Article

Gaseous Elemental Mercury and Total and Leached Mercury in Building Materials from the Former Hg-Mining Area of Abbadia San Salvatore (Central Italy)

Orlando Vaselli [1,2,*], Barbara Nisi [3], Daniele Rappuoli [4], Jacopo Cabassi [1] and Franco Tassi [1,2]

[1] Department of Earth Sciences, Via G. La Pira, 4 – 50121 Florence, Italy; jacopo.cabassi@unifi.it (J.C.); franco.tassi@unifi.it (F.T.)
[2] CNR – Institute of Geosciences and Earth Research, Via G. La Pira, 4 – 50121 Florence, Italy
[3] CNR – Institute of Geosciences and Earth Research, Via Moruzzi, 1 – 56124 Pisa, Italy; b.nisi@igg.cnr.it
[4] Unione dei Comuni Amiata-Val D'Orcia, Via del Colombaio, 98 - 53023 Gallina, Castiglion d'Orcia, Siena , Italy; d.rappuoli@uc-amiatavaldorcia.si.it
* Correspondence: orlando.vaselli@unifi.it; Tel +39 055 2757508

Abstract: Mercury has a strong environmental impact since both its organic and inorganic forms are toxic and it represents a pollutant of global concern. Liquid Hg is highly volatile and it can be released during natural and anthropogenic processes in the hydrosphere, biosphere and atmosphere. In this study the distribution of Gaseous Elemental Mercury (GEM) and the total and leached mercury concentrations on paints, plasters, roof tiles, concretes, metals, dust and wood structures were determined in the main buildings and structures of the former Hg-mining area of Abbadia San Salvatore (Siena, Central Italy). The mining complex (divided into 7 units) covers a surface of about 65 ha and contains mining structures and managers and workers buildings. In this work, nine surveys of GEM measurements were carried out from July 2011 to August 2015 for the buildings and structures located in the units 2, 3 and 6. Moreover, detailed measurements were performed in February, April, July, September and December 2016 in the edifices and mining structures of Unit 6. GEM concentrations showed a strong variability in terms of space and time mostly depending on the distance from the building hosting driers, furnaces and condensers and ambient temperature, respectively. In the Unit 2 surveys carried out in the hotter period (from June to September) showed GEM concentrations up to 27,500 ng m^{-3}, while in the Unit 6 they were on average much higher and occasionally they saturated the GEM measurement device (>50,000 ng m^{-3}). Concentrations of total (in mg kg^{-1}) and leached (in μg L^{-1}) mercury measured in different building materials (up to 46,580 mg kg^{-1} and 4,470 mg L^{-1} for total and leached mercury, respectively) showed for the same type of material highly variable values in dependence on the edifice or mining structure from which they were collected. The results obtained in this study are of relevant interest for the operational cleanings to be carried out during the reclamation activities.

Keywords: gaseous elemental mercury; hg-mining areas; abbadia san salvatore; central italy; total and leached mercury; building material; remediation

1. Introduction

Total Gaseous Mercury (TGM) is referred to the sum of gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM) and particulate bounded mercury (PBM), e.g. [1], the latter two being usually indicated as RM (Reactive Mercury; e.g. [2]). GEM is by far the most abundant form of Hg in the atmosphere (>95%) since it has high stability and volatility and low solubility, at which corresponds a relatively high residence time in the atmosphere that can be evaluated in 0.6 to 2 years ([3,4]). On the contrary, GOM and PBM (defined by Hg^{+2} compounds that consist of mercuric

halides, mercuric sulfate, mercuric nitrite, and mercuric hydroxide [5]) mostly tend to lay down in a relatively short time, i.e. days or weeks [6].

According to [7], TGM related to anthropogenic activities released to the atmosphere is roughly about three times higher than that emitted by natural sources. Coal combustion, waste incineration and cement production are the most important TGM anthropogenic sources (about 2,200 Mg y^{-1}; e.g. [8,9]) whereas those related to natural emissions are mainly due to volcanic and related hydrothermal systems (up to 830 Mg y^{-1}; e.g. [10-13]). Recently, [14] calculated that a higher value for TGM (7,527 Mg y^{-1}), including contributions from both natural (primary emissions + re-emissions) and man-made sources.

The US Government Agency for Toxic Substances and Disease Registry has ranked mercury as the third most toxic substance on planet after arsenic and lead ([15,16]) and its presence widely occurs in the hydrological, pedological and atmospheric geochemical spheres. The effects of mercury affect cellular, cardiovascular, hematological, pulmonary, renal, immunological, neurological, endocrine, reproductive, and embryonic systems of humans, e.g. [17]. According to the review by [18], atmospheric mercury poses two specific risks: i) a direct one, which involves the inhalation of gaseous mercury, causing different problems to human physiology, e.g. [18,19], and ii) collateral risks, which imply variations in the Hg-species, such as transformation from GEM into RGM or RGM into methyl-Hg, the latter being the most toxicant form of mercury, e.g. [20-24]. Many international studies are presently going on to provide detailed information on mercury distribution via monitoring atmospheric surveys, e.g. [25,26]. Moreover, actions to ban new Hg-mines, the closure of those already existing, and the elimination of any Hg-bearing products from the daily life, are presently undertaken (The United Nation's Minamata Convention, [27]).

Serious healthy problems are caused by human exposure to inorganic mercury of workers involved in the extraction of ore containing mercury, especially when Hg-bearing rocks are roasted to produce Hg°, e.g. [28-35], or other occupational activities where mercury is used are carried out, e.g. [36-39].

In this paper, we present new original data on the spatial and temporal distribution of GEM in the main buildings and structures of the former Hg-mining area of Abbadia San Salvatore (Siena, Central Italy) and the total and leached concentrations of mercury determined on different building materials in order to i) assess at which extent the GEM contamination of air and that related to Hg deposition and adsorption affect the most important edifices (including the furnace-bearing structures) and ii) provide indications for minimize the impact to workers who are about to initiate the first phase of remediation, which will mainly consist in the removal of paintings, plasters, roof tiles and dust. Operational activities are also expected to occur in the structures that are still hosting Gould and Nesa furnaces, where the highest concentrations of GEM were recorded [40].

2. The study site

The world-class Hg-mining district of Abbadia San Salvatore is located in Southern Tuscany (central Italy; Figure 1) in close relation to the Mt. Amiata volcanic complex [41,42], whose products, mainly consisting of trachytic to olivine latitic lava flows and domes, were emplaced between 305 and 231 ka [43,44].

The very first exploration studies at Abbadia San Salvatore dates back to 1846. Mercury production started in 1899 when Cermak Spirek furnaces were ignited for the first time. The old mining area also included a large deposit of wood for the furnaces, some driers, and a small water pool that was used to cool down the gaseous mercury passing through condensers. In the following years, new technological apparatus were introduced, e.g. horizontal (Gould) and vertical (Nesa) furnaces, new dryers and transportation belt systems and calcine and slug deposits. The production activity at Abbadia San Salvatore terminated in 1976, since the exploitation of mercury was not economically sustainable and the use of mercury was declining due to its noxious and toxic effects. In 2008, an agreement between the Municipality of Abbadia San Salvatore and the former owner of the mining concession (E.N.I., National Agency for Hydrocarbons, AGIP Division) was signed to transfer the ownership of the reclamation to the public institution. In the agreement, remediation

Peer-reviewed version available at Int. J. Environ. Res. Public Health 2017, 14, , 425; doi:10.3390/ijerph14040425

actions are addressed to an environmentally rehabilitation of the mining areas and buildings for museum purposes and public green [40,45]. It was estimated that, during the activity of the Abbadia San Salvatore mining district, more than 100,000 tons of liquid mercury were produced [46,47], whilst about 10% of the total production was lost as Hg fumes to the atmosphere [45,48].

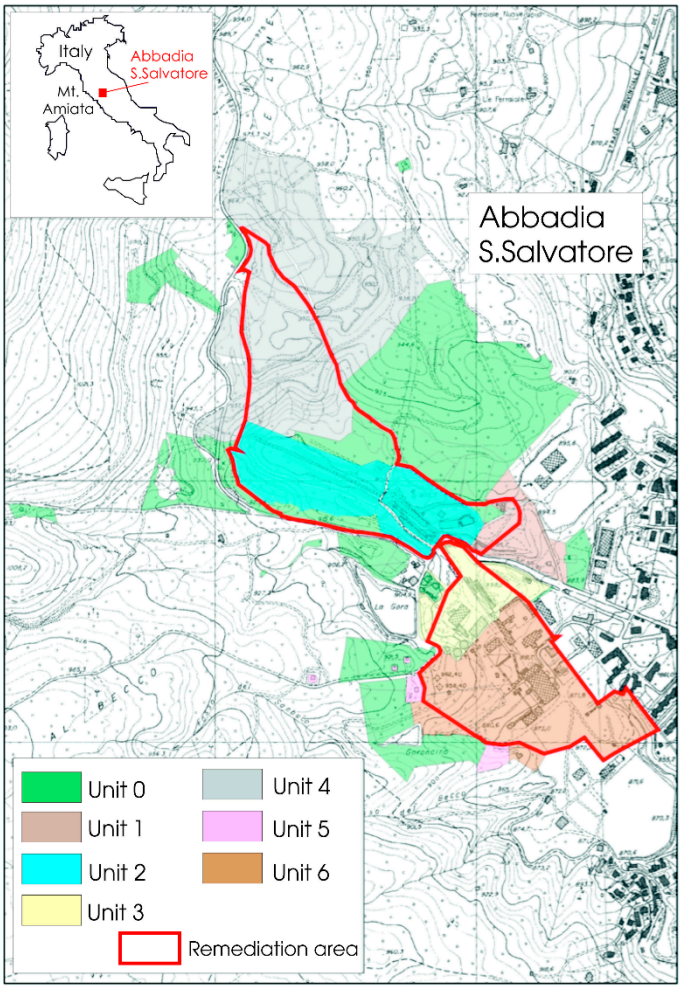

Figure 1. Location of the Hg-mining district of Abbadia San Salvatore (central Italy) and subdivision into 7 units according to the expected different concentrations of mercury present as both GEM and total and leached mercury in the building materials of the edifices hosted in the former mining area.

After the closure of the mining activity, E.N.I.-AGIP Division produced numerous documents where operational activities to remediate the Hg extraction and processing areas were reported, although cessation of the mining activities, which occurred without a scheduled basis, left the decontamination issue open. In fact, metallic mercury is still occurring in the buildings hosting furnaces and condensers, along with the calcine and tailing mounds.

In 1998, the Tuscany regional authorities (Regional Decree n. 1447) produced specific guidelines (named "*Norma Amiata*") for the remediation of the metallurgic activity related to the Hg-mining production areas. The most important points were, as follows: 1) concentrations of Hg in leached soils and terrains and any other kind of material have to be <1 μg L^{-1}; 2) outdoor and indoor concentrations of GEM have to be <300 and <500 ng m^{-3}, respectively.

