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4	An Integrated Approach to the Assessment of
5	Pollutant Delivery Chronologies to Impacted
6	Areas: Hg in the Augusta Bay (Italy)
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# 19 APPENDIX I

#### 20 Seismic survey and sampling

21 The Sub-Bottom Profiler CHIRP operates a frequency sweep between 2 and 7 kHz and provides digital 22 acquisition in SEG-Y format. The acquired seismic data (sampling interval: 125 msec) of the August 23 Bay and Port were processed and interpreted using the software SeisPrho (1). The high resolution (few 24 centimetres) of the CHIRP equipment permits to recognise the internal structures of the sediment 25 layers, discriminating between undisturbed, laminated sediment layers and chaotic sequences. In 26 addition, the excellent repeatability of the produced sonic signals allows the semi-quantitative 27 characterization of the bottom, based on the fact that the reflectivity coefficient (a parameter that 28 quantifies the acoustic energy bounced back by the bottom layer) is directly proportional to the content 29 of sand. Therefore CHIRP profiles of the Augusta Bay and Port and their relative surficial reflectivities 30 provided a reliable picture of bottom sediments in the area, helping identifying the sites where the grain 31 size is mostly fine and the sedimentation is continuous and undisturbed, i.e. those ideal for our research purposes. The seismic survey was realized from 15<sup>th</sup> to 18<sup>th</sup> October, 2003 and the routes are shown on 32 33 the map of Fig. S1. Some examples of the resulting seismic profiles (with the location of cores I, L, A, 34 H and G) and their relative surface reflectivity are also reported.

Sediment cores were collected with a gravity corer especially designed to preserve undisturbed sediment-water interfaces. The relatively large internal diameter (104 mm) also ensures minimal deformation of sediment structures. Dredged and dumping areas (Fig. 1) were carefully avoided, the same for zones close to piers. Table S1 summarises collection dates, coordinates and lengths of the cores.



Fig. S1. Map of the seismic survey realized in the Augusta bay and selected CHIRP profiles with the relative seismic surface reflectivities. Locations
 of the cores collected along the profiles are also shown.

Core	Sampling date	Latitude	Longitude	Length (cm)					
		Northern port							
L	21/10/03	37.2364419	15.2088939	59					
А	18/10/03	37.2284069	15.2113550	56					
В	18/10/03	37.2196539	15.2045261	47					
М	22/10/03	37.2184369	15.2167031	41					
С	18/10/03	37.2056944	15.1892611	1 50					
		Southern port							
D	18/10/03	37.1885481	15.1985639	47					
Ι	21/10/03	37.1838000	15.2018169	58					
Augusta Bay									
Н	21/10/03	37.2152361	15.2634883	41					
G	20/10/03	37.1916339	15.2608589	50					
F	20/10/03	37.1526661	15.2750131	47					
Е	20/10/03	37.1290261	15.2912919	38					

75	Table S1.	Collection d	lates, kil	lometric	coordinates	and l	ength o	f the sam	pled of	cores.
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76 77

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 interpretation of high-resolution seismic reflection profiles. *Comput. Geosci-UK* 2009, *35*, 1497–
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# 82 APPENDIX II

#### 83 Analytical methods

#### 84 <u>Magnetic susceptibility</u>

The collected cores were passed through an induction ring connected to a Bartington meter, measuring the susceptibility on each centimetre every 10 seconds. Background values were estimated with repeated measurements in air before and after the analysis.

88

## 89 <u>X-radiography</u>

90 Core x-radiography were performed in a local facility with a radiogenic industrial tube Gilardoni CPX-91 160 equipped with a Be window and industrial camera films. Cores were kept vertical and shielded by 92 a lead cradle. Exposition was adjusted according to the water content and was repeated when 93 necessary.

94

### 95 *Dry density and water content*

96 Sediments were weighted before and after the liophylization to measure the water content. Porosities
97 and dry densities were defined according to Berner (1), assuming a particle density of 2.5 g cm<sup>-3</sup>.

98

### 99 <u>Organic matter</u>

100 Approximately 10 mg of fine grounded sediments were weighted in silver capsules and treated with

101 HCl 2M to eliminate carbonates. Percent contents of C and N,  $\delta^{13}$ C and  $\delta^{15}$ N were then determined on

- 102 a Carlo Erba CHNS Elemental Analyser.
- 103

### 104 <u>Mineralogy</u>

105 The mineralogical composition was determined on grounded subsamples with a Philips PW 1710 CuK

106 X-ray diffractometre, operating at 30 mA and 40 kV, from 2° to 60°. The semi-quantitative

107 measurement of the percent content for each revealed mineral was based on peak intensity and108 correction for detection factors (2).

