{137}Cs inventories (Figure 3C) with a second order fitting line perfectly approximating the distribution of the four values. Really, the relationship between the "morphological distance" and the ^{137}Cs inventories should be considered as the first part of an exponential decrease, since this trend must reach an equilibrium value for high distance from the coast, where the only source has been the direct fallout. Hence, by subtracting the A7TM inventory to other ^{137}Cs inventories we can observe the distribution of ^{137}Cs with terrigenous origin (Figure 4). This could suggest that coastal to deep-sea transport of sediments deposited at seafloor is strongly driven by morphology and drifting mechanism. Actually, once arrived at the break in slope, sediments undergone an acceleration and a re-disposing primarily driven by the gravity action of the over solid-flows on the slope. In addition, they are under the effects of the attractive action played by canyon axis. In this sense, local morphology plays a major role for sediment distribution, especially for channels and canyons for which the overall dynamic of sediment transport is quite faster with respect to the slope activity (SI Figure S3). It is worth stressing that submarine canyons act as preferential pathway for transport of sediment from the shelf to adjacent basins (e.g., Shepard, 1981), thus strongly influencing the evolution of the shelf itself and the overall sediment displacement of a slope (Canals et al., 2004; 2006; Allen et al., 2009; Piper and Normark, 2009; Puig et al., 2014; 2017; Talling, 2014). Presently, the transport activity and the exchange of sediments with the upper, adjacent, external continental shelf seems to be primarily linked to the tectonic activity and the sediment supply from land. The sediment amount in the uppermost section of the shelf, as a result of anthropogenic activities (e.g., dredging of harbours or natural event like flash floods, etc.), may result in a re-activation of sediment transport along the canyon (Carter et al., 2012; Khripounoff et al., 2012; Puig et al., 2014). This implies that canyons, particularly those located in area characterized by important tectonic activity, may represent efficient focusing systems for pollutants from land (see Micallef et al., 2014 and reference therein). Then, once sediments reach break in slope, they are partially attracted from not incised slopes, partially by not active channel segments or abandoned canyons and, perhaps goes to fill old valleys.

The calculated TE inventories for the different cores show comparable exponential decrease with the distance from land (considering the ^{137}Cs as a reliable tracer; Figure 5) but the slope of this decrease is different for each element, reflecting specific geochemical affinity (sediment–water distribution coefficients, Kd) with sediments (IAEA, 2004). The ΣPAHs-ΣPCBs group shows an analogue behavior although a slightly more complex trend does not exclude other ΣPAHs and ΣPCBs sources and deposition mechanisms from the coastal area.

In this study, we documented very fine correlations of sedimentological and chemical features among dated cores located at different depths and morphologic settings. A primary control of contaminants transport from land to the deep sea via shelf canyons could represent a systematic mechanism of contaminants focusing generating hot spots of pollutants in the uncontaminated ocean sediments from very far point sources on land. Transport mechanisms by shelf canyons could offer unforeseen fast track system of deep sea contamination. A dominant geomorphological feature of the Mediterranean basin in terms of shelf-to-deep sea connection is represented by innumerable canyons, which document geological events modelling the mid- to long-term regional events. These canyons represent natural conduit conveying sediments and associated contaminants from sources on land to very far deep sea environments. Thus, land and deep sea appear much more connected than previously assumed in a region where coastal pollution represents a crucial threat for large areas of the Mediterranean Sea.

Supplementary Material

Additional Information regarding materials and methods are detailed descripted and shown in Figure S1-S4 and Table S1-S2.

Acknowledgments

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References

Allen, E.; Durrieu de Madron, X.; 2009. A review of the role of submarine canyons in deep-ocean exchange with the shelf. Ocean Sci., 5, 607-620.

Aller, R.C.; Cochran, J.K.; 1976. 234Th/238U disequilibrium in near-shore sediment: particle reworking and diagenetic time scales. Earth and Planetary Science Letters, 29, pp. 37-50.

Appleby, P.G.; Oldfield, F.; 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported 210Pb to the sediment. Catena 5, 1–8.

Appleby, P.G.; Oldfield, F.; 1992. Application of lead-210 to sedimentation studies, in: Ivanovich, M., Harman, R.S. (Eds.), Uranium-Series Disequilibrium: Application to Earth, Marine, and Environmental Sciences. Clarendon Press, Oxford.

Baskaran, M.; 2011. Handbook of Environmental Isotope Geochemistry, Media, Advances in Isotope Geochemistry. Springer.

Baskaran, M.; and Santschi, P. H.; 1993. The role of particles and colloids in the transport of radionuclidcs in coastal environments of Texas. Mar. Chem. 43,95-114.

Basso, D.; Thomson, J.; Corselli, C.; 2004. Indications of low macrobenthic activity in the deep sediments of the eastern Mediterranean Sea 68, 53–62. doi:10.3989/scimar.2004.68s353.

Canals M.; Puig P.; Durrieu de Madron X.; Heussner S.; Palanques A.; Fabrés J.; 2006. Flushing submarine canyons. Nature, 444 , 354-357.

