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## PAPER

# Soils and sediments of the Thua Thien-Hue Province (central Vietnam): recognizing trace element sources and the likely influence of natural events

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Trace element concentrations have been measured in soil and sediment samples taken from the Thua Thien Hue (TT-H) Province and the Tam Giang–Cau Hai (TG–CH) Lagoon in 2002 and 2004. Results show that the lagoon is only slightly contaminated by elements such as Ag, Cd, Cr, Cu, Ni, Pb and Zn, whereas As, probably naturally enriched in this Asian region, reaches values above the lowest internationally accepted sediment quality guidelines. Concentrations in soils are ascribable to natural sources and distributions in the TG–CH Lagoon are mainly influenced by river inputs, with Ag and Cd undergoing estuarine desorption processes. However, concentration–depth profiles of most trace elements in sediments show a recent increasing trend that might be linked to the economic development of the area. The comparison of porosity and <sup>210</sup>Pb depth profiles (confirmed also by Cd and As) from repeated samplings of the same core locations in the TG–CH Lagoon seems to account for a loss of 5–10 cm of surficial sediment that took place during the time interval between the two samplings. It is hypothesized that extreme meteorological events (*e.g.* a major typhoon that hit the area in November 2003) could be responsible for such sediment displacement.

#### 1. Introduction

The presence of anthropogenic trace elements in air, soil, and water represents a growing threat to the environment. To the public, trace element contamination and pollution is a problem associated with areas of intensive industrialisation (including metallurgy, coal burning, paper, fertiliser, other chemical productions, *etc.*) but there are many other less expected sources,<sup>1</sup> such as roadways, traffic and, in some cases, military operations. Whatever the source, once released into the environment most trace elements interact with fine particles and, in the aquatic environment, become part of the sediment. When this

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adsorption-settling process is continuous over time, sediments can act as recorders of contaminant inputs, as well as of general environmental changes.<sup>2–6</sup> However, under particular resuspending or redox conditions, they can also represent a source for toxic substances for the overlying waters and may affect wildlife and humans *via* the food chain.<sup>5</sup> For these reasons, the study of sediment cores is important for the definition of contamination history and sources, and for the assessment of potential toxicological effects to the biota. In addition, site sampling repetitions in different years can highlight the effect of short-time scale events (*i.e.* those extending for few days or weeks, such as floods or typhoons) that are difficult to recognize in the records of cores sampled only once.

In Vietnam, the information about pollutant sources and distribution is very poor, despite the Indochinese War-related events (1945–1975) and the recent economic development are supposed to have produced a strong impact on the environment. In this study we aimed at partly filling this gap, presenting the results of trace element analysis in waters and sediments of the TG–CH Lagoon and soils of the surrounding TT-H Province in

#### **Environmental impact**

This paper describes a scientific approach that can be useful for the identification of input sources and natural events' influence on contaminant levels and distributions. In our opinion, this information is essential for an effective management of natural resources. In the present work, we describe the case study of the Thua Thien-Hue province in central Vietnam.

central Vietnam. Furthermore, two lagoon sites were sampled twice to get an insight into the short-term changes of the system.

#### 2. Study area

TT-H is a Vietnamese Province, approximately located in the centre of the country (Fig. 1). Its capital, Hue, was once the imperial capital of Vietnam and is today a small city of about 300 000 inhabitants. The entire province and the city of Hue were the scenes of many military operations during the war, being close to the De-Militarized Zone where most of the conflicts took place (*e.g.* the Tet offensive in January–February 1968<sup>7</sup>), whereas in recent times the area is experiencing an increasing economic development, hosting some industries and large rice fields in the mainland, and aquaculture and fishing facilities along the lagoon shoreline (Fig. 1).

The topography of the province is heterogeneous, from mountains at the Laos–Vietnam border to the sea, passing through hills, plains and the TG–CH lagoon. This latter is the largest lagoon in south east Asia (70 km long and with a surface of 216 km<sup>2</sup>) and is composed of four parts with different shapes and extensions: (1) Tam Giang (27 km long, 0.6–3.5 km wide, up to 2 m deep) the major tributary of which is the O Lau River; (2) Dam Sam ( $5 \times 5.5$  km, 2 m deep) fed by the main tributary of the entire province, the Huong River; (3) Thuy Tu (24.5 km long, 0.8–2.6 km wide, up to 4 m deep), and (4) Cau Hai (a southernmost, semi-circular basin 17 km wide and 1–1.5 m deep) that is subject to the inflow of the small Truoi River (Fig. 1).