109

110 Grain size

111 Wet samples were previously left in  $H_2O_2$  for two days to eliminate the organic matter. The sandy 112 fraction was then separated through wet sieving at 63 µm, dried at 60 °C and weighted. Silt and clay 113 fractions were determined on sodium hexametaphosphate solutions (to avoid flocculation) with a X-ray 114 Micromeritic SediGraph set for analyses on a 4-12  $\varphi$  size range.

115

#### 116 Radionuclides

Alpha spectrometry of <sup>210</sup>Po was used for <sup>210</sup>Pb determinations, assuming secular equilibrium between 117 the two isotopes. <sup>210</sup>Po was extracted from the sediment with hot HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, in the presence of 118 <sup>209</sup>Po as a yield monitor, to account for extraction and counting efficiencies. After separation of the 119 120 leachate from the residue, the solution was evaporated to near dryness and the nitric acid was 121 eliminated using concentrated HCl. The residue was dissolved in 1.5 N HCl, and Po was plated onto a 122 silver disk overnight, at room temperature. Iron was reduced using ascorbic acid (3), and alpha decays 123 were counted by a silicon surficial barrier detector connected to a multichannel analyser. The analyses of the same sample with the two different <sup>209</sup>Po internal standards used at ISMAR (Bologna) and 124 MSRC (Stony Brook) gave nearly identical results, thus suggesting that the analyses were accurate. 125 Nevertheless, the accuracy of <sup>210</sup>Pb analyses was estimated also by repeated measurements of the 126 127 certified standard sediment IAEA 300 (Baltic Sea sediment) and the results were within the standard 128 uncertainties. In addition a successful intercalibration in the framework of the Euromarge-NB project 129 was carried out (4). Precision, calculated from independent analyses of the same sample, was 4.6%. <sup>137</sup>Cs was measured by non-destructive gamma spectrometry of dry samples in standard vessels of 130

131 suitable geometries. The analytical accuracy was periodically checked by counting the international

132 certificate standard IAEA Baltic Sea sediment, and the results were within the standard uncertainties. In 133 addition, two international intercalibrations (IAEA Proficiency test: Determination of Anthropogenic g-134 emitting Radionuclides in a Mineral Matrix, 2002; IAEA Proficiency test: Determination of  $\gamma$ -emitting Radionuclides, 2006) yielded <sup>137</sup>Cs activities within 4.1% and 1.6% of the IAEA accepted values. 135 136 respectively. Precision, estimated by repeated analyses of the same sample, ranged between 2.05 and 137 3.07%. Efficiencies on 10 ml geometries (3.12-3.18%) were calculated through a series of standards 138 obtained by spiking old sediment with a known amount of the Amersham QCY58 multi-peak standard solution. The analytical detection limit for  $^{137}$ Cs was 3 Bq kg<sup>-1</sup>. 139

- 140
- 141 Mercury

Sediments were stored at -18°C and then dried at 40°C, grounded and microwave extracted with 10 mL of conc. HNO<sub>3</sub>, as outlined in the EPA 3051A REV.1 procedure. The solutions were then centrifuged to remove the particulate present in the vessel and HNO<sub>3</sub> was removed by evaporation to near dryness with controlled purge gas.

146 Concentrations were determined following the method EPA 6010 C using an ICP-AES Spectro Ciros 147 and by flameless AAS to confirm the ICP-AES results. Reproducibility, obtained with repeated 148 measurements of the same sample, was 8.2 %. Recovery, defined with the standard MESS-1, was 81%. 149 The analytical detection limit was 0.1 mg kg<sup>-1</sup>.