Canals, M.; Casamor J.L.; Lastras G.; Monaco A.; Acosta J.; Berné S.; Loubrieu B.; Weaver P.P.E.; Grehan A.; Dennielou B.; 2004. The role of canyons on strata formation. Oceanography, 17, 80-91.

Canals, M.; Puig, P.; Durrieu de Madron X.; Heussner, S.; Palanques, A.; Fabrés, J.; 2006. Flushing submarine canyons. Nature, 444, 354-357.

Carroll, J.; Lerche, I., 2003. Sedimentary Processes: Quantification Using Radionuclides. Elsevier, Oxford.

Carter, L.; Milliman, J.D.; Talling, P.J.; Gavey, R.; Wynn, R.B.; 2012. Near-synchronous and delayed initiation of long run-out submarine sediment flows from a record-breaking river flood, offshore Taiwan. Geophys. Res. Lett., 39, Article L12603.

Cossellu, M.; 2007. Sedimentologia e processi deposizionali della piattaforma continentale di Calgiari dal Last Glacial Maximum all'attuale. PhD Thesis, Università degli Studi di Cagliari, pp. 218.

Covaci, A.; Losada, S.; Roosens, L.; Vetter, W.; Santos, F.J.; Neels, H.; Storelli, A.; Storelli, M.M.; 2008. Anthropogenic and naturally occurring Organobrominated compounds in two Deep-Sea fish species from the Mediterranean. Environ. Sci. Technol. 42, 8654–8660. http://dx.doi.org/10.1021/es8016528.

Cutshall, N.H.; Larsen, I.L.; Olsen, C.R. ; 1983. Nucl. Instr. and Meth., 206, p. 309.

Fabres, J.; Tesi, T.; Velez, J.; Batista, F.; Lee, C.; Calafat, A.; Heuss- ner, S.; Palanques, A.; and Miserocchi, S.; 2008. Seasonal and event- controlled export of organic matter from the shelf towards the Gulf of Lions continental slope, Cont. Shelf Res., 28, 1971– 1983.

Fernandez-Arcaya U.; Ramirez-Llodra E.; Aguzzi J.; Allcock A. L.; Davies Jaime S.; Dissanayake Awantha, Harris P.; Howell K.; Huvenne Veerle A. I.; Macmillan-Lawler M.; Martín J.; Menot L.; Nizinski M.; Puig P.; Rowden Ashley A.; Sanchez F.; Van den Beld Inge M. J.; 2017. Ecological Role of Submarine Canyons and Need for Canyon Conservation: A Review. Frontiers in Marine Science 4, 1-5.

Froescheis, O.; Looser, R.; Cailliet, G.M.; Jarman,W.M.; Ballschmiter, K.; 2000. The deep sea as a final global sink of semivolatile persistant organic pollutants? Part I: PCBs in surface and deep-sea dwelling fish in the North and South Atlantic and the Monteray Bay Canyon (California). Chemosphere 40, 661–670. http://dx.doi.org/10.1016/S0045-6535(99)00462-2.

Garcia-Orellana, J.; Sanchez-Cabeza, J.A.; Masqué, P.; Àvila, A.; Costa, E.; Loÿe-Pilot, M.D.; Bruach-Menchén, J.M.; 2006. Atmospheric fluxes of 210Pb to the western Mediterranean Sea and the Saharan dust influence. J. Geophys. Res. Atmos. 111, 1–9. doi:10.1029/2005JD006660.

Hancock, G.; Edgington, D.N.; Robbins, J.; Smith, J.N.; Brunskill, G.; Pfitzner, J.; 2000. Workshop on radiological techniques in sédimentation studies: methods and applications 19.

IAEA; 2004. Sediment distribution coefficients and concentration factors, for biota in the marine environment. International Atomic Energy Agency. Technical report, series 422, Vienna, Austria.

IHO—International Hydrographic Organization; 2008. IHO Standards for Hydrographic Surveys. Special Publication, 44. Published by the International Hydrographic Bureau, Monaco, pp. 28.

Jamieson, A.J.; Malkocs, T.; Piertney, S.B.; Fujii, T.; Zhang, Z.; 2017. Bioaccumulation of persistent organic pollutants in the deepest ocean fauna. Nat. Ecol. Evol. 1, 1–4. http://dx.doi.org/10.1038/s41559-016-0051.

Kalb, C.; 2008. I sedimenti superficiali della Piattaforma interna del Golfo di Cagliari. Relazioni tra moto ondoso, correnti indotte e processi di sedimentazione su sistemi di spiaggia campione. PhD Thesis, Università degli Studi di Cagliari, pp. 295.

Khripounoff, A.; Crassous, P.; Lo Bue, N.; Dennielou, B.; Silva Jacinto, R.; 2012. Different types of sediment gravity flows detected in the Var submarine canyon (northwestern Mediterranean Sea). Prog. Oceanogr., 106, 138-153.