The geological setting of the province is characterized by the presence of Quaternary sedimentary rocks and Paleozoic formations, which emerged during the late-Hercynian folding of the Indochinese shield in the lower Triassic. These formations comprise Cambrian and thick Silurian series (schists, sandstones, *etc.*) and Devonian and Permo-Carboniferous limestones. Lower



**Fig. 1** Location and type of sampling sites in the TT-H Province (central Vietnam) and the TG–CH Lagoon. Major economic activities (large and small industries and aquaculture lots) are evidenced (from Nga<sup>44</sup>).

and middle Triassic series are mainly terrigenous (schists, sand-stones) and volcanic.<sup>8</sup>

The province has one of the world's biggest resources of titanium (as mineral sands) located in the Quang Nam deposit, in the vicinity of Hue, with reserves of 212 000 tons of ilmenite.<sup>9</sup>

#### 3. Methods

Study area and sampling locations for soils, sediments and water are shown in Fig. 1.

Sediments were collected in December 2002 with a manual piston corer that was used to retrieve both surficial samples (subscript "s") and short (50–70 cm) cores (subscript "c"). Sites 02c and 10c were re-sampled in June 2004. After collection, the cores were X-radiographed at the hospital of Hue City, and then extruded and sectioned at intervals of 2–4 cm, with higher resolution at the top. Sediment slabs were then divided into two parts for the different analyses, put in polyethylene vessels and stored in a refrigerator at 0 °C until the arrival to the lab. Afterwards, they were conserved at -18 °C until the analyses.

Water samples were collected in June 2004 by a plastic pump and stored at 4 °C in pre-cleaned Fluorinated Ethylene Propylene (FEP) bottles. They were successively filtered through polycarbonate membrane filters (0.4  $\mu$ m), acidified with 0.2% ultrapure HCl,<sup>10,11</sup> and stored in FEP bottles at -18 °C until analysis.

Soils were sampled in December 2002 around the lagoon (samples A–I, Fig. 1), and in June 2004 along transects that covered most of the TT-H Province (samples D1–4, G1–7, I1–5 and J1–3). They were collected by inserting a Plexiglass tube in the ground to obtain short cores (max 5 cm) that were then divided in two levels (0–2.5 and 2.5–5 cm), put in polyethylene vessels and stored at 4  $^{\circ}$ C until analysis. In case of hard and dry soils it was necessary to use a trowel to insert the tube.

Before analysis, sediments and soils were freeze dried and disaggregated. Sediment porosities were calculated according to Berner,<sup>12</sup> assuming a particle density of 2.5 g cm<sup>-3</sup>.

Grain size analyses were carried out by wet sieving, after a pretreatment with  $H_2O_2$ , to separate sands. Silt and clay fractions were determined with a X-ray sedigraph.

Organic carbon (OC) and total nitrogen (practically corresponding to the organic fraction, ON) contents, together with  $\delta^{13}$ C, were determined by a CHN analyser coupled to a mass spectrometer, after elimination of carbonates using HCl in a silver capsule. The ratio between OC and ON (C/N) was also calculated. Values for  $\delta^{13}$ C are reported as  $\%_{o}$  vs. PDB. Accuracy was tested by analysing Atropine and two certified standards (NIST and IGM), results being within the uncertainty limits. Precisions, estimated by replicate analyses of the same reference materials, were between 1% ( $\delta^{13}$ C) and 4% (%C and %N).