150

#### 151 *Hexa-chlorobenzene*

For HCB analyses, a dried sample of ca. 10 g was spiked with  ${}^{13}C_{12}$ -HCB (CLM351; Cambridge Isotope Laboratories, Woburn, MA, USA) as internal standard and thoroughly mixed. The extraction was performed by ASE 200 (DIONEX Sunnyvale, CA) with a n-hexane/dichloromethane solution. The extracts were cleaned up using the automatic system, Dioxin Prep (Fluid Management System Inc.), then treated with sulphuric acid (98%) and potassium hydroxide (20%) and further eluted through an 157 automatic three-column system (method EPA 8270). The HRGC/HRMS analyses were made using a 158 HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer 159 equipped with a 60-m DB5 ms column (J&W 0.25 mm ID, 0.25-Am film). The quantitative 160 determination was performed by an isotope dilution method using relative response factors obtained 161 from five standard solutions injections (EC1668 Cambridge Isotope Laboratories, Woburn, MA). Three 162 <sup>13</sup>C 12-labeled PCBs (EC4979) were added to the extracts before injection for recovery calculations. 163 Recovery and reproducibility were 86 % and 2.1 %, respectively. The analytical detection limit was 1 164  $mg kg^{-1}$ .

165

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# 179 APPENDIX III

#### 180 Determination of chronologies and sediment accumulation rates

 $^{210}$ Pb<sub>ex</sub> derived sediment accumulation rates (S, cm y<sup>-1</sup>, Table 1) and relative chronologies were calculated assuming constant flux of the radiotracer and constant sedimentation (CF-CS). Under CF-CS assumptions, S is defined by the formula:

184 
$$S = -\lambda / M$$

where  $\lambda$  is the decay constant of the tracer (0.031 y<sup>-1</sup> for <sup>210</sup>Pb) and M is the angular coefficient of the semilogaritmic <sup>210</sup>Pb<sub>ex</sub> activity-depth plot. In this way, each sedimentary level can be associated to a year, providing the chronology of sediment deposition in the analysed cores (see Fig. 2 for <sup>137</sup>Cs profiles). S associated errors have been calculated from uncertainties defined for regression lines and sediment thicknesses.

Fig. S2 reports <sup>210</sup>Pb<sub>ex</sub> profiles for all cores and the regression lines that define M in the majority of 190 191 cases. Two regression lines (and, consequently, two estimates for S) have been calculated for core L (Fig. S2 and Table 1), since the  ${}^{210}$ Pb<sub>ex</sub> profile in this core shows a clear slope change at about 13 cm 192 depth, accounting for a decreased S in the topmost sediment layer. In core I, the <sup>210</sup>Pb<sub>ex</sub> depth 193 194 distribution did not allow the correct reconstruction of a regression line. In this case, a core to core 195 correlation approach was adopted, based on the position of magnetic susceptibility peaks in cores I and D (Fig. S3). The value of S for core I was then estimated as  $1.78 \text{ cm y}^{-1}$  (Table 1). The regression line 196 proposed for core G defines a value for S of 1.08 cm  $y^{-1}$  (Table 1), guite unrealistic when compared 197 with other cores from the Augusta Bay (1). In addition, the increment of  ${}^{210}$ Pb<sub>ex</sub> activity between 20-30 198 199 cm depth suggests that this core is highly disturbed, preventing any further discussion relative to chronology issues. The rapid decline of <sup>210</sup>Pb<sub>ex</sub> activity at 10-15 cm in core F might indicate either 200 201 surface mixing, or an erosional surface/unconformity at that depth. This latter was not evidenced by 202 CHIRP seismic profiles, therefore the hypothesis of surface mixing seems more realistic.

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Fig. S2. <sup>210</sup>Pb<sub>ex</sub> profiles (black) and relative semilogarithic regression lines (grey) for all cores but I, due to its unsuitable <sup>210</sup>Pb<sub>ex</sub> profile. Equations and R<sup>2</sup> values for each regression line are reported. Analytical <sup>210</sup>Pb errors (ca. 4.6% of the measured value, see relative section) are also shown as error bars.

# 214 APPENDIX IV

#### 215 Sediment composition and characteristics

X radiographs (not reported) show no clear structures, despite a diffused presence of shells and lightchanges in density.

Sediments are largely fine grained (Fig. S3), with silt plus clay contents well above 50%. The sole
exception is the surficial level in core E that is slightly coarser (43% of fines, Fig. S2).

Dry bulk densities increase generally with depth (Fig. S3), as a result of progressive downcore sediment compaction and water expulsion. The intermediate sections in cores M and C (i.e. 5-40 cm and 10-50 cm for M and C, respectively; Fig. S3) are characterised by rather constant values, lower than in upper levels. These layers may represent allochthonous material delivered to the sites in a relatively short period of time.