Lecca L.; Panizza V.; Pisano S.; 1998. The sedimentary framework of Cagliari Basin: a Plio-Quaternary underfed rift basin in the southern Sardinia margin. Il Quaternario Italian Journal of Quaternary Sciences, 11(2), 301-318.

Lecroart, P.; Maire, O.; Schmidt, S.; Grémare, A.; Anschutz, P.; Meysman, F.J.R.; 2010. Bioturbation, short-lived radioisotopes, and the tracer-dependence of biodiffusion coefficients. Geochim. Cosmochim. Acta 74, 6049–6063. doi:10.1016/j.gca.2010.06.010.

Ligero, R.; Barrera, M.; Casas-Ruiz, M.; Sales, D.; López-Aguayo, F., 2002. Dating of marine sediments and time evolution of heavy metal concentrations in the Bay of Cádiz, Spain. Environ. Pollut. 118, 97–108. doi:10.1016/S0269-7491(01)00209-3.

Lohmann, R.; Breivik, K.; Dachs, J.; Muir, D.; 2007. Global fate of POPs: current and future research directions. Environ. Pollut. 150, 150–165. http://dx.doi.org/10.1016/j.envpol.2007.06.051.

Masqué, P.; Sanchez-Cabeza, J.A.; Bruach, J.M.; Palacios, E.; Canals, M.; 2002. Balance and residence times of 210 Pb and 210 Po in surface waters of the northwestern Mediterranean Sea. Cont. Shelf. 22, 2127–2146. doi:10.1016/S0278-4343(02)00074-2.

Meleddu, A.; Deiana, G.; Paliaga, E.M.; Todde, S.; Orrù, P.E.; 2016. Continental shelf and slope geomorphology: marine slumping and hyperpycnal flows (Sardinia Southern continental margin, Italy). Geogr. Fis. Dinam. Quat. 39, 183-192, DOI 10.4461/ GFDQ 2016.39.

Micallef, A.; Ribó, M.; Canals, M.; Puig, P.; Lastras, G.; Tubau, X.; 2014. Space-for-time substitution and the evolution of a submarine canyon-channel system in a passive progradational margin. Geomorphology, 221, 34-50.

Munsell, A.H.; 1994. Munsell Soil Color Charts. Rev. ed. Gretag Macbeth, NewWindsor, NY.

Nieuwenhuize, J.; Maas, Y.E.M.; Middelburg, J.J.; 1994. Rapid analysis of organic carbon and nitrogen in particulate materials. Mar. Chem. 45, 217-224.

Orrù, P.E.; Deiana, G.; Meleddu, A.; Paliaga, E.; Todde, S.; 2014. Movimenti di massa in scarpata superiore del Margine meridionale sardo, controllo tettonico e dinamica evolutiva (Golfo di Cagliari - Sardegna Meridionale). Poster. URL http://www.ritmare.it/area-download/category/34-workshop-ritmare-bologna-2014?download=138:05-orru-et-al-sp4.

Pham, M.K.; Povinec, P.P.; Nies, H.; Betti, M.; 2013. Dry and wet deposition of 7Be, 210Pb and 137Cs in Monaco air during 1998-2010: Seasonal variations of deposition fluxes. J. Environ. Radioact. 120, 45–57.

Piper, D.J.W.; Normark, W.R.; 2009. Processes that initiate turbidity currents and their influence on turbidites: a marine geology perspective. J. Sediment. Res., 79, 347-362.

Puig P.; Palanques A.; Martín J.; 2014. Contemporary sediment-transport processes in submarine canyons. Annu. Rev. Mar. Sci., 6, 53-77.

Puig, P.; Durán, R.; Muñoz, A.; Elvira, E.; Guillén, J.; 2017. Submarine canyon-head morphologies and inferred sediment transport processes in the Alías-Almanzora canyon system (SW Mediterranean): On the role of the sediment supply. Marine Geology, 393, 21-34.

Robbins, J.A.; 1978. Geochemical and geophysical applications of radioactive lead isotopes, in: Nriagu, J.O. (Ed.), Biochemistry of Lead. Elsevier.

Robbins, J.A.; Edgington, D.N.; 1975. Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. Geochim. Cosmochim. Acta 39, 285–304. doi:10.1016/0016-7037(75)90198-2.

Scheringer, M.; Jones, K.C.; Matthies, M.; Simonich, S.; van de Meent, D.; 2009. Multimedia partitioning, overall persistence, and long-range transport potential in the context of POPs and PBT chemical assessments. Integrated Environmental Assessment and Management 5, 557–576.

Shepard, R.P.; 1981. Submarine canyons: multiple causes and long-time persistence. Am. Assoc. Pet. Geol. Bull., 65, 1062-1077.

Smith, J.N.; 2001. Why should we believe 210Pb sediment geochronologies? J. Environ. Radioact. 55, 121–123. doi:10.1016/S0265-931X(00)00152-1.