<sup>210</sup>Pb activities were measured through the extraction and alpha counting of the granddaughter <sup>210</sup>Po, considered in secular equilibrium with its parent. The radiotracer was extracted twice with hot HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, taken to dryness, acidified with conc. HCl to eliminate nitrates, dissolved with 1.5 N HCl, treated with ascorbic acid and spontaneously plated on silver discs overnight at room temperature. Alpha decays were counted by a silicon surficial barrier detector connected to a multichannel analyser. <sup>209</sup>Po was used as an internal standard to account for extraction

Table 1	TG-CH sediment characteristics: grain size (as % contents of sand, silt and clay) and organic matter (OC% concentrations,	C/N ratio and
$\delta^{13}$ C). V	Values for cores 02c and 10c are presented as ranges and average values (in <i>italics</i> , between parentheses)	

Sample	%Sand	%Silt	%Clay	%OC	C/N	δ <sup>13</sup> C (‰)
Tam Giang						
2c	4.3-15, (10)	56-66, (60)	27-32, (30)	1.1-1.7, (1.3)	10-12, (11)	-25.7/-24.1, (-25.0)
3s	19	53	28	n.d.	n.d.	n.d.
4s	93	4	3	n.d.	n.d.	n.d.
Dam Sam						
6s	32	55	13	0.21	8.0	-24.4
20s	21	58	21	n.d.	n.d.	n.d.
19s	55	29	16	0.53	8.7	-23.8
Thuy Tu						
18s	29	46	25	n.d.	n.d.	n.d.
17s	19	51	30	n.d.	n.d.	n.d.
16s	89	7	4	0.18	7.4	-23.9
15s	18	51	31	n.d.	n.d.	n.d.
Cau Hai						
11s	55	29	15	n.d.	n.d.	n.d.
7s	54	29	17	n.d.	n.d.	n.d.
8s	18	55	26	n.d.	n.d.	n.d.
9s	6	65	29	n.d.	n.d.	n.d.
10c	0.92-20, (10)	53-69, (61)	23-34, (29)	0.72 - 1.1, (0.90)	8.6-10, (9.5)	-23.5/-21.1, (-21.9)
14s	5	63	32	1.6	9.0	-21.4
13s	11	59	30	n.d.	n.d.	n.d.

and counting efficiencies. <sup>137</sup>Cs determinations were carried out by gamma counting of dry samples in standard vessels of suitable geometries. Analytical accuracy was checked using a Certified Reference Materials (IAEA 300 Sediment). Further details can be found in Bellucci *et al.*<sup>13</sup>

For metal and As analyses of soils and sediments, aliquots of 0.5 g were extracted under reflux with 10 ml of 8 N HNO<sub>3</sub> and 3 ml of 30% H<sub>2</sub>O<sub>2</sub>, at 120 °C for two hours (modified from Bellucci *et al.*<sup>14</sup>). This procedure allows the dissolution of elements bound to Fe–Mn oxides, carbonates and OC, all fractions that are likely available to the living biota; the surficial part of mineral grains is also leached, but the lattices remain untouched. The resulting solutions were filtered, diluted to 100 ml with Milli-Q water and then analysed by ICP-QMS (Agilent 7500) fitted with a standard double-pass spray chamber and a v-groove nebulizer (RF power 1400 W, sample gas 1.20 L min<sup>-1</sup>, sample flow rate 500  $\mu$ L min<sup>-1</sup>, dwell time 20 ms, and 3 points per peak).

Water samples were analysed for trace metals in agreement with the procedure described by Capodaglio *et al.*<sup>10</sup> and Turetta *et al.*<sup>11</sup> Briefly, measurements were carried out by ICP-SFMS (Element 2, Finnigan-MAT) in low resolution mode to determine Ag, Cd and Pb, medium resolution for Cr, Cu, Ni and Zn and high resolution for As. The sample introduction system was directed by a  $\mu$ Flow nebulizer with a Teflon spray chamber (Cr and Zn) or by a  $\mu$ Flow nebulizer coupled with a desolvation unit (Ag, As, Cd, Cu, Ni and Pb). To minimise matrix effects, solutions were diluted 10-fold with Milli-Q water and acidified up to 10% with ultrapure HNO<sub>3</sub> (UPA grade, Romil).

Quantification for all analysed matrices was carried out by a match calibration procedure using four aliquots of CASS-4, filtered coastal seawater certified reference material spiked with a multi-elemental standard solution.<sup>11</sup> Accuracy of results was tested by analysing Certified Reference Materials (CRM BCR-414 for sediments and soils, NRCC-CASS-4 for water). Results were within the uncertainty limits. Precisions, estimated by replicate analyses of the same reference material, were between 2 and 5% for most metals, with the exception of Cd (6%), and Ag (15%).

