Article

Persistent Organic Pollutants and Metals in Atmospheric Deposition Rates around the Port-Industrial Area of Civitavecchia, Italy

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Featured Application: The deposition rate is a relevant and novel issue in air quality evaluation. Particularly, atmospheric micropollutant deposition rate measures represent a strategic element in environmental surveillance and in population exposure evaluation for POPs and metals.

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Abstract: In recent years, studies on climate change have focused on reducing greenhouse gas emissions emitted by various civil and industrial processes. This study highlights the importance of characterizing the total deposition rates of airborne particles (bulk atmospheric deposition) in the surroundings of an industrial area along the north cost of the Lazio Region in Italy, to deepen knowledge about the potential impact of emissions from the coal-fired thermoelectric (CTE) power plant and other possible sources existing in the surrounding area. Four sampling sites were identified, and the monitoring plan was performed a yearlong with monthly collecting observation. The deposition samples were collected monthly and processed for determining organic (polychlorinated dibenzo-*para*-dioxins, PCDDs; polychlorinated dibenzofurans, PCDFs; dioxin-like polychlorinated biphenyls, DL-PCBs; polycyclic aromatic hydrocarbons, PAHs) and inorganic (metals) substances. The samples were collected monthly and sent for chemical characterization. In Europe and Italy, no reference values have been given for the deposition rates of chemicals, while some European countries have determined reference/guide values to which the authors will refer in this study. Therefore, the analytical results show that the deposition rates for PCDD/Fs and DL-PCBs are lower with respects guide values defined by Germany and Belgium; PAHs values are in line with those measured in other rural-type sites, while for metals the analytical results show a situation between rural and urban area. The approach used in this study can help to identify reference values for Italy in deposition rates, with the aim both to characterize the dynamic of pollution in area with multiple risk factors and to describe and protect human health from environmental exposures caused by the contamination of the food chain.

Keywords: deposition rate; sedimentable dust; air quality; climate change; POPs; PCDD/Fs; DL-PCBs; PAHs; metals; industrial area; fossil fuel; emissions; greenhouse effect; chemometric

1. Introduction

Atmospheric pollutant emissions due to anthropogenic activities cause the deposition of airborne particles, with negative effects on human health, environment, food and ecosystem [1–3]. National legislation and European directives define the term total or bulk deposition as “the total mass of pollutants which is transferred from the atmosphere

to surfaces (e.g., soil, vegetation, water, buildings, etc.) in a given area within a given time" [4,5]. The deposition rate is expressed as surface mass for a given reference period, generally in μg of pollutant per m^2 per day ($\mu\text{g m}^{-2}\text{d}^{-1}$). At present, in Italy there are no regulations, guidelines and limits for airborne pollutant depositions. However, we can refer both to measures in similar areas, to the scientific literature and to guidelines and/or rules in force in other countries. For example, about polychlorinated dibenzo-*para*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs), Belgium suggests a maximum value of 8 pg World Health Organization-Toxic Equivalent concentrations (WHO-TE) $\text{m}^{-2}\text{d}^{-1}$ based on the human tolerable weekly intake (TWI) [6]; while Germany, using a guideline approach, for PCDD/Fs and DL-PCBs only, suggests 4 pg WHO-TE $\text{m}^{-2}\text{d}^{-1}$ [7].

Different studies were performed for investigating organic [8–16] and inorganic micropollutants [17–32] in atmospheric deposition using bulk deposition methods. The total depositions (bulk) are collected by passive exposure of a “bottle/cylindrical funnel” system with standardized dimensions, for weekly and/or monthly collecting period in annual monitoring studies. Deposition rates of some atmospheric pollutants measured by means of bulk deposimeter (passive exposure of a “bottle/cylindrical funnel” system of standardized dimensions) is an important tool to evaluate environmental pollution levels and to assess population exposure [33,34]. Deposition samples are particularly suitable to measure the environmental concentration of Persistent Organic Pollutants (POPs), as PCDD/F, PCB and polycyclic aromatic hydrocarbons (PAHs) [34–38]. For these reasons, the pollutant downfall from atmosphere to soil both in environmental surveys and in monitoring networks, are very important for the information on the area’s contamination allowing to perform a comprehensive assessment of the population exposure.

Emissions from different sources (e.g., petrochemicals, refinery, metal industry, large combustion plants, landfill, waste incineration, and cement factories) [39–45] cause contamination of farmlands and a potential subsequent accumulation in the food chain (in which POPs are particularly associated with fats) [46–49]. Italy has drawn up the National Energy Strategy (NES) and the Integrated National Plan for Energy and Climate (INPEC) which contain the national targets for 2030 which provide for the decarbonization of the energy system starting from 2025, with a sharp cut in use of coal for the production of electricity. In this frame, electricity production is a major source of greenhouse gas emissions. Strategies to reduce greenhouse gas emissions from electricity generation include switching to renewable energy sources.