Storelli, M.M.; Losada, S.; Marcotrigiano, G.O.; Roosens, L.; Barone, G.; Neels, H.; Covaci, A.; 2009. Polychlorinated biphenyl and organochlorine pesticide contamination signatures in deep-sea fish from the Mediterranean Sea. Environ. Res. 109:851–856. http://dx.doi.org/10.1016/j.envres.2009.07.008.

Talling, P.J.; 2014. On the triggers, resulting flow types and frequencies of subaqueous sediment density flows in different settings. Mar. Geol., 352, 155-182.

US-EPA (Environmnetal Protection Agency); 2007. Method 7473. Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry.

van Beek, P.; Sternberg, E.; Reyss, J.-L.; Souhaut, M.; Robin, E.; Jeandel, C.; 2009. 228Ra/226Ra and 226Ra/Ba ratios in the Western Mediterranean Sea: Barite formation and transport in the water column. Geochim. Cosmochim. Acta 73, 4720–4737. doi:10.1016/j.gca.2009.05.063.

van Wijngaarden, S. J.; Steeneken, H. J. M.; and Houtgast, T.; 2002. Quantifying the intelligibility of speech in noise for nonnative listeners. J. Acoust. Soc. Am. 111(4), 1906–1916.

Waples, J.T.; Benitez-Nelson, C.; Savoye, N.; Rutgers van der Loeff, M.; Baskaran, M.; Gustafsson, Ö.; 2006. An introduction to the application and future use of 234Th in aquatic systems. Mar. Chem. 100, 166–189. doi:10.1016/j.marchem.2005.10.011.

Figure captions

Figure 1 A) Location Map of Gulf of Cagliari. B) Digital Terrain Model (DTM) of the SE sector of Sardinia. CG= Gulf of Cagliari; BK=Banghittu Knoll; A-TT=Algerian-Tyrrhenian Trough; CR=Carbonara Ridge; CV=Carbonara Valley; SPC, PC, SC and SEC=Spartivento, Pula, Sarroch and San'Elia-Foxi canyons. White capital letters are locations of sampling stations. C) Elevation profile extracted from the DTM (location is in B).

Figure 2 A) and B) ΣPAHs, ΣPCBs, Hg, As and Pb concentrations *vs* age in the A2TM and A3TM sediment cores. Box-whisker plot of silt fraction subdivided in three time intervals (values in %), is also reported for A2TM sediment core. C), D) and E) ΣPAHs, ΣPCBs, Hg, As and Pb concentrations *vs* depth in the A4TM, A6TM and A7TM. Grey bands marks the presence of ^{137}Cs released in the last 60 years.

Figure 3 A) Map showing the distances from Cagliari (which is the main source of sediments in the Gulf of Cagliari) to the sampling stations (A2TM, A3TM, A4TM and A6TM) and the distance *vs* derived ^{137}Cs Inventory plot (B). C) "Morphologic distance" (i.e. the true distance covered by sediments) calculated taking into account the morphology of the seafloor and its corresponding higher fitting distance *vs* ^{137}Cs Inventory plot (D).

Figure 4 The "morphologic distance", previously mentioned, *vs* ^{137}Cs Inventory calculated considering its terrigenous component (i.e. by subtracting A7TM value) and Hg and Zn "normalised" inventories (see text for further details) for A2TM, A3TM, A4TM and A6TM.

Figure 5 ^{137}Cs inventories *vs* ΣHPAHs, ΣPCBs, Hg, Cu, Zn and Pb plots for all sampling stations.

Table captions

Table 1 Table of coordinates and water depth of the studied sediment cores together with sampling site and core length (cm).

Table 2 Inventories values of ^{210}Pb, ^{137}Cs, ΣHPAHs, ΣPCBs and TEs for the studied sediment cores.

Supplementary Figures

Figure S1 ^{210}Pb and ^{137}Cs activity profiles of A2TM, A3TM, A4TM, A6TM, A7TM sediment cores collected in the SE Sardinia with indication of water depth (m).

Figure S2 Comparison between the measured and the estimated value of $^{210}Pbxs$ flux at the water-sediment interface for the studied sediment cores. Fa + Fm = atmospheric + water production $^{210}Pb_{xs}$ flux; Fs = sediment water interface $^{210}Pb_{xs}$ flux.

Figure S3 On the left is shown the slope map derived by the DTM of Cagliari, while the right part of the figure displays the flow patterns of sediments.

Figure S4 Profiles of grain size composition *vs* depth (cm).

Supplementary Tables

Table S1 Mean values of Al, Fe, Mn Cd, Pb, Co, V, As, Cr, Cu, Ni, Zn, Hg, TOC, TN, ΣPAH and ΣPCB.

Table S2 Mean values activity of ^{226}Ra, ^{40}K, and supported ^{234}Th (Bq kg^{-1}, dry weight). ^{234}Thxs downcore mass-depth with in square brackets the depth value in cm. ^{210}Pbxs and ^{137}Cs inventories are also reported.