#### 4. Results

#### 4.1 TG–CH sediment features

Table 1 summarises the results regarding the characteristics of lagoon sediments (grain size and organic matter composition). According to the grain size distribution map of Lan *et al.*,<sup>15</sup> cores 10c and 02c, and the surficial sample at 19s were collected in areas characterized by rather fine sediment composition: fine silt, silt, and very fine sand, respectively. Our results show that both cores present values typical of clayey silt, according to Folk classification, whereas 19s is a silty sand (Table 1). This sample well represents the dynamic environment of the area, deeply influenced by both the mouth of the Huong River and the main lagoon inlet. Other sites located in dynamic environments are represented by samples 11s, 7s (both in the Cau Hai Lagoon), 16s (Thuy Tu Lagoon) and 4s in the Tam Giang Lagoon. These latter samples are the coarsest, being composed almost exclusively of sand (93 and 89%, respectively, Table 1).

The OC content ranges from 1.1 to 1.7% and from 0.72 to 1.1% in cores 02c and 10c, respectively (Table 1). In coarser sediments (6s, 19s and 16s, Table 1) the OC concentration is lower (0.18–0.53%, Table 1). The generally low values could be due to a number of factors, such as low production, high rate of decomposition of autochthonous organic matter, reduced input from rivers and/or dilution by mineral particles. C/N ratios are higher than 10 (10–12, Table 1) in core 02c, whereas values in core 10c range between 8.6 and 10.  $\delta^{13}$ C increases from north to south, passing from a minimum of  $-25.7\%_{00}$  at site 02c to a maximum of -21.1 in core 10c (Table 1).

Concentration-depth profiles of Al, Fe and Mn, measured in samples collected in 2006 at the same sites of cores 02c and 10c (Fig. 5) account for the absence of relevant redox-driven processes taking place in the sedimentary sequence.

Table 2 Tra	2 Trace element concentrations in sediments and waters of the TG-CH lagoon and in soils of the surrounding TT-H province. Values (in mg kg <sup>-1</sup> dw for sediments and soils and in µg L	J <sup>-1</sup> for
waters) are p	) are presented as ranges, whereas the average value is reported ( <i>in italics</i> ) between parentheses. Available international sediment guidelines (ERL and ERM, TEL and PEL in mg kg <sup>-1</sup> ) are	re also
shown		