On the whole, the mining complex has a surface of about 65 ha and contains mining structures and managers and workers buildings (Figure 2). Previous studies, e.g. [32,40,47,49], evidenced the relatively high concentrations of GEM and total mercury in some building material, which showed a heterogeneous distribution in the different edifices. Accordingly, the Municipality of Abbadia San Salvatore divided the mining complex area into 7 different units (Figure 1) [50], the Unit 6 containing the most heavily contaminated structures (Figure 2) [40]:

Unit 0 – This sector is dominated by large green areas, e.g. chestnut trees and Mediterranean scrub, and is located far from any structure, where cinnabar was baked or mercury was condensed or stored, being located outside the remediation area. No intervention is thus expected due to the low contents of mercury in the geological matrices [49].

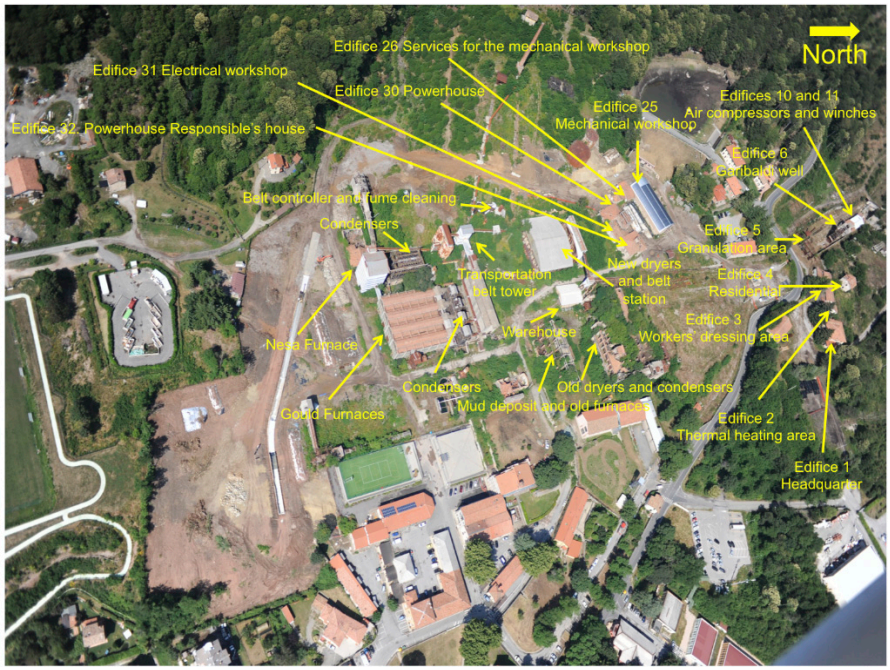

Figure 2. Photos from an ultralight vehicle of the main edifices and mining structures from the units 2, 3 and 6 (see Figure 1) with a description of their use when the mining district was active.

Unit 1 – It is located in the eastern entrance of the mining site and only a part of it is included in the remediation area. No Hg contamination was recorded, being situated far from the sites where mercury was produced [49].

Unit 2 – It includes several edifices such as the headquarter, the workers' dressing room and showers and mining structures, e.g. grounding area, mineral transfer belts, the Garibaldi well;

Unit 3 – It consists of several edifices, among which: the electrical cabin, the mechanical workshops, and an old edifice where furnaces, dryers and condensers were present.

Unit 4 – This area (named "Le Lame") is located to the north of the mining area where most calcines, slugs, and other post-roasting materials were accumulated.

Unit 5 – It is the smallest unit and hosts the armory and the guardian's house. Concentrations of mercury do not raise any concern [49,50].

Unit 6 – It is situated to the south of the mining area at the border of the urban area of Abbadia San Salvatore. Gould and Nesa furnaces, recent condensers and dryers and the main material storing areas are located in this unit.

Such a subdivision in 7 different units is expected to play an important role in the remediation activities. In the case that the concentration limits, reported in the *Norma Amiata*, are not overcome in some edifices and/or areas, no remediation actions are to be adopted. This would allow to save part of the financial resources that could thus be allocated to the remediation activities for the most critical situations, which will be those occurring in the edifices and structures containing driers, furnaces and condensers. As a consequence, in this paper we focused our attention on those edifices and mining structures belonging to the units 2, 3 and 6, which urge a prompt remediation being those buildings where the highest concentrations of mercury were measured [40,49]. GEM measurements and the man-made material investigated in the present study were carried out in the edifices indicated in Figure 2.

3. Materials and Methods

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 March 2017 doi:10.20944/preprints201703.0073.v1

Peer-reviewed version available at Int. J. Environ. Res. Public Health 2017, 14, , 425; doi:10.3390/ijerph14040425

Nine surveys of GEM measurements were carried out from July 2011 to August 2015 for those buildings and structures located in the units 2, 3 and 6 (Figs. 1 and 2). In addition, more detailed GEM measurements were performed in February, April, July, September and December 2016 in 71 selected spots inside and outside edifices and mining structures of Unit 6 (Figure 3).

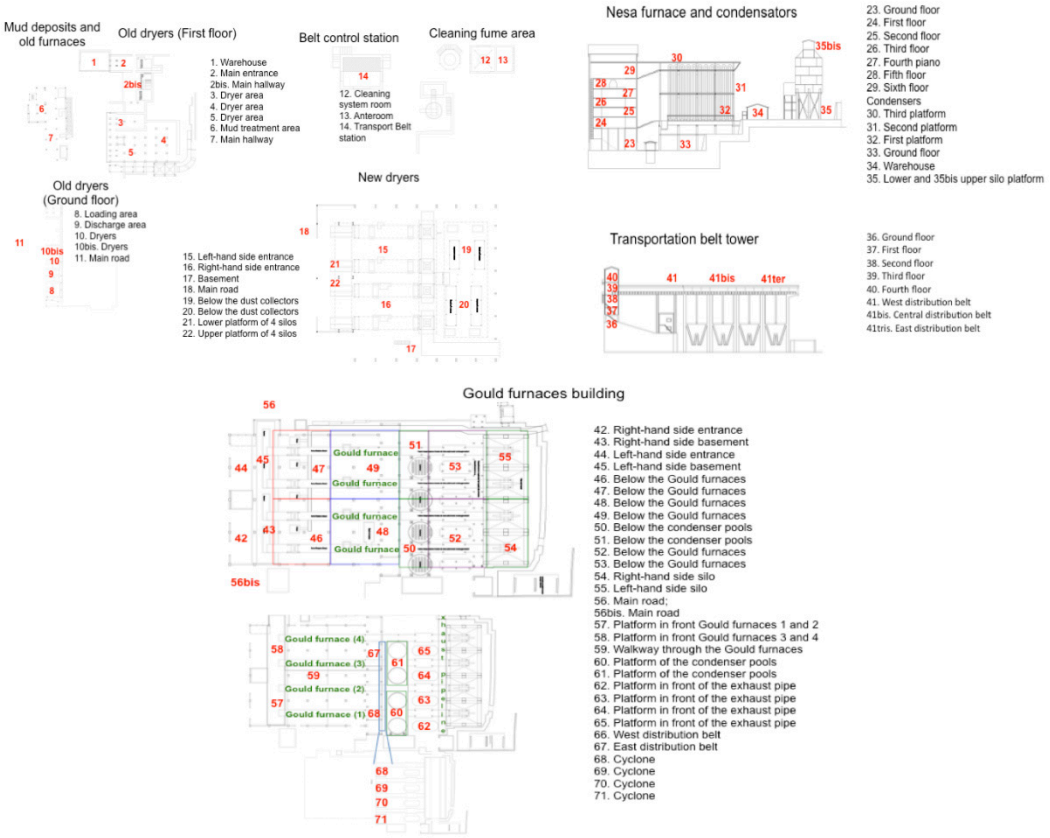

Figure 3. Edifices and mining structures hosted in the Unit 6 and location of the 71 spots (and relative description) where GEM measurements by LUMEX 915+ were carried out.

Real time GEM measurements in air were carried out using a portable Lumex (915+) analyzer, which is based on differential atomic absorption spectrometry using high-frequency modulation of light polarization (ZAAS-HFM; [51]). Application of Zeeman background correction and a multipath analytical cell provided high selectivity and sensitivity. The accuracy of the method is 20% [52]. The detection limit is governed by shot noise and equals CaDL = 2 ng m^{-3} (average measuring time = 5 seconds) and CaDL = 0.3 ng m^{-3} (average measuring time = 30 seconds) at a flow rate of 20 L min^{-1} for GEM determination in ambient air, industrial and natural gases. The dynamic range covers four orders of magnitude (2-50,000 ng m^{-3}).

The GEM portable instrument was maintained at a height of 150 cm from the ground, as the operator was moving around a room. Each measurement was consisting in the acquisition of the GEM data every one second, and calculating the mean values every 30, 60, 90, 120, 150 and 180 seconds. The GEM data were thus referring to the mean value derived by each 30 sec block of measurements. A similar procedure was adopted when measuring GEM outside of most edifices and structures at the distance of about 1 m from the walls.

Paints, plasters, roof tile, dusts, rusts, woods and two soil samples collected at about 10 m from edifice containing the Gould furnaces were analyzed at the Laboratories of Gruppo CSA Ricerche (Rimini) by DMA (Direct Mercury Analyzer)-80, according to the procedure reported by EPA7473 (2007). Samples were grinded and homogenized. According to the expected Hg concentrations, few tens to hundreds milligrams of each sample (analyzed in triplicate) were weighed in a sample boat, thermically decomposed in an oxygen flow at 650 °C, and transferred to an Mn_3O_4-CaO catalyst, which removed possible interference substances, e.g. halogens and nitrogen and sulfur oxides. The

Hg°-rich vapors were interacting with an Au-amalgamator that acted as a selective trap for mercury. Then, mercury was promptly released as the cell where the amalgamator was located by increasing the temperature up to 900 °C and transferred by the O_2 flow to the measurement system that consisted of an atomic absorption. Absorbance was measured at 253.65 nm, obtained by an interferential filter that acted on the radiation emitted by an Hg cold vapor lamp at low pressure. A calibration curve was built with appropriate Hg° standards. Analytical error was <10 %.

Metallic material (e.g. furniture and rust) and the two soils were digested with aqua regia according to the method UNI EN 13657:2004 at the Laboratories of Gruppo CSA Ricerche (Rimini) and analyzed by ICP-AES (Agilent 720ES) following the recommendations described in the UNI EN ISO 11885:2009. Analytical error was <10%.

Samples for leaching tests were collected by using gloves while to remove paints, plasters, rusts, concretes, and woods HCl and acetone cleaned hammer, and chisel and spatula were used. The two soil samples were dried at room temperature and then, sieved at 2 mm. The <2 mm fraction was used for the determination of total and leached mercury.