Table 1

Area	ID station	Latitudine N	Longitudine E	Depth mbsl	Legth cm
Gulf of Cagliari (Sant'Elia-Foxi Canyon; SEC)	**A2TM**	39°05'34"	09°21'29"	625	33
Gulf of Cagliari (Sarroch Canyon; SC)	**A3TM**	39°00'21"	09°18'00"	636	36
Gulf of Cagliari (Carbonara Canyon; CC)	**A4TM**	38°59'01"	09°29'22"	907	28
Gulf of Cagliari (Pula Canyon; PC)	**A6TM**	38°46'05"	09°12'07"	787	29
SE Sardinia (Trough;A-TT)	**A7TM**	38°43'29"	09°40'36"	1153	22

Table 2

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Inventory	^{137}Cs	$\Sigma HPAHs_{antr}$	$\Sigma PCBs_{antr}$	Hg_{antr}	V_{antr}	Cu_{antr}	Pb_{antr}	Zn_{antr}	As_{antr}	Cd_{antr}	Co_{antr}	Cr_{antr}	Ni_{antr}
	Bq m^{-2}	mg m^{-2}	µg m^{-2}	µg m^{-2}	mg m^{-2}	mg m^{-2}	mg m^{-2}	mg m^{-2}	mg m^{-2}	mg m^{-2}	mg m^{-2}	mg m^{-2}	mg m^{-2}
A2TM	740	4.6	66	9724	6019	1077	5004	6250	2165	45	474	2961	1351
A3TM	560	1.6	37	5614	2357	657	1600	2903	628	24	182	1482	617
A4TM	450	1.2	4.1	2724	2491	424	1153	1758	1929	28	205	1759	576
A6TM	360	0.8	5.3	2572	938	292	693	731	816	24	136	730	553
A7TM	110	0.3	2.4	994	146	129	402	251	244	3	43	127	75

Figure 1

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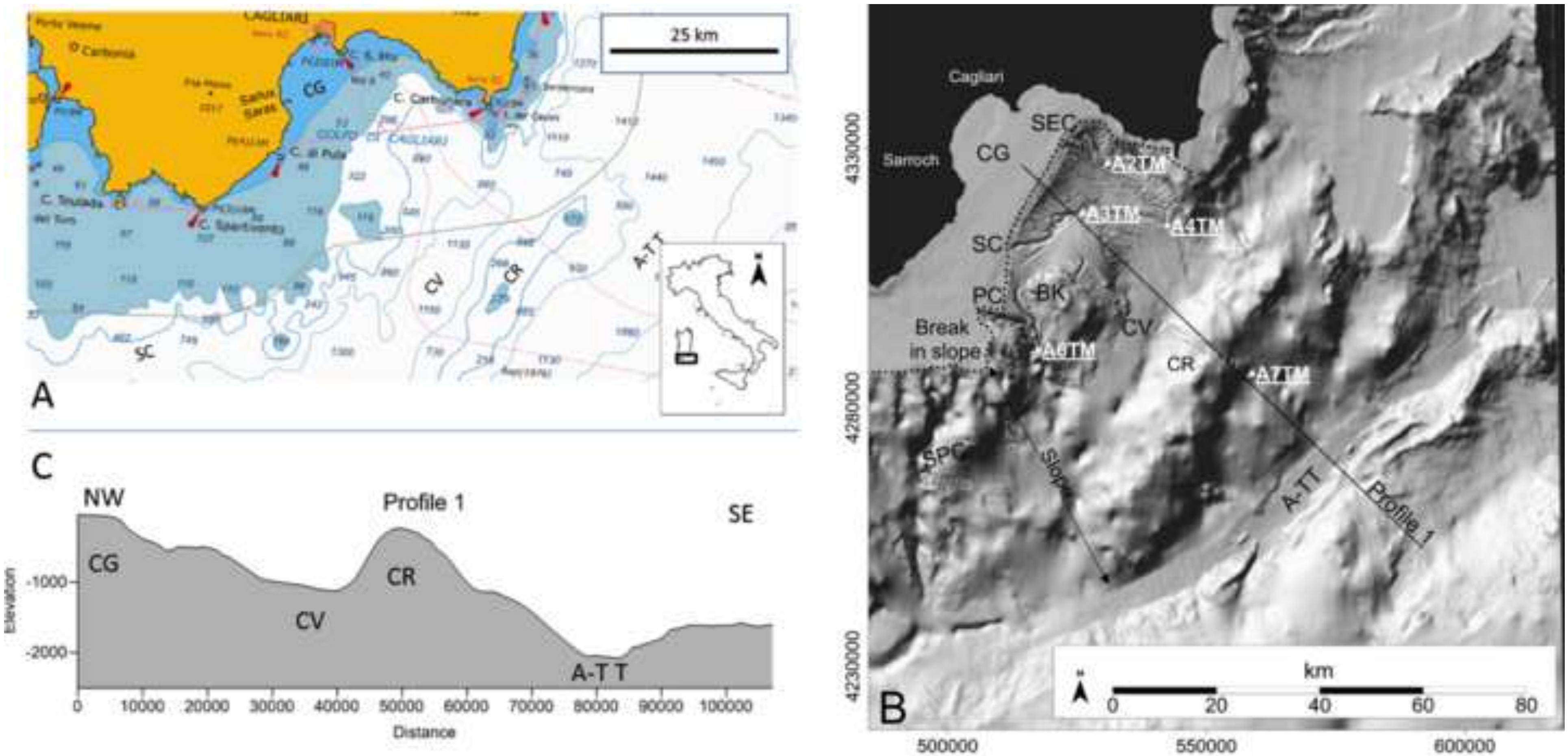