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Area	Samples	Ti	V	Cr	Ni	Cu	Zn	$\mathbf{A}_{\mathbf{S}}$	Ag	Cd	Pb	U
TG-CH	Waters	n.d.	n.d.	0.04-0.27,	0.04 4.4,	0.01 - 0.12,	0.01 - 1.7,	0.21 - 1.6,	$6.1^{*}-0.03$ ,	0.01-0.12,	0.04-0.37,	n.d.
Lagoon				(0.16)	(2.2)	(0.07)	(0.86)	(0.91)	(0.02)	(0.07)	(0.21)	
TG-CH	Sediments	n.d.	8.9–69,	5.2-59,	4.3-32,	2.4-29,	11–90,	3.5-21,	0.06-0.15,	0.02 - 0.46,	3.0_29,	0.44-4.7,
Lagoon			(45)	(40)	(21)	(91)	(69)	(12)	(0.09)	(0.14)	(20)	(2.4)
TT-H	Soils	12 - 1589,	4.1 - 169,	2.9-92,	1.3-24,	2.4-64,	3.9-227,	0.8-33,	0.02 - 0.43,	0.05 - 0.55,	3.2-40,	0.64 - 3.6,
Province		(329)	(44)	(30)	(5.7)	(16)	(25)	(6.8)	(0.13)	(0.18)	(61)	(1.8)
Tam Giang	1-4	n.d.	12-40,	9.1 - 31,	4.7–17,	$3.0{-}18,$	24-82,	5.8 - 13,	0.07 - 0.15,	0.05 - 0.46,	6.1 - 26,	0.72 - 3.1,
Lagoon			(32)	(24)	(13)	(13)	(46)	(II)	(0.11)	(0.22)	(15)	(2.4)
Dam Sam	5, 6, 20, and 19	n.d.	14-69,	13-49,	6.5-26,	5.7-29,	25-72,	3.5-21,	0.06-0.09	0.05 - 0.09,	7.4-23,	0.92 - 2.6,
Lagoon			(35)	(28)	(15)	(15)	(45)	(10)	(0.08)	(0.08)	(14)	(1.5)
Thuy Tu	15-18	n.d.	8.9-57,	5.2-48,	4.3-23,	2.4 - 19,	11-83,	3.8 - 16,	0.06-0.10,	0.02 - 0.09,	3.0-28,	0.44 - 2.7,
Lagoon			(41)	(36)	(18)	(14)	(62)	(12)	(0.08)	(0.07)	(20)	(1.8)
Cau Hai	7–14	n.d.	28–66,	27-59,	15-25,	9.1-22,	53-80,	8.4–13,	0.09 - 0.11,	0.07 - 0.18,	17-29,	1.2-4.7,
Lagoon			(47)	(44)	(20)	(14)	(69)	(10)	(0.10)	(0.12)	(24)	(2.6)
Tam Giang	core 02c	n.d.	40-55,	32-44,	17-25,	15-23,	67–90,	8.3-15,	0.08-0.10,	0.13 - 0.39,	16-18,	2.1-2.9,
Lagoon			(46)	(37)	(20)	(18)	(20)	(12)	(0.09)	(0.22)	(17)	(2.6)
Cau Hai	core 10c	n.d.	45-57,	43-54,	23-32,	13-19,	65-81,	11 - 16,	0.06-0.09	0.06 - 0.11,	21–28,	2.1-2.8,
Lagoon			(53)	(52)	(28)	(17)	(74)	(13)	(0.07)	(0.07)	(23)	(2.4)
ERL-ERM <sup>a</sup>				81 - 370	20.9 - 51.6	34-270	150 - 410	8.2 - 70	1.0 - 3.7	1.2 - 9.6	46.7 - 218	
$\text{TEL-PEL}^{b}$				37–90	18–36	36–197	123–315	5.9–17		0.60 - 3.5	35–91	
<sup><math>a</math></sup> NOAA, 1999 (n.d. = not det	). <sup>b</sup> Burton, 2002. ermined. *: in ng $L^{-1}$	<u>.</u>										

#### 4.2 Trace element distributions and concentrations

Table 2 lists trace element concentration intervals and average values measured in waters, surficial sediments, and cores of the TG–CH lagoon, and in soils of the TT-H Province. Fig. 2 shows the surficial distribution of Cd, As, Ni and Pb in soils and surficial sediments of the Thua Thien Hue Province and the TG–CH lagoon. The spatial distributions of trace element contents were elaborated through the gridding interpolation, a method usually utilized by geoscientists to produces maps (the Generic Mapping Tools-free software<sup>16</sup>). An adjustable tension continuous curvature gridding algorithm was used from gridded values z(x,y). A mask grid with no data was matched on a map grid to limit the computing only to the study area.

Titanium concentrations are quite high, due to the presence of naturally enriched mineral sands in the proximity of Hue City (see above).

Trace element concentrations are unevenly distributed along the territory, with Cd and Ag (this latter is not shown in Fig. 2) presenting higher values in sediments of the northern part of the lagoon (Tam Giang Lagoon, samples 1–4, Table 2), in accordance with related soils. Interestingly, these two metals presented concentrations in waters and sediments of the northern lagoon that were inversely correlated ( $r^2 = -0.999$  and -0.980, respectively). This can be explained as the effect of estuarine-like processes that could cause desorption within the mixing zone between fresh and salt waters, with a consequent transfer from particles into solution. That was confirmed by the correlation between Cd concentration in water and conductivity (chlorinity) in the Tam Giang Lagoon (Fig. 3). No such evident correlation has been observed for the other elements that, in turn, show their maximum concentrations either in the estuarine areas (a pattern particularly evident for Cu in the Dam Sam Lagoon: samples 5, 6, 20, and 19; Table 2) or in the southernmost Cau Hai Lagoon (Cr, Ni, Pb and Zn: samples 7–14; Table 2 and Fig. 2). Although As distribution does not show significant differences between the 4 areas, a slightly higher concentration was observed in the central zone (Dam Sam Lagoon: samples 5, 6, 20, and 19; Table 2 and Fig. 2).