The study, addressed to characterize the related organic and inorganic dust fractions, aims to carry out a characterization of the sedimentable particulate material in the area of Civitavecchia (North Latium, Central Italy) and the neighboring municipalities in order to understand the potential impact on the territory of the emissions of a coal-fired thermoelectric (CTE) power plant and of the other pressure sources existing in the area.

2. Materials and Methods

The locations of the deposimeters (Figure 1) have been identified, taking into account the characteristics of the territory, distributing them on the various municipalities around Civitavecchia (North Latium, Central Italy). The location of Rocca Respampani, in the territory of Viterbo, very far from any known industrial/urban emission source, has been identified as a background location. The monitoring network installed for the study consisted of:

- Location #1: area not affected by industrial and urban sources; positioning: at the Roccaccia Business Center, Tarquinia Agricultural University;
- Location #2: area characterized by the absence of settlements; positioning: Enel Sant’Agostino electrical power station;
- Location #3: area characterized by medium population density; positioning: at the environmental monitoring station of the Management Consortium of the Environmental Observatory of Civitavecchia, at Allumiere;

- Location #4: area not affected by industrial and urban sources; positioning: at the Rocca Respampani Agricultural Company (background site).

Figure 1. (a) Location of the four sampling sites around Civitavecchia and neighboring municipalities; (b) total bulk deposimeter sampler used in this campaign.

An ambient air monitoring network was installed consisting of four stations equipped with total bulk deposimeters (Figure 1b) for determining the atmospheric deposition rate. The determinations of organic (PCDD/Fs, DL-PCBs and PAHs) and inorganic (metals and metalloids) micro-pollutants at (ultra-)trace levels were carried out on all the samples collected. The sampling started at the four sites from June and continued for a whole year, each lasting about 30 days. Each sampling was performed following the indications reported in the Italian Legislative Decree no. 155/2010 [50]: UNI EN 15980:2011 for organic micropollutants [51] and UNI EN 15841:2010 for metals and metalloids [52]. Pyrex glass deposimeters were used for the determination of PCDD/Fs, PCBs and PAHs, while high-density polyethylene (HDPE) deposimeters were used for metals and metalloids.

The samples were filtered on a membrane filter in mixed cellulose esters, diameter 47 mm and porosity 0.45 μm for metals, and in glass fiber, diameter 47 mm, without organic binders, for organic compounds. The mixed cellulose ester filter was then mineralized in a microwave digestion system using concentrated nitric acid and 5% hydrogen peroxide, and the acidified filtrate with high purity concentrated nitric acid for trace analysis, whereas the glass fibers and the filtrate were subjected to extraction with high purity organic solvent for trace analysis (dichloromethane, DCM), respectively, by ultrasound and in a separating funnel. The acid solution coming from the mineralization and the acidified filtrate were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), using the procedure described in UNI EN 15841:2009 [52], whereas the extracts with the solvent were combined, dried, concentrated and analyzed for determining PCDD/Fs by means of gas chromatography coupled with mass spectrometry (GC-MS) according to UNI EN 1948-2:2006 [53], UNI EN 1948-3:2006 [54] and UNI EN 1948-4:2010 [55], and for determining PAHs by means of high performance liquid chromatography-MS (HPLC-MS) according to UNI EN 15980:2011 [51]. In the analytical results, the concentration values below the limit of

detection (LOD) are expressed as 50% of the LOD, as indicated in [32]. The LODs for each compound/metal investigated are reported in Table S1 of the Supplementary Material.

3. Results and Discussion

The approach used in this study has been addressed to maximize all the information: first, the meteorological conditions had been studied, further the deposition rates have been investigated and interpreted in relationship to the related findings. As reported above, the authors would like to underline in Italy no regulations, guidelines and/or limits law limits or national guidelines for airborne pollutant depositions at present: therefore, the authors performed a comparison of observed with guidelines and/or values recommended by other European countries.

3.1. Analysis of the Prevailing Wind Direction

For the analysis of the meteorological conditions present during the monitoring campaign, the data acquired by the station positioned at a height of 120 m, located inside the CTE central station were analyzed. The available data covers the entire sampling period (Figure 2).

Figure 2. Frequency distribution of wind direction month by month.

During the study, the frequencies of the wind direction showed the expected seasonal variability. In general, the winds from the East have low frequencies, in some periods they seem to be absent. The most frequent directions are those associated with the whole sector that goes from South-West to North-West, the winds from the South are predominant in the months of October and February, whereas the North-East sector is present with higher frequencies in the months of September, October, November and March.

The wind directions change during the hours of the day: this occurs during the whole year. Until mid-morning the main frequency of wind directions are from North-East and from South-East; in the afternoon, the wind direction turns, and the West and North-West directions are predominant, with the North-North West sector prevalent during 16–19.