Leaching tests were performed by weighing about 10 g of fine-grained material into a 100 mL beaker at which 50 mL of MilliQ water saturated with CO_2 were added. To obtain saturated MilliQ water with CO_2, for each 100 mL of MilliQ water, pure CO_2 was bubbled in a Pyrex® bubbler, previously cleaned with ultrapure HCl (1:1), for 15 minutes until a pH of 4.5 was reached. The suspension was periodically swirled for about 3h and let decanting overnight. The surnatant was filtered at 0.45 µm with cellulose nitrate filters. Mercury was then analyzed by ICP-AES at the Laboratories of Gruppo CSA Ricerche (Rimini).

4. Results

4.1. Hg° measurements in the main edifices and mining structures

The GEM data measured in the nine surveys carried out from July 2011 to August 2015 in the edifices and structures of the Abbadia San Salvatore mining district and belonging to the units 2, 3 and 6 are reported in the Supplementary Material 1 (hereafter SM 1) along with the respective layouts, whilst those related to the same period and those determined in the Unit 6 in February, April, July, September and December 2016 are listed in the Supplementary Material 2 (hereafter SM 2) and described in Figure 3.

Strikingly high variations were observed during the different surveys, mostly related to seasonal variations although for those buildings belonging to Unit 2, where relatively high GEM concentrations were measured during the very first surveys. It is worth to mention that doors and windows from edifices from units 2 and 3 have been closed for many years after the closure of the mining activity and they were containing old furniture, metallic spare parts and pieces of wood, rock samples and so forth. These materials were then removed to verify whether they were possible GEM emitters and analyzed for total and leached Hg before their disposal (see below). Consequently, the air quality of most rooms was improved. For the sake of clarity, here below we summarize the most relevant results obtained during the nine (units 2 and 3) and fourteen (unit 6) surveys, whilst the full set of data are reported in the SM 1 and 2. Specific considerations on GEM temporal variations are described in the discussion.

Edifices belonging to Unit 2 and the respective GEM concentrations (in ng m^{-3}) were, as follows:

Edifice 1 (headquarter) consists of 5 and 14 rooms at the ground and first floor, respectively. GEM concentrations were from 20 to 182 ng m^{-3} (ground floor) and from 5 to 602 ng m^{-3} (first floor). GEM measurements carried out along the perimeter of the edifice were between 8 and 56 ng m^{-3}.

Edifice 2 (thermal heating area), represented by a single room, showed GEM values always <50 ng m^{-3}.

Edifice 3 (workers dressing area, Figure 4a) is formed by three blocks: ground and first floors and mezzanine, the latter being almost completely destroyed due to large collapsed areas of the roof. The ground floor has six rooms where GEM reached values up to 932 ng m^{-3}, with the exception of one value (1,686 ng m^{-3}) measured in September 2014 (room A, SM 1). In the first floor, GEM was

<144 ng m^{-3}, while in the mezzanine due to safety reasons, GEM values, sporadically determined, were up to 113 ng m^{-3}.

Edifice 4 (residential), consisting of two floors. Most of this house is falling apart and few GEM measurements (up to 111 ng m^{-3}) were carried out due to risk of collapse.

Edifice 5 (granulation area) is characterized by a ground floor and three basements, the highest GEM values being measured in July 2011 in the first, second and third basement (1,100, 1,250 and 13,600 ng m^{-3}, respectively). GEM values of the ground floor did not exceed 280 ng m^{-3}.

Edifice 6 (Garibaldi well; Figure 4b). GEM measurements were carried out close to the main entrance of the well, now closed for safety reason, with values ≤267 ng m^{-3}.

Edifices 10 and 11 (air compressor and winch areas, respectively), related to the supply of the elevator of the Garibaldi well, showed GEM values <100 ng m^{-3} in the inner rooms, whilst in the perimetral area they were <66 ng m^{-3}. Previous to its collapse in 2105, GEM values measured at the roof of the westernmost room were up to 85 ng m^{-3}.

The edifices belonging to Unit 3 and the respective GEM (in ng m^{-3}) values were, as follows:

Edifice 25 (mechanical workshop) is a wide building (about 1,000 m^2) with a mezzanine and three small rooms. GEM measurements were carried out in three sectors of the building, whose highest concentrations were up to 3,608, 3,968 and 2,131 ng m^{-3}, while the mezzanine showed values up to 2,350 ng m^{-3}. Eventually, GEM concentrations in the three rooms were <2,350 ng m^{-3}, whilst those outside the building were up to 368 ng m^{-3}.

Edifice 26 (services for the workers of the mechanical workshop and pigment production area) was divided in 9 areas where GEM concentrations up to 4,453 ng m^{-3} were measured. Perimetral values were up to 497 ng m^{-3}.

Edifice 30 (powerhouse), consisting of two floors made up of one single room each, showed relatively variable GEM concentrations, the highest and lowest values being up to 950 and down to 58 ng m^{-3}.

Edifice 31 (electrical workshop) is made up of 4 rooms with GEM concentrations up 1,551 Hg° ng m^{-3}.

Edifice 32 (house of the supervisor in charge of the powerhouse) has a small basement and two floors. GEM values were relatively high, being mostly comprised between 333 and 2,358 ng m^{-3} and 168 and 6,896 ng m^{-3} at the ground and first floors, respectively.

As previously mentioned, Unit 6 contains the main structures that were used to produce liquid mercury and GEM concentrations were measured with two different approaches. From July 2011 to August 2016, Lumex measurements were carried out in order to highlight the most critical sites in terms of GEM concentrations. Then, from February to December 2016, 77 sites belonging to the different edifices were systematically and repeatedly measured as reported in Figure 3 where for each measuring site a specific description is provided. The complete set of data related to gaseous mercury is fully listed in the SM 2, while GEM concentrations (in ng m^{-3}) recorded from February to December 2016 for the 71 sites (Figure 3) are listed in Table 1.

Old dryers and condensers, mud deposits and old furnaces (Figure 2; points marked from 1 to 11 in Figure 3, SM 2 and Table 1). These old buildings partly collapsed (Figs. 4c,d). GEM concentrations were highly variable in terms of space and time. The highest values were measured at points 6 (2,480 up to ng m^{-3}), 9 (up to 3,660 ng m^{-3}) and 10bis (up to 1,133 ng m^{-3}).

Belt control station and cleaning fume area (Figure 2; points marked from 12 to 14 in Figure 3, SM 2 and Table 1). GEM contents were >200 ng m^{-3}, the highest concentrations recorded being 1,630 ng m^{-3}.

New dryers (Figure 2; points marked from 17 to 22 in Figure 3, SM 2 and Table 1). GEM concentrations were spatially and temporally highly variable since, for example, at points 16 and 17, they were spanning from 47 to 6,606 and from 161 to 4,910 ng m^{-3}, whereas the lowest values (up to 625 ng m^{-3}) were measured at point 15, 16, 21 and 22, the latter two being located in the belt transportation area.

Table 1. Concentrations of GEM in the 71 spots from the Unit 6 measured in February, April, July, September and December 2016. The location of each site is reported in Figure 3.

Progressive number	25 February	04 April	07 July	02 September	22 December
			ng m^{-3}		
1	166	877	982	787	312
2	49	98	713	121	28
2bis	52	106	420	54	22
3	33	152	60	31	17
4	39	214	88	30	12
5	37	138	221	164	14
6	130	1036	746	145	729
7	105	742	937	275	387
8	276	388	804	615	489
9	1070	1562	1939	3660	1214
10	108	639	1534	279	325
10bis	98	533	1133	297	311
11	43	515	283	84	309
12	544	493	1100	474	283
13	277	455	1596	1535	212
14	326	678	1483	1630	325
15	73	462	420	279	32
16	50	522	431	308	47
17	161	757	4910	1341	1293
18	143	252	722	31	107
19	109	522	888	80	469
20	89	343	2822	112	447
21	50	217	382	43	360
22	131	282	625	198	594
23	177	296	3914	723	1081
24	83	885	2429	1642	843
25	104	485	784	577	394
26	133	415	1179	561	508
27	111	261	1226	593	471
28	245	353	1670	707	434
29	156	588	1767	914	475
30	24	225	420	290	78
31	62	146	523	575	155
32	124	3280	4728	1477	575
33	429	4077	6091	2960	737
34	618	3531	3453	8509	762
35	17	528	10096	1137	458
35bis	n.d.	138	1258	2480	364
36	137	57	3192	1796	525
37	180	234	1332	10835	638
38	258	133	1009	1569	637
39	136	146	2906	1100	568
40	155	201	1530	1535	374
41	210	814	1577	2260	480
41bis	226	278	845	749	315
41ter	411	199	509	621	479
42	974	5845	18851	11261	1879
43	3569	4715	18581	4600	993
44	271	999	7481	8523	4159
45	762	1954	9924	13603	4158
46	2080	4002	5236	7991	3285
47	985	4616	6809	8943	3390
48	4613	8858	18053	7874	3459
49	1930	5745	10624	8575	4252
50	2221	8833	14161	15227	6695
51	3306	6795	14029	11812	9101
52	1291	4180	16581	3747	4180
53	2178	5112	17989	1286	4829
54	1851	4020	20017	2477	3577
55	1217	5700	13694	1002	4027
56	251	912	4088	2734	1146
56bis	1211	4794	1643	240	307
57	929	1729	5133	2298	1710
58	970	1418	6016	4329	2092
59	1542	3505	4927	7972	1960
60	2138	4683	21123	11713	2953
61	2680	8830	10686	8218	3768
62	1233	4753	3940	813	990
63	576	8634	5229	3531	2469
64	375	742	10068	9135	2008
65	473	2064	10137	2754	1850
66	2768	4963	8774	6107	1774
67	380	2083	3903	5561	1448
68	2633	3467	6947	2885	1258
69	2261	3086	14935	6168	1549
70	1701	2763	3870	7781	1570
71	310	14299	19124	1780	709

Nesa furnace, condensers, silo platforms and warehouse (Figure 2; points marked from 23 to 35bis in Figure 3, SM 2 and Table 1). Nesa furnace is hosted in an about 30 m high edifice (Figure 4e).

Peer-reviewed version available at Int. J. Environ. Res. Public Health 2017, 14, , 425; doi:10.3390/ijerph14040425

It was built in the 1960's and was functioning for a very short time due to stability problems. Some mining material is still present in both the furnace and the silos. GEM measurements at the platforms of the silo were only performed in 2016. As previously remarked for other edifices, strong variations of GEM concentrations were observed during the surveys. With the exception of the GEM measurements carried out in the upper platforms of the condensers (points 30 and 31), the other measurement sites were characterized by values >1,000 ng m^{-3} at least during one of the surveys. The highest GEM concentrations (up to 10,096 ng m^{-3}) were measured at points 32 to 35.

Belt transportation tower (Fig, 2; points marked from 36 to 41ter in Figure 3, SM 2 and Table 1). This building consists of five floors and a more than 50 m long horizontal belt area, which was divided into three parts for these surveys. GEM concentrations were highly variable and ranged from 57 to 3,192 ng m^{-3}, with the exception of point 37 where a value of 10,835 ng m^{-3} was measured in September 2016.