Values measured in sediment and soils of the TT-H Province and the TG–CH Lagoon can be considered relatively low in comparison to those found in human impacted areas, as shown in Fig. 4. Here, mean concentrations of Ni, Cu, Zn, As, Cd, and Pb in



-Cd conc. in water

Fig. 3 Trends of cadmium concentrations in waters and sediments and conductivity *vs.* distance from the O Lau estuary.



**Fig. 2** Spatial distribution of Cd, As, Ni and Pb in soils of the TT-H Province and in surficial sediments of the TG–CH Lagoon. The software used is the GMT, released under the GNU General Public License. Values are in mg kg<sup>-1</sup>. Major economic activities (see Fig. 1) are evidenced.

surficial sediments of the lagoon and in soils of the province are plotted together with selected literature results from all over the world. Sediment data are separated into three major groups, to account for different anthropogenic pressures and environmental settings: industrial areas,<sup>14,17,18</sup> coastal zones,<sup>19–22</sup> and lagoons.<sup>14</sup> For soils, literature values are grouped between areas influenced by human activities ("anthropogenic influences", Fig. 4)<sup>23–25</sup> and natural levels ("natural matrices", Fig. 4).<sup>26–29</sup> The average values measured in the TG–CH and TT-H Province are among the lowest, being comparable to the average values for other coastal environments. As for the soils of the TT-H Province, the measured concentrations do not exceed the ranges of natural reported values. Also element concentrations in water (Table 2) do not suggest significant contamination, being comparable to those detected in other coastal and lagoon areas.<sup>30,31</sup>

#### 4.3 Core chronologies

The assessment of a reliable core chronology based on radiotracer analysis (<sup>210</sup>Pb and <sup>137</sup>Cs) is weakened by the absence of a useful <sup>137</sup>Cs signal, as already reported by Frignani *et al.*,<sup>32</sup> and Giuliani *et al.*<sup>33</sup> Moreover, the most common conceptual models for the calculation of rates and dates with excess <sup>210</sup>Pb depth distributions <sup>34–36</sup> require specific conditions (*e.g.*, constant inputs of particles and/or radiotracer onto the sediment) that are not strictly met in a dynamic environment such as the TG–CH Lagoon.<sup>32</sup> Therefore, sediment accumulation rates (SARs) of 0.31 and 0.60 cm y<sup>-1</sup>, assigned to cores 10c and 02c, respectively, (on the basis of excess <sup>210</sup>Pb profile and the correlation between porosity and grain size downcore distributions<sup>32,33</sup>), have to be considered as apparent and probably overestimated values. Due



Fig. 4 Comparison with literature data of average surficial values for Ni, Cu, Zn, As, Cd and Pb in sediments of the TG–CH Lagoon and soils of the TT-H Province.

to these uncertainties, no dates are here associated to core depths at sites 02c and 10c.

#### 4.4 Depth profiles of trace elements and sediment parameters

Concentration-depth profiles for the analysed trace elements in cores 02c and 10c, collected in 2002 in the TG-CH Lagoon, are shown in Fig. 5. Values are quite constant, with core 02c presenting lower values at surface with respect to deeper sediments (*i.e.* V, Cr, Ni, Cu and Ag; Fig. 5), while core 10c shows slight minima for most parameters at 12–14 cm depth, a level characterised by a coarser grain size.<sup>32</sup> Lower surficial values are displayed in core 02c also by Zn and Cd profiles that, in addition, show consistent subsurface maxima between 35 and 45 cm depth. As, Pb and U depth profiles are characterized by values that are higher in the upper part of the core than at depth. The same is observed at 10c for V, Cr, Zn, Ag, Cd and Pb, with a more evident increasing trend for Pb in the uppermost 10 cm of the sedimentary section.