The wind speeds show a variability related to the sector of origin of the winds. On average, higher speeds are associated with winds from North-East and South-East (Figure 3).

Figure 3. Distribution of wind speeds for each wind sector.

3.2. Atmospheric Deposition

3.2.1. Annual Deposition Rates

The atmospheric deposition investigation was carried out on four locations taking into account the characteristics of the territory under study. Each sampling system consists of two deposimeters (1 for organic fraction and 1 for inorganic) to carry out the analytical determinations of organic and inorganic chemical contaminants in the airborne particle deposition. The analysis was performed for determining organic, i.e., PCDD/Fs, DL-PCBs and PAHs, and inorganic-metal, i.e., As Ba Be Cd Co, total Cr, Cu, Mn, Ni, Pb, Sb, Se, Sn, Sr, Te, Ti, Tl, V, Zn, micro-pollutants.

Table 1 summarizes the main regulation developed by various European countries [32] both on atmospheric deposition rate and on the content of PCDD/Fs + DL-PCBs and on some metals.

Table 1. Reference values of deposition rates for dust, some metals and PCDD/Fs + DLPCBs in some European legislations [32].

	Dust ¹	As ²	Cd ²	Hg ²	Ni ²	Pb ²	Tl ²	Zn ²	PCDD/Fs + DL-PCBs	
									Monthly ³	Annual ³
Austria	210	–	2	–	–	100	–	–	–	–
Belgium	350	–	2	–	–	250	–	–	21	8.2
Croatia	350	4	2	1	15	100	2	–	–	–
Germany	350	4	2	1	15	100	2	–	–	4
UK	200	–	–	–	–	–	–	–	–	–
Switzerland	200	–	2	–	–	100	2	400	–	–
Slovenia	200	–	2	–	–	100	–	400	–	–

¹ Expressed as mg m^{−2}d^{−1}; ² as µg m^{−2}d^{−1}; ³ pg WHO-TE₁₉₉₈ m^{−2}d^{−1}.

Table S2 of the Supplementary Material shows the measurements of the deposition rate of the total sedimentable dusts for each location and season. This measure is an important indicator of particular local environmental conditions, such as fouling, deposit on crops and soil, with possible exposure of the population by ingestion, etc., which is given increasing attention.

European and national legislation does not indicate limit values for the deposition rate of sedimentable dusts. Consequently, an assessment of the extent of the phenomenon can be obtained by comparison with reference values or limits suggested in guidelines or in legislative acts of other European countries (Table 1) [32].

The deposition rates based on monthly collecting period, measured at the Allumiere, S. Agostino, Roccaccia and Rocca Respampani stations, vary between $8.1 \text{ mg m}^{-2} \text{ d}^{-1}$ recorded in the autumn 2015 season at the Roccaccia station, to the $49.3 \text{ mg m}^{-2} \text{ d}^{-1}$ recorded in the spring 2016 season again in Roccaccia (Table S1 of the Supplementary Material).

On the other hand, the deposition rates based on annual collecting period measured in the entire period in the four stations, are, respectively, reported in Table 2.

Table 2. Deposition rate (expressed as $\text{mg m}^{-2} \text{ d}^{-1}$) of the total sedimentable dusts in each location.

Season	Roccaccia	S. Agostino	Allumiere	Rocca Resp.
Annual	21.5	35.8	18.8	27.9

The analysis of these data shows that the stations do not show areas with high rates of atmospheric deposition of total sedimentable dusts, compared to what is reported both in the legislation of different countries and in the scientific literature.

Autumn has the lowest dustiness in all locations, while the Allumiere location, also the winter season, is associated with low dustiness. Spring appears to be the season with the highest dustiness in all locations. In fact, a seasonal variability can be observed that sees the atmospheric depositions of total sedimentable dusts increase, when passing from the humid season to the drier one. This trend can be explained by the greater contribution to the total depositions brought about by the rising phenomena of the total sedimentable dusts from the ground.

The measured total sedimentable dusts rates show both short and long-term (annual average) values that are approximately one order of magnitude lower than the more restrictive limits ($200 \text{ mg m}^{-2} \text{ d}^{-1}$) reported in Table 1 by some countries.

3.2.2. PCDD/Fs and DL-PCBs

Table 3 summarizes the PCDD/Fs + DL-PCBs values in WHO-TE₁₉₉₈, for each location and season. The estimated annual value is also reported on the basis of seasonal data (Table S3 of the Supplementary Material).

Table 3. Mean atmospheric deposition rate (expressed as $\text{pg WHO-TE}_{1998} \text{ m}^{-2} \text{ d}^{-1}$) of PCDD/Fs + DL-PCBs by season and location.