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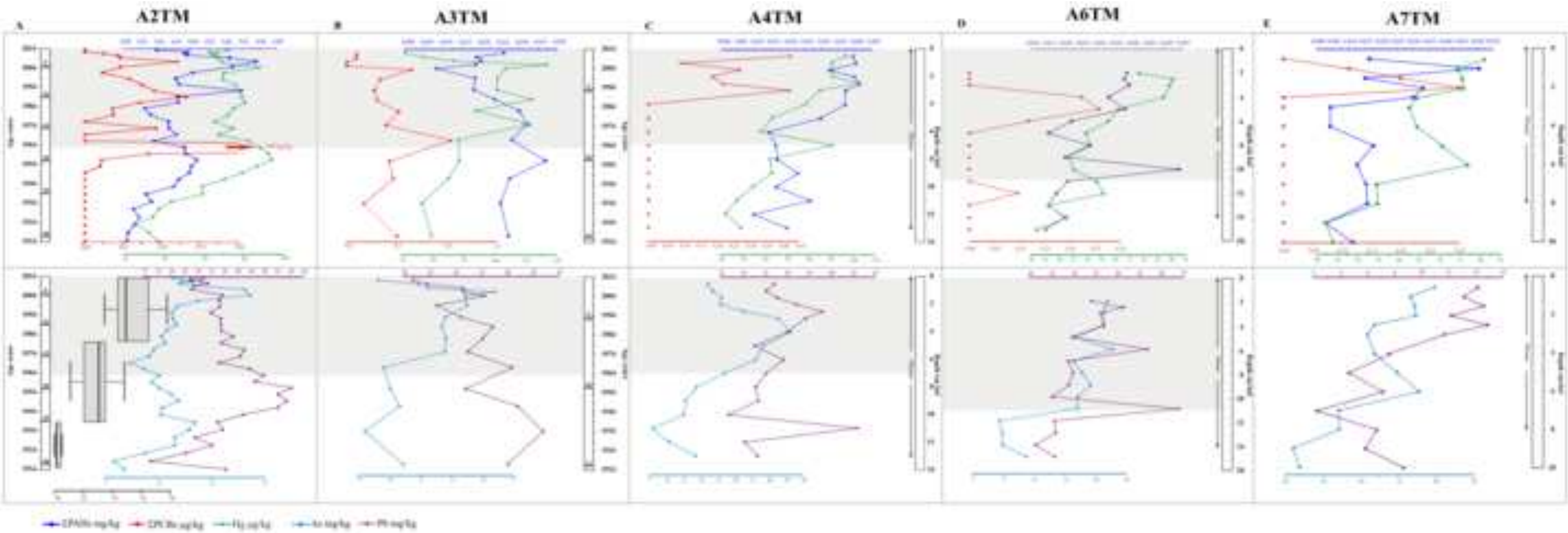