Gould furnaces building (Figure 2; points marked from 42 to 71 in Figure 3, SM 2 and Table 1). This is the edifice where liquid mercury was produced and consists of 4 Gould furnaces (Figure 4f), condensers, condensation pools, cyclones to force the fumes of the furnaces to the condensers, an exhaust pipeline, different silos used for the storage of the mining material before roasting, and distribution belts. In this area, liquid mercury is still condensing and occasionally, small liquid mercury pools are observed [45]. As expected, this building is to be regarded as the most contaminated site among all the edifices and mining structures of the former mining area of Abbadia Sal Salvatore. In some of the investigated sites, GEM concentrations were >50,000 ng m^{-3}. More than 200 spots were measured during the 14 surveys and in almost 90% of them GEM concentrations were >1,100 ng m^{-3}, >60% were >3,000 ng m^{-3} and >30% were >10,000 ng m^{-3}.

Figure 4. Examples of buildings and mining structures analyzed in this work: a) dressing building of miners; b) the Garibaldi well; c) the Old driers and condensers; d) the Mud deposit and old furnaces; e) the Nesa furnace and related condensers; f) the building hosting the Gould furnaces.

4.2. Total and leached mercury

Concentrations of total (in mg kg^{-1}) and leached (in µg L^{-1}) mercury measured in different building materials and rock fragments still present in the transportation belts are listed in Table 2. Total mercury showed for the same type of material highly variable values in dependence on the edifice or mining structure from which it was collected. For example, roof tiles were characterized by the lowest total Hg contents, being comprised between 0.8 and 17.5 mg kg^{-1} for those edifices located relatively far from the liquid mercury production area, whereas those collected in the mining structure hosting the Old driers and Gould furnaces, total Hg concentrations were of 36.2 and 485 mg kg^{-1}, respectively both showing relatively high contents of leached Hg (0.2 and 485 µg L^{-1}, respectively).). It is to remark that the roof tile sample collected in the area of the Gould furnaces edifice shows a relatively low concentration of total Hg (4.1 mg kg^{-1}) although that of leached Hg was >1 µg L^{-1}. Similarly to what evidenced for the roof tiles, concrete samples showed a relatively wide range in terms of both total and leached mercury (from 2.2 to 46,580 mg kg^{-1} and <0.1 and 4,470 µg L^{-1}), the highest values being related to concrete samples collected where the Nesa and Gould furnaces are located.

The total Hg concentrations in ordinary and tuff bricks, which were commonly used for different buildings in the mining area, ranged from 4.8 and 11,535 mg kg^{-1}, while those of leached Hg were between 0.3 and 2,250 µg L^{-1}, the highest values being found in the mining structure of Unit 6. To notice that tuff bricks showed, on average, a higher content of leached Hg, being relatively more porous than the ordinary bricks. In this respect, both the total and leached Hg values measured in drilled cores of various tuff bricks from Edifice 25 (Figure 2) were systematically higher than those measured at the brick surface (Table 2). Similarly, paints were characterized by higher concentrations of both total and leached mercury (from 5.5 to 281 mg kg^{-1} and from <0.1 to 37.6 µg L^{-1}, respectively) when compared to the underlying plasters (from 10.8 to 708 mg kg^{-1} and from <0.1 to 392 6 µg L^{-1}, respectively). Unfortunately, where the highest concentrations of mercury in plasters were found paint was scanty or even absent.

All the abandoned machineries and instrumentations were partially covered by rust; thus, several samples from different edifices and mining structures were also analyzed for total and leached mercury, the former varying from 1.3 (railing rust, Edifice 3) to 3,390 (rust in the Nesa furnace) mg kg^{-1}. Leached mercury in rust from Unit 6 (from Nesa and Gould furnaces) was measured only on two samples (351 and 717 µg L^{-1}, respectively).

Three samples of dust covering part of the edifices hosting the Old and New driers were analyzed for total and leached mercury with values up to 13,680 mg kg^{-1} and 1,020 µg L^{-1}, respectively.

In mineral wool from the Nesa furnace total mercury was 420 mg kg^{-1}, whereas leached mercury concentrations was 833 µg L^{-1}.

One wood pylon, girder and table showed concentrations of total mercury up to 57.2 mg kg^{-1}. In the wood girder from the edifice that was hosting mud deposit and old furnaces, leached mercury was only measured with a content of 0.4 µg L^{-1}.

Condensers connected to the Nesa and Gould furnaces are made of crystalline isotactic polymer (Moplen®). A significant difference in terms of total and leached mercury was measured since fragments from the condensers of the Gould furnaces showed higher concentrations than those related to the Nesa furnace, the former being 3,020 mg kg^{-1} and 660 µg L^{-1} whereas the latter were 420 mg kg^{-1} and 1.1 µg L^{-1}, respectively.

Table 2. Concentrations of Total (mg kg^{-1}) and Leached (µg L^{-1}) in the different material collected from the former mining area of Abbadia San Salvatore.

	Total Hg (mg kg^{-1})	Leached Hg (µg L^{-1})		Total Hg (mg kg^{-1})	Leached Hg (µg L^{-1})
Edifice 1			**Edifice 31**		
Basement (room A): Painting	29.6	n.d.	Ground floor (room C): plaster	50.0	<0.1
Ground floor (room C): Painting	28.3	<0.1	Ground floor (room C): painting	67.0	2.2
Ground floor (room N): Painting	57.1	<0.1	Roof tile	0.8	<0.1
First floor (room H): Painting	11.5	<0.1	**Edifice 32**		
Roof tile	6.8	n.d.	Basement (room A): plaster	34.0	<0.1

Edifice 2		
Ground floor: plaster	12.8	<0.1
Mineral wool	18.5	n.d.
Rust	2.2	n.d.
Edifice 3		
Ground floor (room C): Painting	165	<0.1
Ground floor (room D): Painting	14.3	n.d.
Ground floor (room E): Painting	20.5	n.d.
First floor (room C): Painting	13.8	<0.1
First floor (room E): Painting	17.8	<0.1
First floor (room F): Painting	15.3	<0.1
First Floor (room C): Railing Rust	1.3	n.d.
First Floor (mezanine): Aerator Rust	24.3	n.d.
Roof tile	6.0	n.d.
Outer stair: Painting	19.0	<0.1
Main facade: Painting	n.d.	<0.1
Edifice 4		
Ground floor (room A): painting	5.5	n.d.
Ground floor (room C): Painting	44.0	n.d.
Roof tile	17.5	n.d.
Main facade: Painting	86.5	<0.1
Edifice 5		
Basement (first floor): hopper rust	4.8	n.d.
Basement (first floor): vibrating screen rust	16.0	n.d.
Basement (first floor): concrete	31.0	<0.1
Concrete close to the transporting belt	471	<0.1
Grinded rock on the transporting belt	222	n.d.
Gangue	10800	n.d.
Supporting pylons of the trasporting belt: rust	554	n.d.
Supporting pylons of the trasporting belt: wood	57.2	n.d.
Supporting pylons of the trasporting belt: wood	240	n.d.
Edifice 6		
Ground floor: stairs rust	15.6	n.d.
Ground floor: girder rust	13.7	n.d.
Ground floor: wood table in the Garibaldi well cockpit	19.8	n.d.
Ground floor: door rust of the Garibaldi well cockpit	479	n.d.
Ground floor: mining truck rust	30.6	n.d.
Ground floor: rocky retaining wall	1.2	<0.1
Edifice 10		
Ground floor (room A): painting	50.6	<0.1
Ground floor (room A): painting	21.2	n.d.
Ground floor (room A): painting	40.7	n.d.
Edifice 11		
Ground floor (room A): painting	281	<0.1
Rails outside Edifice 10: rust	42.0	n.d.
Edifice 25		
Ground floor (room B): tuff wall (0-2 mm)	159	1.0
Ground floor (room B): tuff wall (inner part)	6.4	n.d.
Ground floor (room B): tuff wall (outer part)	21.8	12.0
Ground floor (room A): tuff wall (0-2 mm)	8.2	26.4
Ground floor (room B): tuff brick at 10 cm depth	6.2	0.3
Ground floor (room B): tuff brick at surface	19.7	0.8
Ground floor (room C): concrete (surface)	469	52.6
Ground floor (room D): concrete (inner pat)	2.2	n.d.
Ground floor (room D): concrete (outer part)	6.7	n.d.
Ground floor (room D): concrete	80.9	1.2
Edifice 26		
Ground floor (room E): painting	122	37.6
Ground floor (room E): painting	81.9	n.d.
Ground floor (room E): plaster	18.4	n.d.
Ground floor (room F): painting	89.2	0.6
Ground floor (room F): plaster	19.9	1.0
Main facade	42.8	n.d.
Edifice 30		
First floor (room B): plaster	10.8	<0.1
First floor (room B): painting	25.8	<0.1
Roof tile	2.6	<0.1
Ground floor (room G): plaster	51.9	4.2
Ground floor (room G): painting	184	5.1
Ground floor (room D): plaster	25.4	0.1
Ground floor (room D): painting	63.8	1.0
Stairs (room E): painting	69.3	2.1
First floor (room G): painting	95.6	<0.1
First floor (room G): plaster	74.9	<0.1
Roof tile	3.3	<0.1
Material removed and disposed from edifices 1 and 3		
Wood girders 1	1.9	<0.1
Wood girders 2	25.6	<0.1
Wood girders 3	0.8	<0.1
Wood girders 4	8.4	<0.1
Wood furniture 1	3.9	0.2
Wood furniture 2	9.17	<0.1
Metal furniture 1	2.5	0.7
Metal furniture 2	6.7	6.1
Wood roof 1	98.5	3.3
Wood roof 2	907	<0.1
Wood roof 3	34.6	<0.1
Wood roof 4	176	<0.1
Unit 6		
Rock wall (Old driers)	486	0.4
Tuff bricks (Old driers)	37.6	29.2
Dust (Old driers)	5880	1.0
Bricks (Old driers)	76.6	0.2
Plaster (Former grinding area in the Old driers)	129	0.5
Roof tile (Old driers)	36.2	0.2
Plaster (Carpentry close to the Old driers)	708	183
Tuff bricks (water depuration area close to the Old driers)	11535	2160
Concrete (Mud deposit and old furnaces)	156	0.3
Wood girders (Mud deposit and old furnaces)	56.3	0.4
Bricks (Mud deposit and old furnaces)	9442	288
Reinforced concrete (New driers)	14.3	<0.1
Dust (New driers)	1100	85.7
Concrete (New driers)	69.6	0.9
Concrete (from the silo area in the New driers)	3160	185
Dust (from the silo area in the New driers)	13680	1020
Tuff bricks (New driers)	31.9	1.5
Mineral wool (New driers)	58.7	2.8
Mineral wool (New driers)	63.4	1.4
Concrete (New driers)	23.6	0.2
Concrete close to the transporting belt (New driers)	76.8	9.8
Concrete (support of the New driers)	90.9	0.2
Concrete (condensation pools, Nesa)	64.4	1.4
Crystalline isotactic polymer (Moplen) condensers (Nesa furnace)	17.9	7.7
Mineral wool (Nesa furnace, first floor)	420	1.1
Mineral wool (Nesa furnace, third floor)	336	833
Rust (Nesa furnace)	3390	351
Reinforced concrete (Condensers Nesa furnace)	46580	4470
Mining material on the belt (Transportation belt tower)	435	3.2
Bricks (Transportation belt tower)	267	2550
Concrete (Gould furnaces edifice)	1045	1470
Concrete (condensation pools, Gould furnaces edifice)	257	14.7
Concrete close to the silos (Gould furnaces edifice)	109	6.8
Plaster (Gould furnaces edifice)	353	34.4
Concrete (close to the calcine deposit; Gould furnaces edifice)	76.1	20.2
Rust (Gould furnaces)	2490	717
Brick (Gould furnace condensers)	6830	1690
Concrete (exhaust pipe; Gould furnaces edifice)	186	1.3
Bricks (liquid mercury bottling area)	4.8	10
Lime (liquid mercury bottling area)	181	105
Plaster (liquid mercury bottling area)	210	392
Plaster (liquid mercury bottling area)	325	0.66
Crystalline isotactic polymer (Moplen) condensers (Gould furnaces)	3020	660
Roof tile (Gould furnaces edifice)	4.1	1.3
Roof tile (Gould furnaces edifice)	485	140
Soil in front of the Gould furnaces 1	73670	6640
Soil in front of the Gould furnaces 2	51770	260