Season	Roccaccia	S. Agostino	Allumiere	Rocca Resp.
Summer	14.1	0.33	0.39	1.04
Autumn	0.90	2.70	0.29	0.82
Winter	0.53	0.33	0.59	0.27
Spring	0.19	0.21	0.14	0.16
Annual average	3.93	0.89	0.35	0.57

The comparison of the deposition rates for the PCDD/Fs + DL-PCBs shows a substantial homogeneity among the sampling sites with the exception of Roccaccia where the mean deposition rate is from 4 to 11 times higher, with a maximum in summer. These average deposition rates are significantly lower than the limit ones envisaged in the legislation and guidelines of various European countries [32]. In particular, in Germany the guide values for PCDD/F and DL-PCBs in deposition define a target value (annual average) of $4 \text{ pg WHO-TE}_{1998} \text{ m}^{-2} \text{ d}^{-1}$, and $9 \text{ pg WHO-TE}_{1998} \text{ m}^{-2} \text{ d}^{-1}$ is the reference for some industrial areas. In the Roccaccia and Allumiere stations, the highest concentrations of PCDD/Fs are recorded in winter and autumn seasons with much lower concentrations in summer and

spring. S. Agostino shows the highest total PCDD/F concentrations in spring and autumn. Rocca Respampani shows the highest concentrations in winter, but the values are still more comparable between the different seasons. The Roccaccia station is the one that shows a significantly higher value (in WHO-TE).

Table 4 shows the average rates profile of such micropollutants, expressed as $\text{fg m}^{-2} \text{d}^{-1}$ and in equivalent toxicity (WHO-TE₁₉₉₈). Tables S4–S7 of the Supplementary Material report the data of the PCDD/F and DL-PCB rates profiles in each season and location, expressed both in $\text{fg m}^{-2} \text{d}^{-1}$ and in equivalent toxicity with respect to the International Toxicity Equivalent (I-TE) factors, WHO-TE₁₉₉₈ and WHO-TE₂₀₀₅.

Table 4. Mean annual levels of PCDD/Fs and DL-PCBs determined in the four investigated locations.

Congener	Roccaccia		Rocca Respampani		Allumiere		S. Agostino	
	$\text{fg m}^{-2} \text{d}^{-1}$	WHO-TE ₁₉₉₈	$\text{fg m}^{-2} \text{d}^{-1}$	WHO-TE ₁₉₉₈	$\text{fg m}^{-2} \text{d}^{-1}$	WHO-TE ₁₉₉₈	$\text{fg m}^{-2} \text{d}^{-1}$	WHO-TE ₁₉₉₈
2,3,7,8-TCDD	38.0	38.0	15.4	15.4	15.4	15.4	24.8	24.8
1,2,3,7,8-PCDD	509	509	15.4	15.4	29.1	29.1	15.4	15.4
1,2,3,4,7,8-HxCDD	399	39.9	15.4	1.54	22.1	2.21	15.4	1.54
1,2,3,6,7,8-HxCDD	609	60.6	36.5	3.65	31.4	3.14	38.2	3.82
1,2,3,7,8,9-HxCDD	218	21.7	27.8	2.78	46.3	4.62	15.4	1.54
1,2,3,4,6,7,8-HpCDD	8513	85.1	417	4.17	498	4.98	489	4.89
OCDD	137.09	13.7	4023	0.402	5533	0.552	5630	0.565
2,3,7,8-TCDF	419	41.9	119	11.9	134	13.4	99.2	9.92
1,2,3,7,8-PCDF	810	40.5	67.3	3.36	76.1	3.81	45.8	2.29
2,3,4,7,8-PCDF	1033	516	69.7	34.9	96.4	48.2	44.2	22.1
1,2,3,4,7,8-HxCDF	1173	117	72.9	7.29	155	15.6	64.6	6.46
1,2,3,6,7,8-HxCDF	1199	119	71.0	7.10	95.1	9.51	62.0	6.2
2,3,4,6,7,8-HxCDF	637	63.7	84.7	8.48	140	14.0	75.3	7.53
1,2,3,7,8,9-HxCDF	27.2	2.72	29.9	2.99	34.5	3.45	15.4	1.54
1,2,3,4,6,7,8-HpCDF	2231	22.3	245	2.45	768	7.69	283.9	2.84
1,2,3,4,7,8,9-HpCDF	49.2	0.492	27.0	0.270	48.9	0.487	24.5	0.245
OCDF	2899	0.287	1155	0.117	1222	0.122	690	0.0675
Total	158,072	1694	6493	122	8947	207	7634	112
77-CB	127,165	12.7	25,277	2.53	12,750	176	44,216	4.42
81-CB	3814	0.382	765	0.078	12,750	1.27	44,216	0.240
105-CB	3,9632,69	396	652,429	65.2	445	0.045	2405	116
114-CB	336,172	168	52,101	26.0	301,770	30.2	1,169,450	53.9
118-CB	1,399,6455	1399	2,265,709	227	9780	4.89	10,7856	487
123-CB	1,145,574	114	890,431	89.0	954,798	95.5	4,873,182	29.5
126-CB	893	89.3	154	15.4	48,220	4.82	294,745	47.405
156-CB	108,006	54.0	46,223	23.1	154	15.4	474	28.3
157-CB	1443	0.722	769	0.385	46,336	23.2	56,507	0.697
167-CB	48,895	0.488	14,061	0.140	1088	0.545	1396	0.222
169-CB	280	2.80	154	1.53	12,630	0.125	22,097	2.96
189-CB	1568	0.155	769	0.077	154	1.54	296	0.167
Total	19,733,537	2239	3,948,844	450	1159	0.117	1669	772