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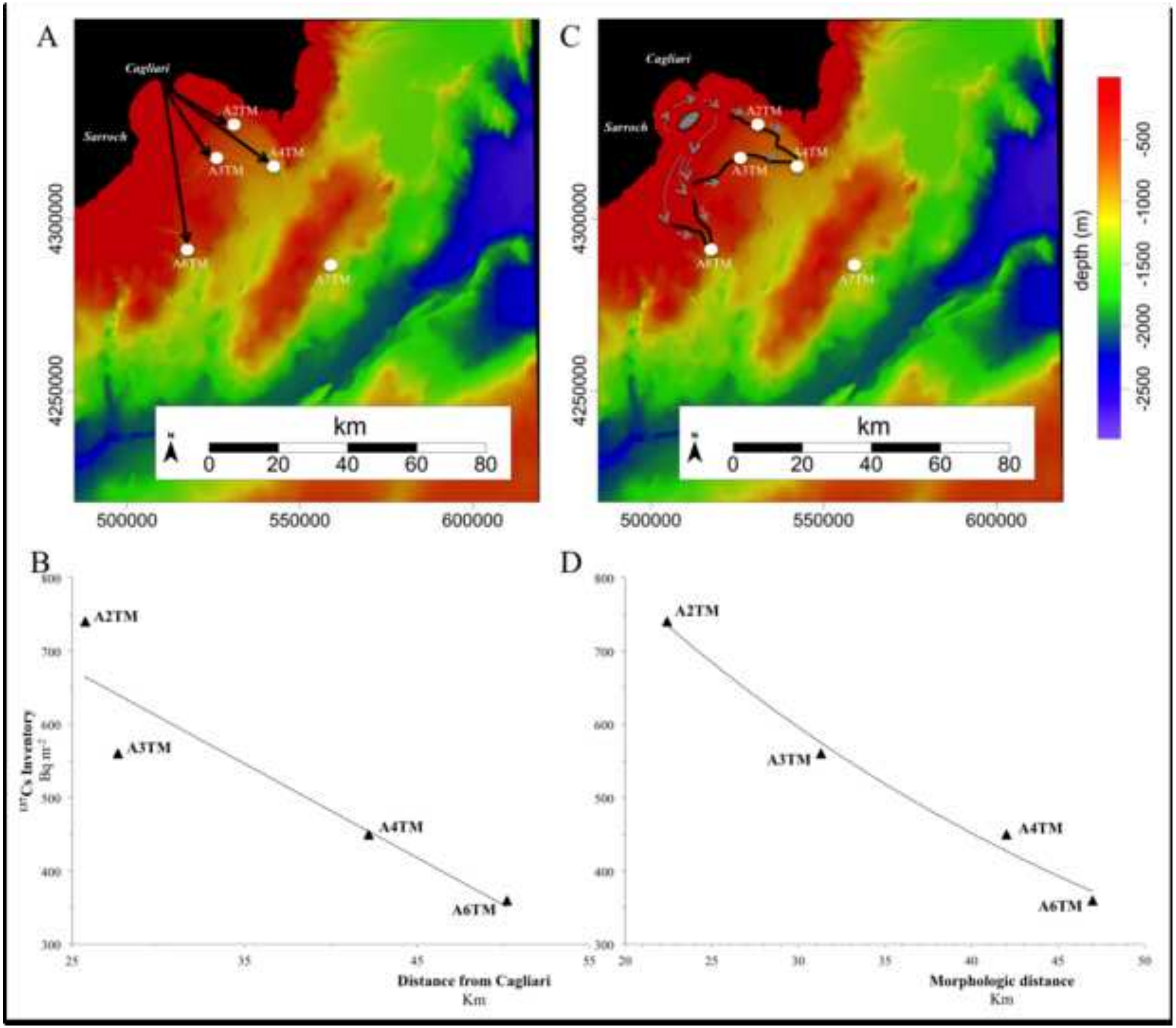

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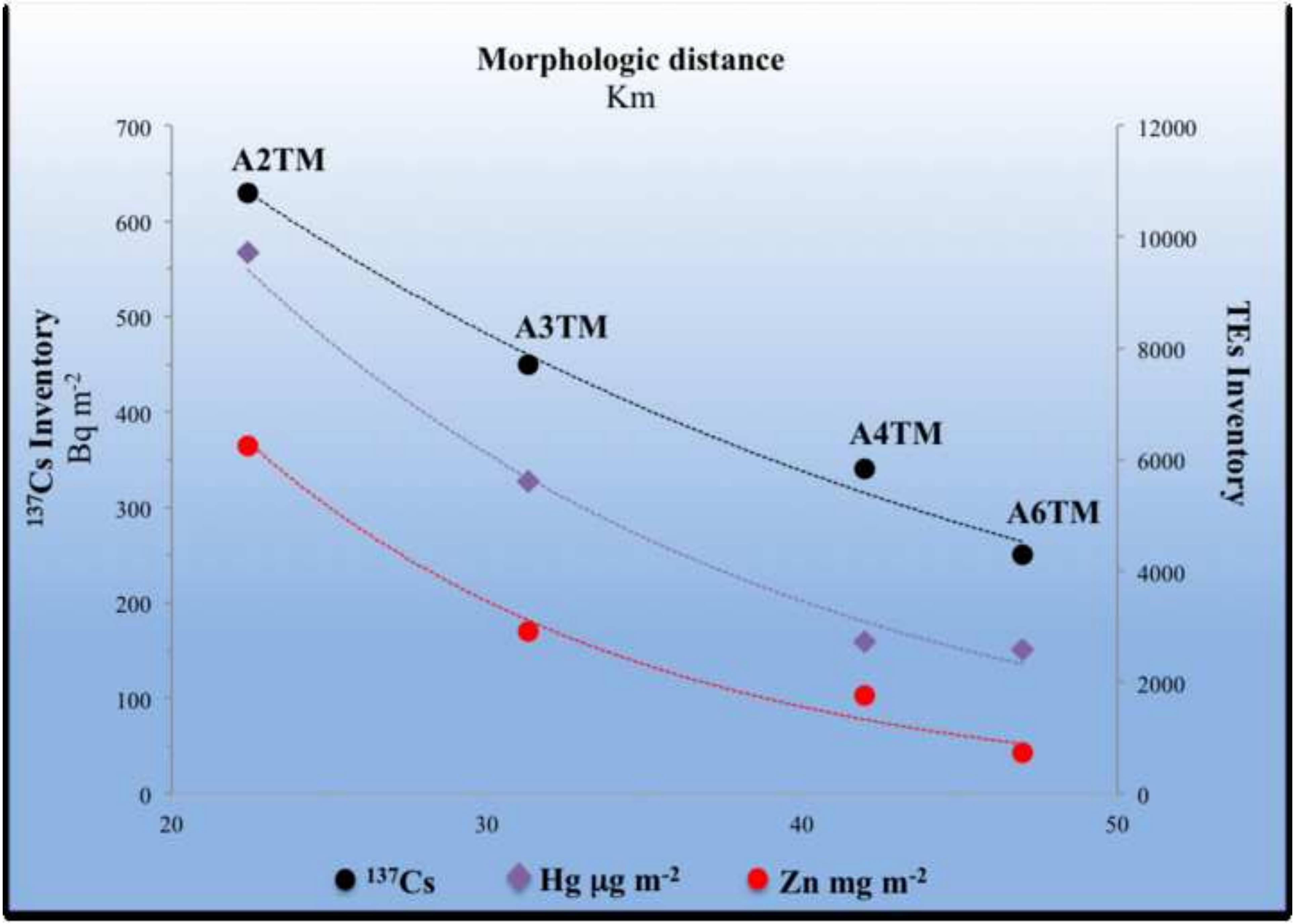