As previously mentioned, most (metal and wood) furniture, rock samples and wood girders and roofs (the latter related to collapsed parts of some buildings) were removed from edifices 1, 2 and 3 and stored outside and piled-up separately according to the different material. Wood and

metal furniture and wood girders and roofs were analyzed for total and leached mercury by collecting fragments from each accumulation, which were consisting of about 1-2 tons each (Table 2). The highest total mercury contents were measured for the wood roofs (34.6 to 907 mg kg^{-1}) and the lowest ones were found in the metal furniture (2.5 to 6.7 mg kg^{-1}), although the latter showed a relatively high leached mercury concentration (0.7 to 6.1 µg L^{-1}).

Eventually, two samples of rocky material still present in the transporting belts, one lime sample located in the liquid mercury bottling area and two soil samples, collected in front of the building hosting the Gould furnaces, were also analyzed (Table 2), although leached mercury was not measured in the rocky material. It is worthwhile to mention that the terrain in front of the Gould furnaces was mainly consisting of discharge material (calcine, bricks, slug, and so forth) [45]. Strikingly high concentrations were thus not only recorded in the geological material present in the transporting belts (up to 10,800 mg kg^{-1}) but also in the terrains (up to 73,670 mg kg^{-1}), the latter showing high contents of leached mercury (up to 6,640 µg L^{-1}). The lime sample had values of total and leached mercury of 181 mg kg^{-1} and 105 µg L^{-1}, respectively.

5. Discussion

5.1. Spatial and temporal distribution of GEM

Mercury vapor is absorbed through inhalation, e.g. [53,54], it bonds to S-bearing amino acids and can reach the brain, e.g. [55]. Prolonged exposure to mercury vapor may induce neurological dysfunction and even low-level exposures are reported to produce weakness, anorexia, weight loss and so forth [56]. Changes in personality, loss of memory, depression and occasionally delirium were reported as some of the symptoms when man is exposed to high-level of mercury vapor [57]. [32] evidenced that miners of Abbadia San Salvatore did not suffer exposure to Hg° since no native mercury was present in the ore deposit. Differently, workers involved in the smelting process, cinnabar pigment production, soot purification, laboratory work and bottling showed high concentrations of mercury in their blood and urine. The high GEM values measured in this study for those buildings where native mercury was produced and treated may affect the operational activity of the operators during remediation processes.

The GEM concentrations in the edifices and mining structures of the former Hg-mining area of Abbadia San Salvatore showed a strong variability in terms of space and time (SM 1 and SM 2 and Table 2), mostly depending on the distance from the building hosting driers, furnaces and condensers and ambient temperature, respectively. To better evidence such differences, time variations (from July 2011 to August 2015) for selected buildings located in the units 2 and 3 are reported in Figure 5. Surveys carried out in the hotter period (from June to September) showed the highest values, although for Edifice 1 and Edifice 3 GEM concentrations did not exceed the maximum values defined by the Tuscany Region for air quality, i.e. 500 ng m^{-3}. Values well above 500 ng m^{-3} were instead measured in the edifices where machineries related to the processing of the geological material for the extraction of mercury from are still present (Edifice 5), or where workers and miners were constantly present, i.e. Edifice 31 and Edifice 32. Furthermore, these edifices are not far from the production area of Unit 6 (Figure 2) and winds blowing from the south likely favored air contamination in these edifices of GEM released from the furnace areas [40]. This would also explain some sporadic spikes of GEM measured in the colder periods.

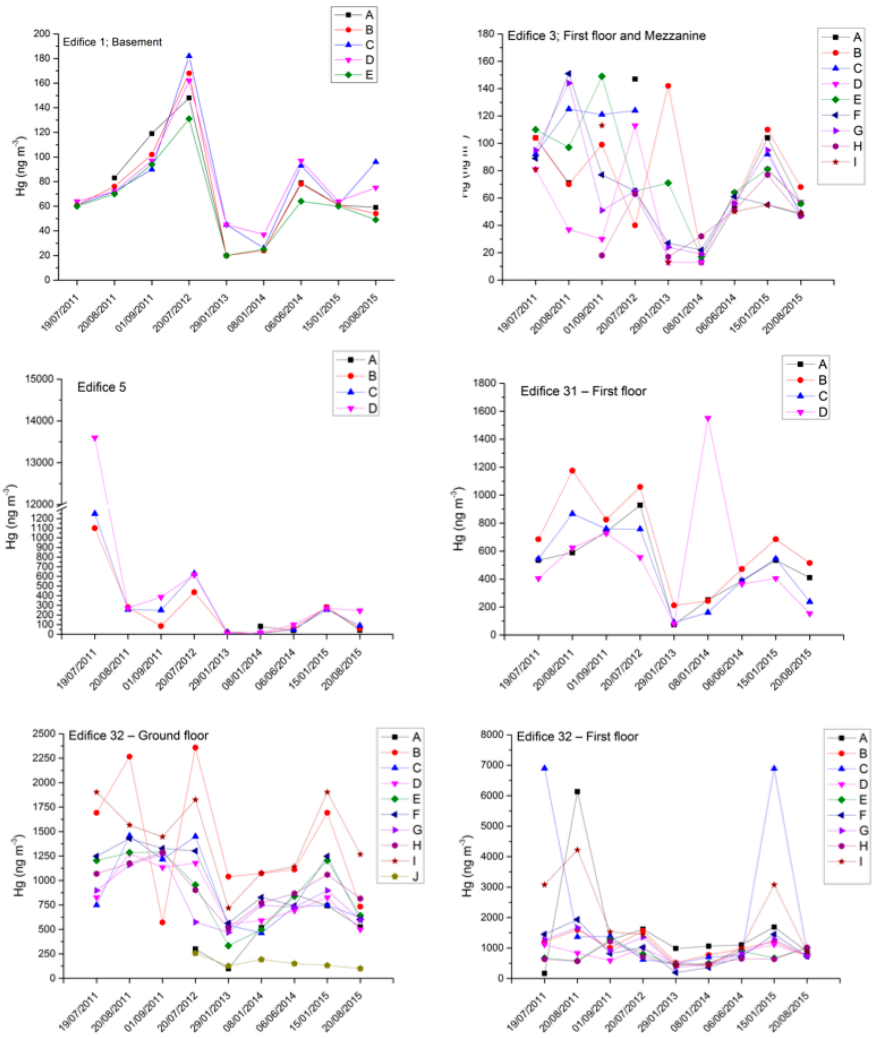

Figure 5. GEM concentrations (in ng m^{-3}) versus time (from July 2011 to August 2015) for selected edifices located in the units 2 and 3. The full set of GEM data is reported in SM 1.

In the Unit 6, GEM concentrations were undoubtedly much higher than those recovered from the edifices previously described and listed in SM 1, as occasionally they saturated the GEM measurement device (>50,000 ng m^{-3}). The spatial and temporal GEM variability in the Unit 6 can clearly be shown by separately considering the five surveys carried out in 2016 (Table 1), during which 71 spots were systematically analyzed in February, April, July, September and December. As shown in Figure 6, in the hotter period GEM showed the highest concentrations, especially in July 2016, when the highest values were measured and a bell-shape temporal pattern is clearly visible for any of the 71 spots. Nevertheless, in some cases relatively high concentrations were also detected in September. During the colder months, the GEM concentrations strongly decreased, occasionally dropping down to <500 ng m^{-3}. It is worth to mention that even those edifices that had collapsed (e.g. the buildings hosting the mud deposits, the old furnaces, and the old driers), hence more affected by meteorological events with respect to the closed structures (e.g. the mining structures hosting the Nesa and Gould furnaces), showed GEM concentrations >500 ng m^{-3}.

The most important finding is that GEM concentrations almost systematically were higher than the in-door threshold of 500 ng m^{-3}, although they were much lower than those recorded by Bellander et al. (1998) in 1982, when the mining activity was practically stopped. GEM values up to 250,000 ng m^{-3} were indeed measured. Nevertheless, any remediation activity in most edifices from units 2, 3 and 6 should not be carried out without any personal protective equipment. It is expected that cleaning operations can last for months in the Gould and Nesa furnaces and other critical areas

and if appropriate precautions are not adopted operators may face serious health problems. In particular, it can be recommended that workshifts should be shortened and they can occasionally be transferred to less exposing GEM concentrations for limited periods before returning into the sites were high GEM concentrations were documented. Since operational cleanings will likely raise dust, GEM concentrations may increase in the working environment. This implies that a monitoring activity of GEM concentrations is to be performed.