In Roccaccia, the predominant contributions are from OCDD which range from 36–96%, depending on the season, with the highest percentage in winter and autumn; in S. Agostino from 64% to 84%, with the greatest contribution in autumn and spring; in Allumiere from 44% to 77% with the highest contribution in autumn and in Rocca Respampani site a variable contribution from 47% to 75% with the highest values in autumn and spring. Heptachlorodibenzo-*p*-dioxin (HpCDD) and PCDF are the other congeners that contribute significantly to the rate profiles even if with very variable percentage contributions.

Many reports, studies and/or communications reporting in the scientific literature describe data on PCDD/F levels in Bulk sedimentable dust deposition: Table 5 shows a comparison among different sites across Italy and Europe.

Table 5. Comparison of PCDD/F levels (pg I-TE m⁻² d⁻¹) in deposition rates among our values and other studies in different Italian and European locations.

Locations	PCDD/Fs	Ref.
Aosta (North-West Italy)	urban sites: 0.6–3.0 industrial sites: 3.7	[56]
Venice (North-East Italy)	urban sites: 13–200 industrial sites: 15–2767	[21]
Mantua ^a (North Italy)	urban site: 1.2–4.2 industrial site: 1.3–5.1 rural area: 1.3–2.7	[57]
Stroncone-Terni (Central Italy)	urban site: <5.0	[58]
Taranto (South Italy)	industrial site: 0.57–45 rural sites: 1.6–33	[59]
Melfi ^a (South Italy)	industrial site: 1.7–2.1 rural area: 1.2–2.7	[32,60]
Belgium	urban site: <1–12 rural area: <1–3.1	[61]
Germany	urban site: <0.5–464 rural area: 7–17	[62,63]
UK	urban site: <1–312 rural area: 0–517	[33]
Denmark	urban site: 300–31,600 rural area: 300–1700	[64,65]
France	urban site: 100–147 rural area: 20–50	[66]
North Latium (Central Italy)	urban site: 1.4–7.1 industrial site: 1.4–4.6 rural area: 1.4–3.9	This study

^a site with presence of an incineration plant.

3.2.3. PAHs

The annual average deposition rates of each PAH measured at the four sites are shown in Table 6 while the seasonal variability is illustrated in Figure 4. Table S8 of the Supplementary Material reports the deposition rates of each PAH by season.

Table 6. Mean annual PAH levels ($\text{ng m}^{-2}\text{d}^{-1}$) determined in the four investigated locations.

Compound	Roccaccia	Rocca Respampani	Allumiere	S. Agostino
Benz[a]Anthracene	3.593	4.515	6.268	2.510
Benzo[b]Fluoranthene	4.760	100.493	6.320	2.587
Benzo[j]Fluoranthene	4.995	1.538	3.403	1.538
Benzo[k]Fluoranthene	3.763	1.538	3.190	3.325
Benzo[a]Pyrene	5.873	2.325	3.950	2.165
Dibenzo[a,h]Anthracene	1.553	1.538	1.538	1.538
Dibenzo[a,e]Pyrene	2.073	1.538	1.538	1.538
Dibenzo[a,h]Pyrene	1.553	1.538	1.538	1.538
Dibenzo[a,i]Pyrene	2.323	1.538	1.538	1.538
Dibenzo[a,l]Pyrene	1.553	1.538	1.538	1.538
Indeno[1,2,3-cd]Pyrene	4.853	1.538	2.428	1.538
Acenaphthene	34.663	7.178	212.348	11.710
Acenaphthylene	36.023	9.028	18.228	16.213
Anthracene	13.465	10.295	7.953	6.145
Benzo[g,h,i]Perilene	5.670	1.538	4.695	1.538
Crysene	6.228	4.193	9.175	4.065
Phenanthrene	103.723	77.238	72.873	51.878
Fluoranthene	14.000	8.473	15.990	10.693
Fluorene	84.898	78.830	88.820	47.730
Naphthalene	164.510	67.385	103.665	68.620
Pyrene	11.433	7.058	15.128	7.745
Total PAHs	511.498	390.853	582.118	247.690