Profiles of As and Cd measured at the same locations resampled in 2004 are reported in Fig. 6, with surface values at 10c slightly higher than deeper layers, while core 02c presents recent increasing trends that determine surface values that are still below the subsurface maxima at 50–60 cm depth. The similarity of 2002 and 2004 profiles allowed the exclusion of any consistent lateral discontinuity.

In the same Fig. 6 are shown also the profiles of porosity and <sup>210</sup>Pb measured in the TG–CH cores collected during the two sampling campaigns. In all cases repeated profiles are quite similar, with generally higher values at the surface. Some differences are evidenced when considering the locations of minima and maxima, that, in 2004, are to be found at lower depths (from 5 to 10 cm in cores 02c and 10c, respectively) than 2002.

#### 5. Discussion

#### 5.1 Origin of trace elements in soils and lagoon sediments

Trace element concentrations in soils of the TT-H Province do not allow the recognition of any particular anthropogenic input.

On the contrary, the measured levels are consistent with those characterising different types of parent rocks (i.e. sandstone, limestone and granite; Fig. 4) that can be found in the territory.<sup>8,9</sup> The observed distributions (Fig. 2) are then to be ascribed almost exclusively to natural variations. It is true, however, that surficial concentration maxima have been measured in samples close to industrial zones (Cd, As, and Ag, this latter is not shown in Fig. 2) or near Hue City (Ni, Fig. 2), whereas Pb and Cr (this latter is not shown in Fig. 2) have a more homogeneous spatial distribution. Therefore, it seems that, even if the impact due to human activities cannot yet be discriminated from natural sources, some evidence in this regard are starting to appear. A further confirmation of a recent increasing influence of anthropogenic inputs is testified by TG-CH sediment core profiles that show slight increasing values in surface layers. The increases are more consistent in the southernmost Cau Hai basin, whose proximity to larger industrial settings and the slacker hydrodynamics in normal conditions<sup>37</sup> might enhance input and retention of pollutants in the sediments.

On the other hand, the distributions in surficial soils and lagoon sediments suggest a clear relationship between levels measured in sediments and inputs from the rivers that flow into the lagoon (Fig. 2). In addition, while minimum concentrations in sediments and soils are comparable, maximum values are always higher in soils except for Ni (Table 2 and Fig. 2). This picture provides a reliable evidence of the prevailing influence of fluvial loadings to the TG-CH Lagoon with respect to other sources (atmosphere and direct discharges). For example, Cd and Ag in soils are characterized by the highest values in the northernmost part of the TT-H Province, influencing directly the two sections of the TG-CH lagoon (Tam Giang and Dam Sam) where the city of Hue and the two main tributaries (O Lau and Huong rivers) are located (Fig. 1). Similarly, As and Ni (together with Cu and Zn, not shown in Fig. 2) present high values also in the southern catchment areas leading to the Thuy Tu and Cau Hai sections of the lagoon, where the Truoi river is located (Fig. 1).

The influence of terrestrial inputs in the northern sector of the TG–CH Lagoon is evidenced also by the presence of C/N ratios higher than 10 and  $\delta^{13}$ C values lower than –23 at site 02c (Table



Fig. 5 X-radiographs and depth distribution of trace elements, Al, Mn and Fe in cores 02c and 10c of the TG–CH Lagoon. X-Radiographs reveal fairly homogeneous sediment layers, with traces of bioturbation that are more evident at depth in core 10c.



Fig. 6 2002 vs. 2004: comparison of porosity, <sup>210</sup>Pb, Cd and As depth profiles in cores 02c and 10c.

1),<sup>38</sup> whereas a mixed terrestrial–autochthonous origin has to be considered for site 10c.

