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SUPPORTING MATERIAL

Characterization of urban pollution in two cities of the Puglia region in Southern Italy using field measurements and air quality (AQ) model approach

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Content

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Text S1. Description of the sampling sites

The urban areas of Bari and the sub-urban site of San Vito Taranto, are characterized by different industrial activities and urban organization. The city of Bari (11 620 km^2, 320 475 town inhabitants) is the capital of the Puglia region. Bari has industrial importance in growing development, especially in the mechanical sector, in the alimentary, and in wood and clothing industries. The urban center is characterized by high motor-vehicle traffic density. On the other hand, San Vito Taranto is a sub-urban southern fraction of the city of Taranto (217 km^2, 191 810 town residents) and is located at 2.5 km from Taranto. In the city of Taranto is situated the Europe's largest iron and steel integrated complex, and close to the steel factory is located one of the largest oil refineries in Italy.

Text S2. PAHs and PCBs screened and the target/qualified ions, and oven conditions

PUF disk samples were extracted in Soxhlet for 24 h using petroleum ether (300 ml), extracts were concentrated by rotary evaporation and blow down under a gentle stream of nitrogen to 0.5 ml and solvent exchanged to isooctane. Mirex (100 ng) was added as internal standard to correct for volume difference. Analysis of PUF disk extracts for PAHs and PCBs were carried out by gas chromatography-mass spectrometry (GC-MS) on a GC-Trace^{TM} GC 2000 (equipped with auto sampler AS3000), and MS *Polaris*Q ionic trap (ThermoFinnigan), using positive electron impact-selected ion monitoring (EI-SIM). PUF disk samples were analyzed for a suite of target of 15 PAHs listed by the US EPA as priority pollutants (excluded naphthalene). PAHs compounds and target/qualified ions were monitored as follow: acenaphthylene (152), acenaphthene (154), fluorene (166), phenanthrene (178), anthracene (178), fluoranthene (202), pyrene (202), benz(*a*)anthracene (228), chrysene (228), benzo(*b*)fluoranthene (252), benzo(*k*)fluoranthene (252), benzo(*a*)pyrene (252), indeno(*1,2,3-cd*)pyrene (276), dibenzo(*a,h*)anthracene (278/276), benzo(g,h,i)perylene (276) (Supelco Analytica, USA). PCBs congeners were: PCBs-3Cl: 28, 37 (256/2589), PCBs-4Cl: 52 (290/292), PCBs-5Cl: 95, 101, 99, 110, 105, 114, 118, 123, 126 (326/328), PCBs-6Cl: 138, 141, 146, 149, 151, 153, 156, 157, 167 (360/362), PCBs-7Cl: 170, 177, 180, 183, 187, 189 (394/396), PCB-10Cl: 209 (496/498) (Supelco Analytica, USA).

For PAHs and PCBs, GC separation as performed on a capillary column ZB-5ms (30m · 0,25 mm internal · 0,25 µm) from the Phenomenex. The oven temperature program was as follows: start at 50 °C (hold 2 minute), 50-120 °C at 30 °C min-1, 120-280 °C at 6 °C min-1 (hold 15 minute) at 6 °C min-1. A sample of 2 µL was injected on splitless mode at 250 ºC.

Text S3. Modeling set up

PCB and PAHs simulations were carried out for the year 2012 over the Italian basin with a spatial resolution of 12 km x 12 km and 16 terrain-following vertical levels irregularly spaced from the ground to 10 000 m above surface level, with the first four layers placed at 20, 75, 150 and 250 m.

The meteorological input fields to FARM were produced by the prognostic, non-hydrostatic meteorological model RAMS, run in a 2-way nested grids configuration: an outer grid covering large part of Central Europe and the Mediterranean Sea, with a horizontal resolution of 48 km × 48 km, and an inner grid, including the Italian domain for the air quality simulations, with a resolution of 12 km × 12 km. Initial and boundary conditions have been based on NCEP operational analyses with a horizontal space resolution of 1. degrees and a time frequency of 3 hours.