Figure 4. Concentrations (expressed as $\text{ng m}^{-2}\text{d}^{-1}$) of each PAH in the deposition rates in the four locations for each season. For the acronyms: BaA Benzo[a]Anthracene; BbF Benzo[b]Fluoranthene; BjF Benzo[j]Fluoranthene; BkF Benzo[k]Fluoranthene; BaP Benzo[a]Pyrene; DhA Dibenzo[a,h]Anthracene; DeP Dibenzo[a,e]Pyrene; DhP Dibenzo[a,h]Pyrene; DiP Dibenzo[a,i]Pyrene; DiP Dibenzo[a,i]Pyrene; DiP Dibenzo[a,i]Pyrene; IcdP Indeno[1,2,3-cd]Pyrene; ACE Acenaphthene; ACY Acenaphthylene; ANT Anthracene; BbP Benzo[g,h,i]Perylene; CRY Chrisene; Phen Phenanthrene; FLT Fluoranthene; FLU Fluorene; NaP Naphtalene; PyR Pyrene.

As already observed in the previous study [67], the highest contribution is due to the lighter PAHs. In atmospheric deposition, the heavier PAHs (i.e., over benzo[a]pyrene, B[a]P, molecular weight, 252.32 Da) are observed with higher frequencies than those detected in PM_{2.5} and PM₁₀ fractions. The background station of Rocca Respampani records, on average, lower PAH rates than the other stations, with the exception of a single observation of benzo(b)fluoranthene in summer [68] which is very high compared to all other stations during all sampling periods.

B[a]P was selected as a marker of the carcinogenic potencies of the six PAHs (i.e., Benzo[a]Anthracene, Benzo[b]Fluoranthene, Benzo[j]Fluoranthene, Benzo[k]Fluoranthene, Indeno[1,2,3-cd] Pyrene and Dibenzo[ah]Anthracene) [22,69–72].

The comparison of the deposition rates for B[a]P in the four sites (Table 6) shows a substantial homogeneity of the annual average rates recorded in the Roccaccia and Allumiere sites which are, respectively, equal to 5.9 and 3.9 ng m⁻² d⁻¹, and significantly lower deposimetric rates in the S. Agostino 2.3 ng m⁻² d⁻¹ and Rocca Respampani 2.2 ng m⁻² d⁻¹ stations, which constitutes the blank site. These annual average deposition rates are in line with those measured in remote/reference and urban Italian areas (see Table 7).

Table 7. Levels of B[a]P in other studies in different Italian and European locations (ng m⁻²d⁻¹).

Locations	Benzo[a]Pyrene	Ref.
Aosta (North-West Italy)	urban site: 28 reference site: 5.0	[57,73]
Venice (North-East Italy)	urban site: 30 rural area: 6–9	[21]
Perugia (Central Italy)	urban site: 5.0–14	[74]
Terni (Central Italy)	urban sites: 10–11 industrial sites: 18–27	[74]
Melfi (South Italy)	urban sites: 3.2–4.1 industrial sites: 4.6–6.9 rural site: 140 remote/reference sites: 1.9–5.7	[22,32]
Taranto (South Italy)	urban sites: 2.0–182 industrial site: 57–555 rural area: 5.6–42	[59]
Finland ^a	remote sites: 51–280 rural area: 2–10	[17]
Rorvik (Sweden)	rural area: 5–17	[75]
Paris (France)	urban site: 25	[18,19]
Cardiff, Manchester ^a (UK)	urban area: 219–300	[33]
North Latium (Central Italy)	urban site: 1.4–7.1 industrial site: 1.4–4.6 rural area: 1.4–3.9	This study

^a annual average.

3.2.4. Metals

The atmospheric depositions collected with the deposimeters in the Roccaccia, S. Agostino, Allumiere and Roccarespampani stations were analyzed to determine the deposition rates of the following metals and metalloids which are toxic for human exposure: As, Ba, Be, Cd, Cu, Cr, Mn, Ni, Hg, Pb, Sb, Sr, Sn, Te, Tl, V, and Zn. Even with regard to metals and metalloids in depositions, the Italian and European regulations do not provide any

reference and it is therefore necessary to take into account the reference values adopted by other European countries.

The atmospheric deposition rates measured in the Roccaccia, S. Agostino, Allumiere and Rocca Respampani stations all year long (Table 8 for the annual average whereas Table S9 of the Supplementary Material for each season) show a small variability among seasons with the exception of the Sn in Allumiere and S. Agostino (autumn/spring and winter/summer seasons) and Zn in Roccaccia (autumn/winter season), whose atmospheric deposition rates are significantly higher than in Rocca Respampani. This small seasonal variability shows a different pattern among the sampling sites.