#### 5.2 Potential toxicity of trace metals

The potential threats to biota of lagoon sediments can be evaluated through the comparison of measured concentrations with internationally accepted Sediment Quality Guidelines (SQGs) that define threshold values above which adverse effects might be observed. Table 2 shows that most values for the measured elements lay below the NOAA ERL (Effect Range Low) threshold<sup>39</sup> and hence adverse effect on biota are unlikely to happen. Only As is higher than ERL in most soils and sediments. This means that this element could sometimes cause adverse

biological effects, but its higher-than-usual concentration in sediments and soils of the TT-H Province probably results from natural enrichment processes that affect the entire Indochinese region.<sup>40</sup>

The Threshold Effect Level (TEL) and the Probable Effect Level (PEL) guidelines for marine sediments<sup>41</sup> are generally more restrictive than NOAA ERL and ERM (Table 2), and using these values some more surficial sediments and soils exceed the lower limit for Cr, Cu, Ni and Pb, especially those located in the southernmost Cau Hai Lagoon and in proximity of the Huong river estuary (Table 2). This is also an indication that the concentrations of trace elements in the TT-H Province might generate adverse effects to the ecosystem, although specific bioassays should be carried out to assess the real ecotoxicity and to determine chemical reference levels specific for the Province and the whole Vietnamese coastline.

## 5.3 Sedimentary sequences and the influence of extreme meteorological events

The comparison of selected parameters measured in cores 02c and 10c collected in 2002 and 2004 (Fig. 6) evidences a change in the sedimentary sequences, *i.e.* the loss of the topmost layers in the time lag between the first sampling in 2002 and its repetition in 2004. This removal is clearly suggested by porosity and <sup>210</sup>Pb (Fig. 6), in that parts of the 2002 surficial profiles are lacking in 2004, the missing layer being about 10 cm at 02c and 5 cm at 10c, corresponding to 10.3 and 5.2 g cm<sup>-2</sup> of the sediment removed between the repeated samplings. This removal appears confirmed also by Cd, As, and Zn (this latter is not shown in Fig. 6) depth profiles in 2002 and 2004.

Although just two cores are not sufficient to draw conclusions for the whole lagoon, the presented results seem to give value to the hypothesis that sediments were resuspended around sites 02c and 10c and then displaced elsewhere. Since no information relative to dredging operations in the TG-CH Lagoon (or other heavily impacting human actions) has been reported between 2002 and 2004, such hypothetical removal should have had a natural cause, e.g. a particularly strong event that interested both Tam Giang and Cau Hai basins at the same time. The most important meteorological event in the period December 2002-June 2004 was the typhoon Nepartak<sup>42</sup> that hit the Philippines in mid-November 2003, then made its way northwest, towards Vietnam. On November 17th, 2003, the eye of the storm was just off the coast of Vietnam,43 with maximum sustained winds of 75 knots (*ca.* 140 km  $h^{-1}$ ). We believe that the typhoon was strong enough at that time to be able to resuspend the TG-CH sediments and cause the observed bias in the 2004 sequences.

It must be noticed that relevant changes seem to have recurred already in the TG–CH area. Indeed also Frignani *et al.*<sup>32</sup> hypothesized a past major environmental change through the observation of porosity, sand content, C/N ratio and  $\delta^{13}$ C profiles in cores 02c and 10c. This environmental change has been recorded in both basins, even though variations seemed more regular in the Cau Hai sector. However, the authors could not identify what originated that change, while a plausible explanation was possible in the present case, thanks to the sampling repetition over a short (~18 months) time scale.

#### 6. Conclusion

This paper describes the scientific approach developed for the study of trace element sources and distributions, together with dynamic processes in the TG–CH Lagoon (central Vietnam). This approach is based both on the sampling of different environmental matrices (soil, sediment, and water) and on the repetition of core sampling at the same lagoon sites in two different years.

The analysis of soil samples collected over the TT-H Province permitted to determine trace element (Ag, As, Cd, Cr, Cu, Ni, Pb and Zn) concentrations and distributions that are in good agreement with those observed in surficial sediments of the TG– CH lagoon collected in 2002, with concentration ranges in soils generally higher than in sediments. These results provided a reliable evidence of the greater influence of fluvial inputs to the lagoon with respect to other sources (*e.g.* atmosphere and direct discharge).

The influence of anthropogenic inputs could not be clearly evidenced, but recent increasing trends could be the effect of their growing importance. Therefore attention must be paid to avoid the worsening of the environmental quality with the rapid economic development of the area.

The impact of extreme climatic events has been hypothesized to explain the removal of significant amounts of sediment, as evidenced by depth profiles of some parameters in core samples at the same location after 1.5 years.

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