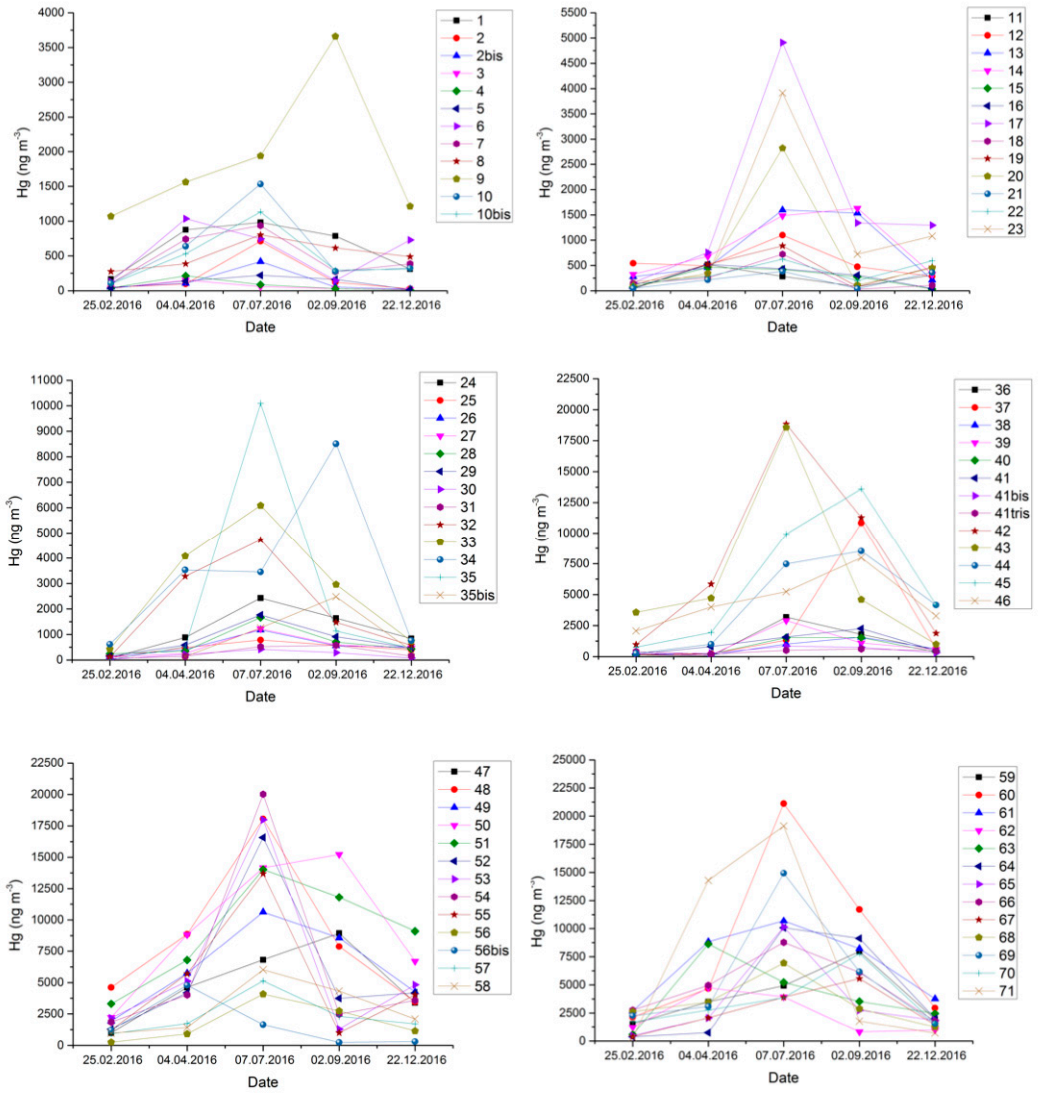

Figure 6. GEM concentrations (in ng m^{-3}) versus time (from February to December 2016) for selected edifices and mining structures located in the Unit 6. The full set of GEM data is reported in SM 2 and Table 1.

5.2. Total and leached mercury concentrations in the building and stored materials

To the best of our knowledge, no reference total and leached mercury concentrations are available for building materials exposed to mercury contamination and consequently, a comparison between unaffected and contaminated concrete, wood furniture, rust, dust and so forth is not presently viable. Of particular importance is the leached mercury (the value of 1 µg L^{-1} is the highest value admitted for the disposal of any material in ordinary landfill), which can be regarded as indicator of mercury availability since it strictly reflects the amount of mercury that has been adsorbed both during the mining activity and after the closure of the production plant. The total Hg/leached Hg ratio, along with the GEM concentrations, can be also considered critical parameter

to evaluate the quality of the environment for workers, users and researchers. No mercury speciation for total and leached mercury was performed. It is to remind that, during the production of liquid mercury, >100 ktons were produced and 10 ktons were lost in the atmosphere. Presently, the buildings where the Nesa and Gould furnaces are located, as well as those containing the (old and new) driers and the condensers (Figure 2), are still emitting GEM, as evidenced by the measurements in air (Table 2 SM 2). This confirms that just after the closure of the mining activity, the GEM concentrations in air affecting the analyzed material were much higher [49] than in the present. Thus, the measured concentrations of total and leached mercury mostly represent the amount of mercury absorbed during the mining- and post-mining activity, when air contamination was at the higher level (Bellander et al., 1998). The spatial distribution of total mercury in the analyzed material collected from 1 to 32 edifices (Figs. 7 and 8) showed increasing trends approaching the Unit 6 (Figure 2, SM 1 and Table 2), the highest total mercury concentrations being measured in the granulation area (Edifice 5) close to the Garibaldi well (Edifice 6). As previously evidenced, paints are more enriched in mercury than plasters underneath, suggesting that mercury absorbed at the surface only partly diffuses inside the analyzed wall. Tuff bricks, concretes and rust appear to be good mercury absorbers (Figure 7).

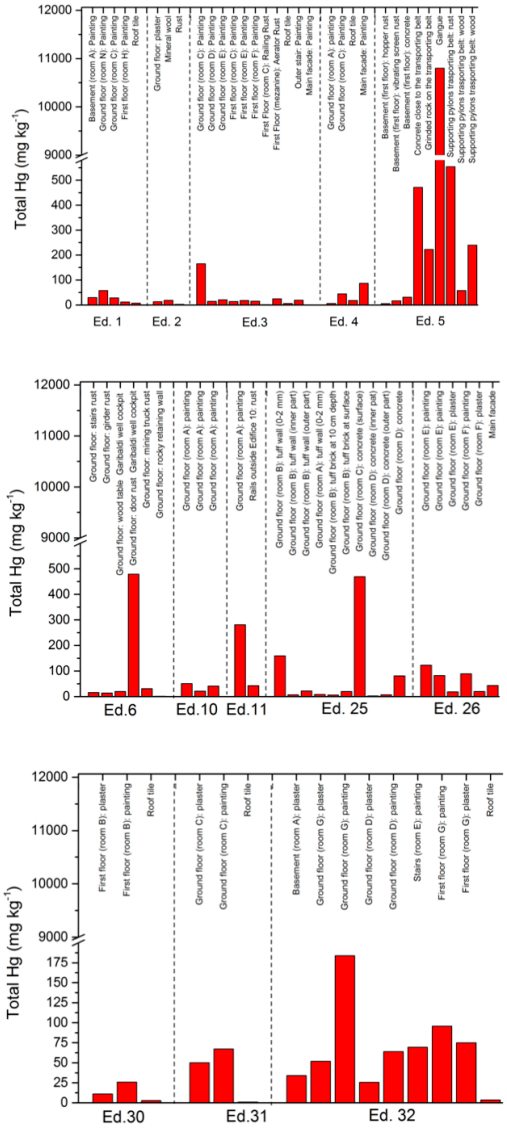

Figure 7. Bar diagrams for total Hg concentrations (in mg kg^{-1}) measured in different building materials from units 2 and 3. For each material the relative location is also described as reported in SM 1.

Setting aside the materials from Edifice 5, those analyzed from the Unit 6 showed concentrations of total mercury one order of magnitude higher than those recorded in the edifices from units 2 and 3, independently on the type of analyzed material. However, concretes, paints, mineral wools, and crystalline isotactic polymers of the condensers showed the highest concentrations of total mercury likely because they were exposed (and still they are) for longer time to GEM-rich fumes.

It is strikingly surprising the persistency of gaseous mercury in contaminated sites despite the fact that the mining activity at Abbadia San Salvatore terminated in 1976. However, high GEM concentrations were also measured in other abandoned mining districts (e.g. Almaden, Spain, and Idrija, Slovenia; Higueras et al., 2014) or even in apartments and studios built at Hoboken (New Jersey, USA) where a tool-and-dye company and, successively, a factory of manufactured mercury valor lamps operated [58,59]. High Hg concentrations were found in the urine of 29 people living in those apartments and studios after the reconversion and decrements of some neurobehavioral performances were likely related to the high contents of gaseous mercury [60], whose concentrations were >1,000 ng m^{-3}. Unfortunately, no data on paints and plasters from such environments are available but according to our findings it is matter of fact that building materials are able to adsorb mercury as it is was observed in the edifices and mining structures analyzed in this study.

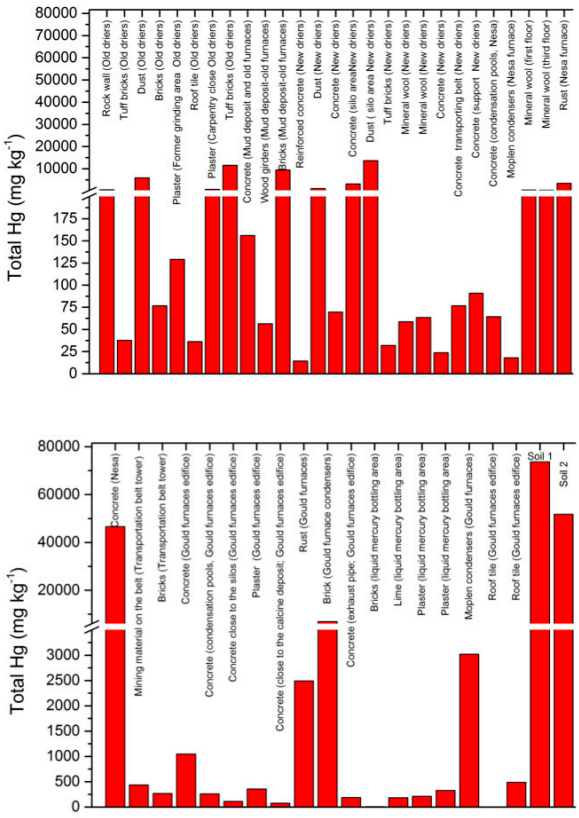

Figure 8. Bar diagrams for total Hg concentrations (in mg kg^{-1}) measured in different building materials from Unit 6. For each material the relative location is also described as reported in Figure 3.

Studies on Hg mobility have been carried out in order to proceed with soil-remediation techniques in mining areas, e.g. [61] and references therein. [62] assessed that adsorpion/desorption processes control the behavior of Hg in the soil, suggesting that mercury can be occurring in dissolved, non-specifically and/or specifically adsorbed, chelated or precipitated forms. [63] evidenced that Hg mobility depends on its chemical speciation that can be dictated by soil parameters, including pH and redox potential [62,64], and their interactions. In addition, Hg

transformations operated by microbial activity, via methylation and demethylation processes (likely not applicable to building materials we are dealing with in this paper), may further mobilize or stabilize mercury, e.g. [65] and references therein).