Table 8. Mean levels of metals ($\mu\text{g m}^{-2} \text{d}^{-1}$) determined in the atmospheric depositions at the four investigated locations.

Metals	Roccaccia	Rocca Resp.	Allumiere	S. Agostino
As	0.073	0.084	0.441	0.409
Ba	1.470	2.947	4.583	1.541
Be	0.009	0.037	0.016	0.012
Cd	0.013	0.009	0.020	0.072
Co	0.083	0.092	0.105	0.082
Cr	0.452	0.435	0.758	0.588
Cu	0.858	0.550	0.751	0.869
Mn ¹	4.773	3.266	3.581	3.034
Ni	0.394	0.300	0.470	0.479
Pb	1.105	1.452	0.921	2.553
Sb	0.024	0.042	0.059	0.048
Se	0.025	0.025	0.025	0.027
Sn	12.881	14.402	17.955	113.356
Sr ¹	1.519	2.998	3.534	1.592
Tl	0.006	0.016	0.015	0.006
Te ¹	0.001	0.001	0.001	0.001
Ti ¹	1.227	2.181	1.327	1.292
V	0.375	0.487	0.592	0.531
Zn	6.174	3.846	6.115	5.449
Total	31.460	33.168	41.265	131.941

¹ detected only in winter and spring seasons.

The typical concentrations of metals, detected in different European areas, using bulk deposimeters, are summarized below, considering diverse types of areas [32,76]. The legislations of several European countries establish limit values expressed as an annual average for As, Cd, Hg, Ni, Pb, Tl, Zn and sedimentable dusts [32]. Table 9 resumes such limit values present in the related various legislations.

Table 9. Limit value concentrations ($\mu\text{g m}^{-2} \text{d}^{-1}$) reported in European legislation for different areas.

Metals	Type of Area		
	Rural	Urban	Industrial
As	0.082–0.43	0.22–3.4	2.0–4.3
Cd	0.011–0.14	0.16–0.90	0.12–4.6
Ni	0.03–4.3	5–11	2.3–22

The comparison of the atmospheric depositions rates observed in this study with the limit values shown in Table 9 [32] describes an area in the lower ranges of the atmospheric deposition values as expected in the different countries. Using the intervals rates suggested by the European Commission, the monitored sites of this study would be classified as rural areas for Ni and Cd, and urban for As.

3.3. Chemometric Approach

A chemometric investigation has been carried out on the average deposition rates of annual collecting data, for a better knowledge of the relationships among the main species occurring in the deposition rates. Cluster analysis (CA) and principal component analysis (PCA) were used to achieve similarities among the different species as well as for understanding how the dataset can be divided [77–79]. First, CA among the data of each location was run. As it can be seen in Figure 5, data collected at the two locations such as Rocca Respampani and Allumiere show high similarities whereas ones collected at S. Agostino site show very high dissimilarity in comparison with the previous ones. Roccaccia has an intermediate behavior among the sites.

Figure 5. Cluster Analysis (CA) related to the different sampling points.

This behavior can be explained taking into account both the four sampling points (Figure 1) and the direction of the prevailing winds, i.e., North-West and South-East (Figure 2). The S. Agostino site is located both close to the power plant and close to the port-industrial area in Civitavecchia [67] whereas Allumiere and Rocca Respampani are in the inner part of the region, far from the anthropogenic sources. Roccaccia is located north of S. Agostino, along the same direction as the prevailing winds but farther from anthropogenic sources, i.e., power plant and port-industrial area. These occurrences can explain the Allumiere and Rocca Respampani profiles cluster as well as Roccaccia one whereas S. Agostino is totally different.

The authors would like to investigate the overall data (inorganic and organic fractions) both for finding out similarities among the different species and for evidencing possible presence of outliers that could affect the analysis. First, the CA shows the presence of three clusters:

- cluster # 1 1 compound: Sn;
- cluster # 2 5 compounds: 118-CB, Ba, Mn, Sr, Zn;
- cluster # 3 62 compounds: all other compounds/elements.

For a better representation, the authors would like to show the PCA (Figure 6): the three clusters are well evidenced with the related species.

Figure 6. Principal Component Analysis (PCA) of the overall data. Component 1: organic fraction; Component 2: inorganic fraction.