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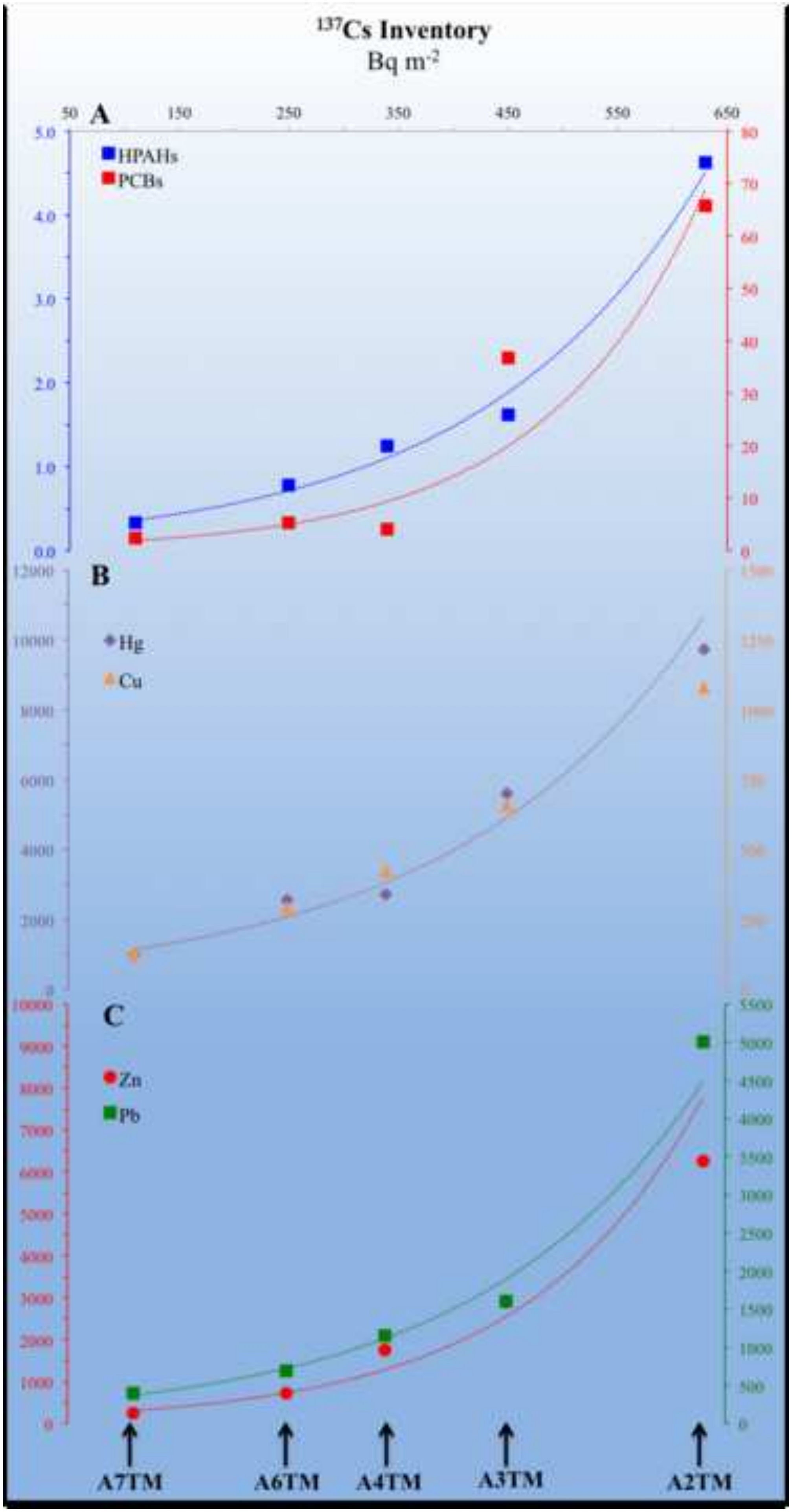

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