Magnetic susceptibility varies from a maximum of 3901 (core E, Fig. S3) to a minimum of 43 (core I, Fig. S3), probably as a consequence of different spatial and temporal accumulation of ferromagnetic and paramagnetic materials originating from the volcanic activity of Mount Etna. The contribution from this latter source might be evidenced by the many peaks observed at various depths (Fig. S3), and therefore we used magnetic susceptibility profiles to provide further confirmations to the <sup>210</sup>Pb<sub>ex</sub> chronology, as discussed in detail in the manuscript text.

231 The mineral composition is characterized by the predominance of calcite and quartz (Table S2) with 232 limited contribution of other minerals. Interestingly, pyrite has been detected only in cores collected 233 within the port and in core G (Table S2), as if the presence of this mineral in the area were linked to 234 well defined point sources, such as direct input from industrial settlements or autigenic formation in 235 sediments subject to strong anoxic conditions. Pyrite detection at site G might be the result of the 236 illegal dumping of dredged port materials along the routes to the disposal sites (Fig. 1). In turn, clay 237 minerals are higher in cores collected in the bay (Table S2), where the composition of sediments is 238 supposed to be less impacted by human activities.

Organic carbon (both %C and  $\delta^{13}$ C) and nitrogen ( $\delta^{15}$ N) compositions differentiate cores D and I from the others, in that they present the highest carbon content of the whole dataset, coupled with the most depleted  $\delta^{13}$ C and  $\delta^{15}$ N values (Table S2). These features account for the predominance of terrestrial and petrogenic sources (soils and plants for N, coal and crude oil for C) in the southern sector of the port where cores D and I are located.





257 Fig. S3. Profiles of magnetic susceptibility, dry density and percent silt plus clay contents.

$\gamma$	5	Q
4	$\mathcal{I}$	0

Core	Calcite	Quartz	Mg- calcite	Aragonite	Plagioclase	K- feldspar	Pyrite	Halite	Dolomite	Clay minerals	% C	%N	$\delta^{13}C$	$\delta^{15}N$
L	30/36	14/20	n.d./8	5/10	7/12	8/13	n.d./6	7/16	n.d./2	n.d./10	2.3/3.9	2.0/3.3	-19/-21	2.6/5.1
А	31/50	15/23	n.d./10	5/9	7/18	n.d./17	n.d./6	4/12	n.d.	n.d./7	2.2/3.1	0.2/0.3	-20/-21	1.5/5.1
В	29/44	15/20	n.d./8	5/9	7/28	7/20	n.d./5	4/10	n.d./3	n.d./3	2.1/2.6	0.2	-21/-22	3.5/4.3
Μ	27/39	15/20	n.d./22	8/17	5/9	6/8	n.d./5	6/11	n.d./2	n.d./7	2.2/4.4	0.1/0.3	-19/-21	0.9/4.2
С	38/70	12/24	n.d./9	n.d./11	8/18	n.d./12	n.d./4	2/7	n.d./3	n.d./3	1.7/2.6	0.1/0.2	-22/-24	0.9/3.7
D	37/65	12/20	n.d./12	8/16	n.d./8	n.d./15	n.d./3	2/21	n.d./6	n.d./2	2.4/6.2	0.2/0.3	-21/-24	-1.8/3.0
Ι	37/70	6/19	n.d./18	10/17	n.d./5	n.d./8	n.d./5	n.d./13	n.d./6	n.d./6	2.3/5.7	0.1/0.3	-21/-25	-3.1/3.4
Н	22/32	28/38	n.d./5	3/7	6/11	8/13	n.d.	3/8	n.d./3	5/14	1.1/1.5	0.1	-20/-22	3.6/5.2
G	23/35	20/32	n.d./9	5/11	6/23	6/13	n.d./4	3/7	n.d./4	2/11	1.3/2.2	0.1/0.2	-20/-23	3.4/4.6
F	18/33	28/35	n.d./7	5/8	7/19	6/14	n.d.	2/8	n.d./3	9/12	0.8/1.4	0.1	-21/-23	3.3/5.0
E	19/31	22/37	n.d./16	5/14	7/37	n.d./16	n.d.	3/5	n.d./2	3/12	0.6/0.9	0.1	-21/-22	3.8/4.5

**Table S2.** Mineral and organic matter composition (as % ranges) for the sampled cores.

n.d.= not detected