As it can be seen, the only different species is Sn, which makes group by itself and very distant from the other clusters. In these conditions, Sn could be considered an outlier: this consideration is confirmed looking at the data reported in Table 8 where Sn concentration value determined at S. Agostino site reaches high annual average level ($113 \mu\text{g m}^{-2} \text{d}^{-1}$). The data reported in Table S8 of the Supplementary Material confirm and stress this consideration. The data determined in summer and autumn seasons are 100 to 12,000 times higher than those determined in the other seasons; further, the seasonal values greatly range among them, with a very high level in autumn ($449 \mu\text{g m}^{-2} \text{d}^{-1}$) at S. Agostino site. These factors lead to the hypothesis that Sn could be considered an outlier. Following this assumption, the PCA among sites was performed using all the data but omitting the Sn values, as shown in Figure 7. Component 1 represents the organic fraction, distinguished in the positive values associated with PCBs (mainly, 118-CB, 105-CB, 123-CB, 114-CB) and PCDD/Fs (mainly, OCDD) and the negative values associated with PAHs: Roccaccia is the station with the highest content of PCDD/Fs and PCBs, while Allumiere is the station with the highest values of PAHs and S. Agostino is the one with the lowest contribution of organic compounds. Component 2 represents the inorganic fraction (mainly, Ba, Zn, Sr, Mn): once again, Allumiere shows the highest metal content.

This finding could be reasonable considering the map reported in Figure 1, and especially the distance among the emission points, i.e., the power plant and the port-industrial area of Civitavecchia, and each sampling site: Roccaccia and Rocca Respampani, which are further away from these points than the other two locations, are the main receptors of the organic compounds according to the wind direction whereas the Allumiere and S. Agostino sites mainly suffer of inorganic contamination.

Figure 7. PCA of the four investigated locations. Component 1: inorganic fraction; Component 2: organic fraction.

4. Conclusions

The monitoring of deposition airborne particle greatly contributes to the knowledge on the dynamic of pollution in an area allowing to study the deposition fluxes, the pollutants environmental fate with the aim to address the potential exposure for population. Total depositions (bulk) are particularly suitable to measure the environmental POPs concentration. The data collected by bulk deposition are useful to estimate contamination of farmlands and a subsequent accumulation in the food chain (in which POPs are particularly associated with to fats). In this study, we want to replicate the approach already used in countries like Belgium, Germany and France for PCDD/Fs and PCBs to identify reference values (TDI/deposition) for the Italian situation. Particularly, the results of the chemical characterization of the depositions show that the major differences between the sites are attributable to the PCDD/Fs content. In fact, the total metal content and the total PAHs one are comparable between the four sites, whereas PCDD/Fs and DL-PCBs between the Roccaccia and Rocca Respanpami sites are 3/4 orders of magnitude higher than the other two locations. This suggests that what has been observed is due to activities carried out locally, probably attributable to livestock and agricultural activities. This is conceivable by observing the seasonal differences in the content of PCDD/Fs and DL-PCDs in the different sites: in fact, higher contributions of PCDD/Fs and DL-PCBs in the depositions are observed mainly in summer and autumn. Even the meteorological characteristics of the summer may have contributed to the increase in these depositions. Furthermore, it is highlighted that the results of the chemical characterization of the depositions do not distinguish the potential contribution due to the CTE plant, unlike the results of the airborne PM chemical characterization study [67], performed in the same area. At present, it is necessary to establish specific guidelines and/or limits at European level to better manage the particularly difficult environmental and health situations of the population that are observed in the various national contexts. Finally, it is also desirable find a European consensus on sampling procedures, analytical methods and assessment methods for a unique, accurate and effective evaluation approach.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2076-3417/11/4/1827/s1>, Tables S1–S9: Table S1. Limit of Detections (LODs) for each compound/metal determined in this study. LODs were determined according to the methods reported in International guidelines [51–55]; Table S2. Deposition ($\text{mg m}^{-2}\text{d}^{-1}$) of the total sedimentable particulate matter (PM) per season at each location; Table S3. Atmospheric deposition of PCDD/Fs + DL-PCBs per season at each location; Table S4. Levels of PCDD/Fs and DL-PCBs expressed as equivalent toxicity I-TE, WHO-TE₁₉₉₈ and WHO-TE₂₀₀₅ at Roccaccia location; Table S5. Levels of PCDD/Fs and DL-PCBs expressed as equivalent toxicity I-TE, WHO-TE₁₉₉₈ and WHO-TE₂₀₀₅ at S. Agostino location; Table S6. Levels of PCDD/Fs and DL-PCBs expressed as equivalent toxicity I-TE, WHO-TE₁₉₉₈ and WHO-TE₂₀₀₅ at Allumiere location; Table S7. Levels of PCDD/Fs and DL-PCBs expressed as equivalent toxicity I-TE, WHO-TE₁₉₉₈ and WHO-TE₂₀₀₅ at Rocca Respampani location; Table S8. Seasonal levels of the deposition rates ($\text{ng m}^{-2}\text{d}^{-1}$) for PAHs determined in the four investigated locations; Table S9. Seasonal levels of the deposition rates ($\mu\text{g m}^{-2}\text{d}^{-1}$) for metals determined in the four investigated locations.

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