In the absence of specific investigations that may shed light on the Hg forms occurring in the different materials analyzed in the present study, a binary diagram of total (in mg kg^{-1}) versus leached mercury (in µg L^{-1}) for those material where the two parameters were available is displayed in Figure 9 to test the availability of mercury by grouping the different materials according similar features. A positive correlation (Pearson's r = 0.7) between the two parameters is observed and, consequently, the higher the total mercury the higher its removal with a simple leaching procedure. With the exception of the two soil samples collected in front of the building hosting the Gould furnaces, which represent a contaminated material less affected by exposure to high mercury concentrations, being characterized by Hg-rich matrices, the exposure to Hg (either GEM or RM or both) is favoring the increment of mercury in the building materials.

The equation of the straight line depicted by total (THg) versus leached (LHg) mercury (Figure 9) is:

$$LHg = -1.0472 + 0.90177 * THg \quad (1)$$

Assuming that no leachable mercury should be occurring in such material, we may speculate that the value of 1.16 mg kg^{-1} might be considered a sort of reference concentration for uncontaminated building materials. The THg/LHg ratios is relatively variable and is comprised between 105 and 588,0000, suggesting that at high concentrations of total Hg, leached Hg is relatively high (Figure 9) although in percentage the latter represents a small fraction. This may indicate that most Hg is present is a stable form and water-saturated CO_2 is able to remove a minimal quantity of Hg, though often higher that the limit defined by the *Norma Amiata* (1 µg L^{-1})

Nevertheless, inhalation of microparticles of any building material during its partial (via abrasive-blasting devices) or total removal by operators may introduce mercury in their lungs. As a consequence, personal protective equipments are evidently compulsory but it is highly recommended to proceed with a hydro-blaster, which allows to protect workers and to recapture the water with consequent waste reduction and minimization of the environmental impact.

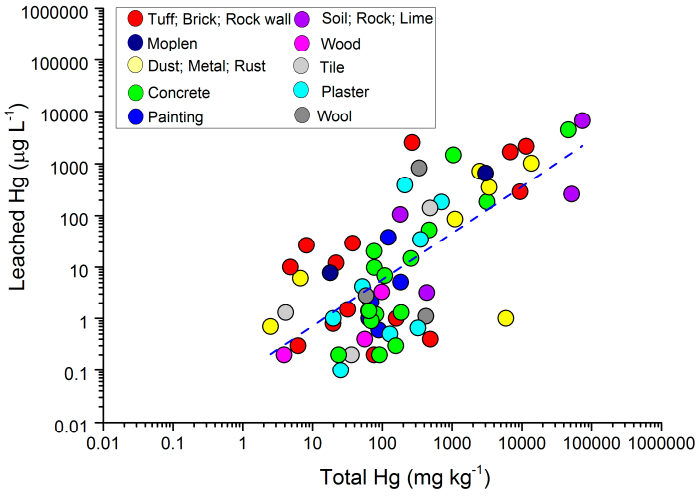

Figure 9. Binary diagram of total (in mg kg^{-1}) versus leached mercury (in µg L^{-1}) for different materials collected from building and mining structures of units 2, 3 and 6 and grouped according to similar features.

6. Conclusions

GEM concentrations in the former Hg-mining area of Abbadia San Salvatore (Tuscany, central Italy) from July 2011 to August 2015 in most edifices of units 2 and 3 (Figs. 1 and 2) and from July 2011 to December 2016 in the mining structures of Unit 6 (Figure 3) showed in most cases

concentrations >500 ng m^{-3} and a large variability from colder to hotter period, the latter being characterized by the highest values recorded in the study area (>10,000 ng m^{-3}). High concentrations of total and leached mercury were also detected in the building materials (e.g. tuff bricks, roof tiles, concretes), suggesting that they act as Hg-adsorbers when affected by high GEM concentrations.

The reclamation project in the former mining area of Abbadia San Salvatore is still at the beginning and it has not yet interested nor the buildings of the workers nor the liquid mercury production areas. Thus, the results obtained in this study are of relevant interest for the operational cleanings to be carried out during the reclamation activities. Operators are expected to dress appropriate personal protective equipments and act with machineries (e.g. hydro-blasters) that avoid the dispersion of GEM and RM in the environment during the removal of paints, plasters, dust, rust and so forth. This is highly recommended for both the operators' safety and that of the inhabitants living nearby, the urban centre of Abbadia San Salvatore bordering the former mining area (Figure 1). To better monitor the operational activities, continuous acquisition of GEM data is suggested and samples of urine, blood and hair for mercury concentrations should be collected in statistically significant populations of operators prior and after the reclamation since several months are likely necessary to complete the cleaning activity particularly in the most contaminated sites.

Acknowledgments: Many thanks are due Andrea Esposito and Marcello Niccolini for their help during the collection of the building materials and the measurements of Hg° in the studied area. Luciano Giannini is warmly thanked for the photos taken by an ultralight vehicle. This work was funded by a contract between the Municipality of Abbadia San Salvatore (Resp. D.R.) and the Department of Earth Sciences of Florence (Resp. O.V.).

Author Contributions: Orlando Vaselli and Daniele Rappuoli conceived and designed the experiments; Orlando Vaselli, Barbara Nisi and Jacopo Cabassi performed the experiments; Orlando Vaselli, Barbara Nisi, Jacopo Cabassi and Franco Tassi analyzed the data; Orlando Vaselli, Daniele Rappuoli, Jacopo Cabassi and Fanco Tassi contributed analysis tools; Orlando Vaselli and Barbara Nisi wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fu, X. W., Feng, X., Shang, L.H., Wang, S.F., Zhang, H., 2012. Two years of measurements of atmospheric total gaseous mercury (TGM) at a remote site in Mt. Changbai area, Northeastern China. Atmos. Chem. Phys., 12, 4215–4226.
2. Weiss-Penzias, P., Amos, H.M., Selin, N.E., Gustin, M.S., Jaffe, D.A., Obrist, D., Sheu, G.-R., and Giang, A., 2015. Use of a global model to understand speciated atmospheric mercury observa- tions at five high-elevation sites, Atmos. Chem. Phys., 15, 1161– 1173.
3. Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury—an overview. Atm. Environ. 32, 809–822.
4. Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E., Seigneur, Ch., 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition, Ambio 36, 19–32.
5. Gustin, M.S., Huang, J., Miller, M.B., Peterson, C., Jaffe, D.A., Ambrose, J., Finley, B.D., Lyman, S.N., Call, K., Talbot, R., Feddersen, D., Mao, H., Lindberg, S.E., 2013. Do we understand what the mercury speciation instruments are actually measuring? Results of RAMIX. Environ. Sci. Technol. 47, 7295-306.
6. Gustin, M., Jaffe, D., 2010. Reducing the Uncertainty in Measurement and Understanding of Mercury in the Atmosphere, Environ. Sci. Technol., 44, 2222–2227.
7. Mason RP, Fitzgerald WF, Morel FMM. 1994. The biogeochemical cycling of elemental mercury: anthropogenic influences. *Geochim. Cosmochim. Acta* 58:3191–98.
8. Pacyna, E.G., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic mercury emission inventory for 2000. Atmos. Environ. 40, 4048–4063.
9. Wilson, S.J., Steenhuisen, F., Pacyna, J.M., Pacyna, E.G., 2006. Mapping the spatial distribution of global anthropogenic mercury atmospheric emission inventories. Atmos. Environ. 40, 4621–4632.
10. Varekamp, C.V., Buseck, P.R., 1986. Global mercury flux from volcanic and geothermal sources. Appl. geochem. 1, 65–73.

11. Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E., Pirrone, N., 2000. Volcanoes as emission sources of atmospheric mercury in the Mediterranean Basin. Sci. Total Environ. 259 (1–3), 115–121.
12. Nriagu, J., Becker, C., 2003. Volcanic emissions of mercury to the atmosphere: global and regional inventories. Sci. Total Environ. 304, 3–12.
13. Pyle, D.M., Mather, T.A., 2003. The importance of volcanic emissions for the global atmospheric mercury cycle. Atmos. Environ. 37, 5115–5124.
14. Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R.B., Friedli, H.R., Leaner, J., Mason, R., Mukherjee, A.B., Stracher, G.B., Streets, D.G., Telmer, K, 2010, Global mercury emissions to the atmosphere from anthropogenic and natural sources. Atm. Chem. Phys. 10(13), 5951-5964.
15. US Department of Health and Human Services, Public Health Service, 1999. Toxicological profile for mercury. Atlanta: US Department of Health and Human Services; p. 1-600
16. Clifton, J.C. 2nd, 2007. Mercury exposure and public health. Pediatr. Clin. North Am. 54, 237-269.
17. Rice, K.M., Walker Jr, E.M., Wu, M., Gillette, C., Blough, E.R., 2014. Environmental Mercury and Its Toxic Effects. J. Prev. Med. Public. Health 47, 74-83.
18. Higueras, P.L., Oyarzun, R., Kotnik, J., Esbrí, J.M., Martínez-Coronado, A., Horvat, M., López-Berdonces, M.Á., Llanos, W., Vaselli, O., Nisi, B., Mashyanov, N., Ryzov, V., Spiric, Z., Panichev, N., McCrindle, R., Feng, X., Fu, X., Lillo, J., Loredo, J., García, M.E., Alfonso, P., Villegas, K., Palacios, S., Oyarzún, J., Maturana, H., Contreras,, F., Adams, M., Ribeiro-Guevara, S., Ribeiro-Guevara, L.F., Giammanco, S., Huremović, J., 2014. A compilation of field surveys on gaseous elemental mercury (GEM) from contrasting environmental settings in Europe, South America, South Africa, and China: separating fads from facts. Environ. Geochem. Health, 36, 713–734.
19. Clarkson, T.W. & Magos, L., 2006. The toxicology of mercury and its chemical compounds. Critical Reviews in Toxicology, 36, 609–662.
20. WHO, 2000. Air quality guidelines for Europe.WHORegional Publications European Series 91, World Health Organization Regional Office for Europe, Copenhagen, 288 pp.
21. Grandjean P., Weihe P., White R. F., Debes F., Araki S., Yokoyama K., Murata K., Sorensen N., Dahl R., Jorgensen P. J. , 1997. Cognitive deficit in 7-year-old children with prenatal exposure to methylmercury. Neurotox. Terat. 19(6), 417–428.
22. Grandjean, P., Satoh, H., Murata, K., Eto, K., 2010. Adverse effects of methylmercury: Environmental health research implications. Environmental Health Perspectives, 118, 1137–1145.
23. Davidson P.W., Palumbo D., Myers G.J., Cox C., Shamlaye C.F., Sloane-Reeves J., Cernichiari E., Wilding G.E., Clarkson T.W., 2000. Neurodevelopmental outcomes of Seychellois children from the pilot cohort at 108 months following prenatal exposure to methylmercury from a maternal fish diet. Environ. Res. 84, 1–11.
24. Mergler, D., Anderson, H.A., Chan, L.H.M., Mahaffey, K.R., Murray, M., Sakamoto M., Stern, A.H., 2007. Methylmercury Exposure and Health Effects in Humans: A Worldwide Concern. AMBIO 36, 3-11.
25. Mason R.P., Pirrone N. (Eds.), 2009. Mercury Fate and Transport in the Global Atmosphere. Emissions, Measurements and Models Springer, New York, p. 627.
26. Pirrone, N., Cinnirella, S., W. Aas, Ebinghaus, R., Hdgecock, I.M., Pacyna, J., Sprovieri, F., Sunderland, E.M., 2013. Toward the next generation of air quality monitoring: Mercury. Atm. Environ. 80, 599-611.
27. AMAP/UNEP, 2013. Technical background report for the global mercury assessment. Arctic Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland (2013).
28. Vouk, V.B., Fugas, M., Topolnik, Z., 1950. Environmental conditions in the mercury mine of Idria. Br. J. Ind. Med. 7, 168-176.
29. Ladd, C, Zusin, E., Valic, F., Almonte, J.B., Gonzales, T.V., 1966. Adsorbtion and excretion of mercury in miners. J. Occup. Med. 3, 127-131.
30. Gonzales-Fernandez, E., Caballero, J.D., Espanol, S., 1992. Long-term exposure to elemental mercury vapors in the Almaden miners. A follow-up 3-year study (abstract). In International Occupational Hygiene Association, First International Scientific Conference, Bruxelles, Belgium 7-10 December 1992.
31. Kishi, R., Doi, R., Fukuchi, Y., Satoh, H., Satoh, T., Ono, A., Moriwaka, F., Tashiro, K., Takahata, N., and the Mercury Workers Study Group, 1993. Subjective symptoms and neurobehavioral performances of ex-mercury miners at an average of 18 years after the cessation of chronic exposure to mercury vapor. Environ. Res., 62, 289-302.

32. Bellander, T., Merler, E., Ceccarelli, F., Boffetta, P., 1998. Historical Exposure to Inorganic Mercury at the smelter works of Abbadia San Salvatore, Italy. Am. Occup. Hyg. 42, 81-90.
33. Drake, P.L., Rojas, M., Reh, C.M., Mueller, C.A., Jenkins, F.M., 2001. Occupational exposure to airborne mercury during gold mining operations near El Callao, Venezuela. Int. Arch. Occup. Environ. Health 74, 206-212.
34. García Gómez, M., Caballero Klink JD, Boffetta P, Español S, Sällsten G, Gómez Quintana, 2007. J.Exposure to mercury in the mine of Almaden. Occup. Environ. Med. 64, 389-95.
35. Soto-Jiménez, M.F., Flegal A.R., 2011. Childhood poisoning from a smelter in Torreon, Mexico. Environ. Res. 111, 590-596.
36. Sikorski, R., Juszkiewicz, T., Paszkowski, T., Szprengier- Juszkiewicz, T., 1987. Women in dental surgeries: reproductive hazards in occupational exposure to metallic mercury. Int. Arch. Occ. Environ. Health 59, 551-557.
37. Letz, R., Gerr, F., Cragle, D., Green, R.C., Watkins, J., Fidler, A.T., 2000. Residual neurologic deficits 30 years after occupational exposure to elemental mercury. Neurotoxicology 21, 459-474.
38. Neghab, M., Norouzi, M.A., Choobineh, A., Kardaniyan, M.R., Zadeh, J.H., 2012. Health Effects Associated With Long-Term Occupational Exposure of Employees of a Chlor-Alkali Plant to Mercury. Int. J. Occ. Saf. Ergon., 18, 97–106.
39. Al-Batanony, M.A., Abdel-Rasul, G.M., Abu-Salem M.A., Al-Dalatony, M.M., Allam, H.K., 2013. Occupational exposure to mercury among workers in a fluorescent lamp factory, Quisna industrial zone, Egypt. Int. J. Occup. Environ. Med. 4, 149-156.
40. Vaselli, O., Higueras, P., Nisi, B., Esbrì, J.M., Cabassi, J., Martìnez-Coronado, A., Tassi, F., Rappuoli, D., 2013. Distribution of gaseous Hg in the Mercury mining district of Mt. Amiata (Central Italy): A geochemical survey prior the reclamation project. Environmental Research 125 (2013) 179–187.
41. Ferrari, L, Conticelli, S., Burlamacchi L., Manetti, P., 1996. New geologic and volcanological data on the Mt. Amiata silicic complex. Acta Vulcanol., 8, 41–56.
42. Conticelli, S., Melluso, L., Perini, G., Avanzinelli, R., Boari, E., 2004. Petrologic, Geochemical and Isotopic characteristics of potassic and ultrapotassic magmatism in Central-Southern Italy: inferences on its genesis and on the nature of mantle sources. Per. Mineral. 73, 135-164.
43. Conticelli, S., Boari, E., Burlamacchi, L., Cifelli, F., Moscardi, F., Laurenzi, M.A., Ferrari Pedraglio, L., Francalanci, L., Benvenuti, M.G., Braschi, E., Manetti, P., 2015. Geochemistry and Sr-Nd-Pb isotopes of Monte Amiata Volcano, Central Italy: evidence for magma mixing between high-K calc-alkaline and leucititic mantle-derived magmas. It. J. Geosci. 134, 266-290.
44. Laurenzi, M.A, Braschi, E., Casalini, M., Conticelli, S., 2015. New ^{40}Ar-^{39}Ar dating and revision of the geochronology of the Monte Amiata Volcano, Central Italy. It. J. Geosci 134, 255-265.
45. Vaselli, O., Nisi, B., Rappuoli, D., Bianchi, F., Cabassi, J., Venturi, S. Tassi, F., Raco, B., 2015. Geochemical characterization of the ground waters from the former Hg-mining area of Abbadia San Salvatore (Mt. Amiata, central Italy): criticalities and perspectives for the reclamation process. It. J. Sci., 134, 23-31.
46. Nriagu, J.O., 1979. Production and uses of mercury. In: Biogeochemistry of Mercury in the Environment (J.O. Nriagu, Ed.), Elsevier, Amsterdam, pp. 23-40
47. Ferrara, R., Mazzolai, U.B., Edner, H., Svanberg, S., Wallinder, E., 1998. Atmospheric mercury sources in the Mt. Amiata area, Italy. Sci Total Environ., 213, 12–23.
48. Bombace, M.A., Cigna Rossi, L., Clemente, G.F., Zuccaro Labellarte, G., Allegrini, M., Lanzola, L., Gatti, L., 1973. Ricerca ecologica sulle zone mercurifere del Monte Amiata. Igiene Sanità Pubblica 29, 191-237.
49. Bacci, E., Gaggi, C., Lanzillotti, E., Ferrozzi, S., 1998. Studio per l'individuazione dei residui di mercurio in forme mobili e della presenza di altri elementi in traccia di interesse tossicologico ai fini della predisposizione di un progetto di bonifica dell'area di pertinenza della ex miniera di mercurio di Abbadia San Salvatore (SI), Proprietà ENI S.P.A. - Divisione AGIP: relazione finale. Per conto della Società Mining Italiana S.p.A. (Gruppo ENI), Roma, 161 pp.
50. Bianchi, F., Corti, F., Vaselli, O., Rappuoli, D., 2012. Bonifica area mineraria Lotto 6: relazione conclusiva sulle indagini e studi degli anni 2011 e 2012. Modalità operative per la bonifica. Technical Report, Municipality of Abbadia San Salvatore – Unità di Progetto Bonifica, p. 53. In Italian.
51. Sholupov, S., Pogarev, S., Ryzhov, V., Mashyanov, N., Stroganov, A., 2004 Zeeman atomic absorption spectrometer RA-915+ for direct determination of mercury in air and complex matrix samples. Fuel Process. Technol., 85, 473-485.

52. Sholupov, S.E., Ganeyev, A.A., 1995. Zeeman atomic absorption spectrometry using high frequency modulated light polarization. Spectrochim. Acta, Part B, 50, 1227–1236.
53. Hursh, J.B., Clarkson, T.W., Cherian, M.G., 1976. Clearance of mercury (Hg-197, Hg-203) vapor inhaled by human subjects, Archives of Environmental Health 31, 302–309.
54. Bernhoft, R.A., 2012. Mercury Toxicity and Treatment: A Review of the Literature. J. Environ Public Health 2012, 1-10, doi:10.1155/2012/460508.
55. Nordberg, G.F., Serenius, F., 1969. Distribution of inorganic mercury in the guinea pig brain. Acta Pharmacol. Toxicol. 27, 269–283.
56. Baldi, G., Vigliani, E.C., Zurlo, N., 1953. Mercury poisoning in hat industry. La Medicina del Lavoro 44, 160–199.
57. Berglund, A., Pohl, L., Olsson, S., Bergman, M., 1988. Determination of the rate of release of intra-oral mercury vapor from amalgam," J. Dental Res. 67, 1235–1242.
58. Orloff, K.G., Ulirsch, G., Wilder, L., Block, A., Fagliano, J., Pasqualo, J., 1997. Human exposure to elemental mercury in a contaminated residential building. Arch. Environ. Health. 52, 169–172.
59. Gochfeld, M., 2003. Cases of mercury exposure, bioavailability, and absorption. Ecotoxicol. Environ. Saf. 56, 174–179.
60. Fiedler, N., Udasin, I., Gochfeld, M., Buckler, G., Kelly McNeil, K., Kipen, H., 1999. Neuropsychological and stress evaluation of a residential mercury exposure. Environ. Health Perspect. 107, 343–347.
61. Xu, J., Bravo, A.G., Lagerkvist, A., Bertilsson, S., Sjöblom, R., Kumpiene, J., 2014. Sources and remediation techniques for mercury contaminated soil. Environ. Internat. 74, 42–53.
62. Schuster, E., 1991. The behaviour of mercury in the soil with special emphasis on complexation and adsorption processes□a review of the literature. Water Air Soil Pollut. 56, 667–680.
63. Yin, Y., Allen, H.E., Huang, C.P., Sparks, D.L., Sanders, P.F., 1997. Kinetics of mercury (II) adsorption and desorption on soil. Environ. Sci. Technol. 31, 496–503.
64. Robles, I., Lakatos, J., Scharek, P., Planck, Z., Hernández, G., Solís, S., Bustos, E., 2014. Characterization and Remediation of Soils and Sediments Polluted with Mercury: Occurrence, Transformations, Environmental Considerations and San Joaquin's Sierra Gorda Case. In: Environmental Risk Assessment of Soil Contamination (Ed. Maria C. Hernandez-Soriano), p. 827-850.
65. Hu, H., Lin, H., Zheng, W., Tomanicek, S.J., Johs, A., Feng, X., Elias, D.A., Liang, L., Gu, B., 2013. Oxidation and methylation of dissolved elemental mercury by anaerobic bacteria. Nat. Geosci. 6, 751–754.