The emissions used in this study came from the ISPRA National Emissions Inventory (ISPRA, 2009) for the Italian basin and from the EMEP Centre on Emission Inventories and Projections (CEIP) [http://www.ceip.at] for surrounding countries. The ISPRA inventory is compiled at the national level, by multiplying activity data and emission factors (EF) that express emission of pollutant per unit of activity. The inventory has been then disaggregated at provincial level (NUTS3) using activity-related proxy data. The inventory follows the CORINAIR methodology defined by the European Environmental Agency (EEA, 2009): emissions sources are classified according to the SNAP (Standard Nomenclature for Air Pollution) scheme, allowing an easy individuation of the relative contribution of different emission activities. In the inventory emission sources are available as: point sources and diffuse sources. Point sources are mostly large industrial facilities and energy production plants; these sources are individually characterized with geographic coordinates, physical and thermodynamic parameters (stack height and diameter, gas exit velocity and temperature). Related emissions are either directly measured or estimated through process-specific EF starting from fuel consumptions or activity levels and accounting for abatement techniques that can be in place. Diffuse sources are all other sources that cannot be considered on an individual basis and whose activities take place over a larger area; their emissions are usually estimated through statistical data of the underlying activities. National PCB emissions were provided by EMEP while the ISPRA inventory was used for PAHs. The further disaggregation of these species in their congeners was performed using proper speciation profiles for each activity. Boundary conditions to the national domain have been derived from background domain results.

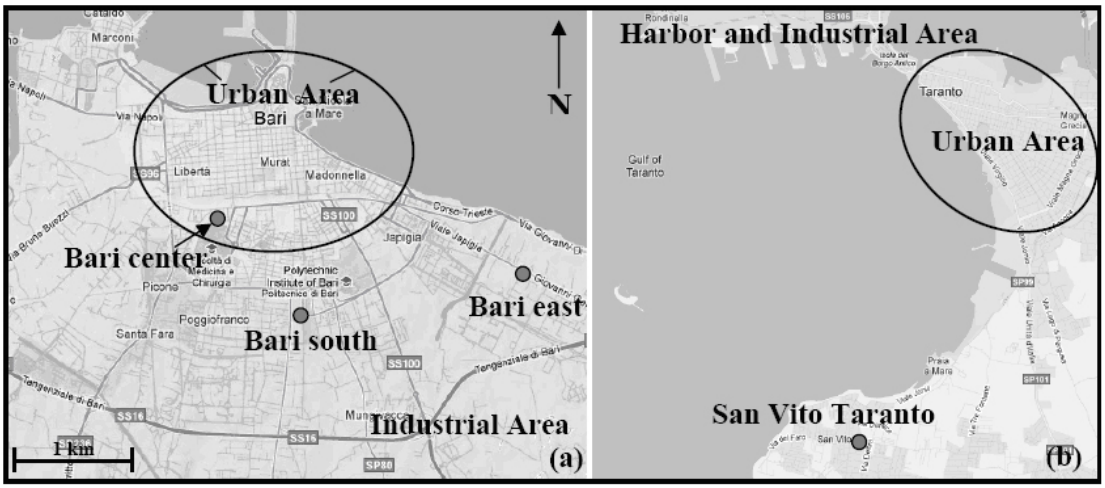

Figure S1. *Map of sampling sites: (a) Bari, and (b) Taranto.*

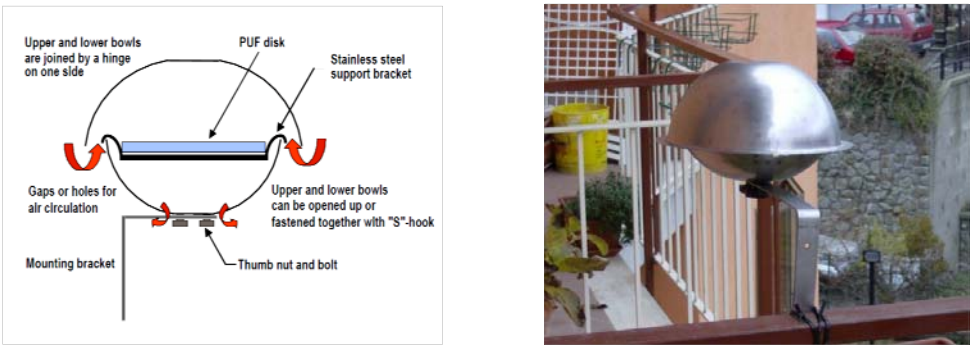

Figure S2. *Schematic representation of the PUF disk sampler and photo of a PAS deployed.*

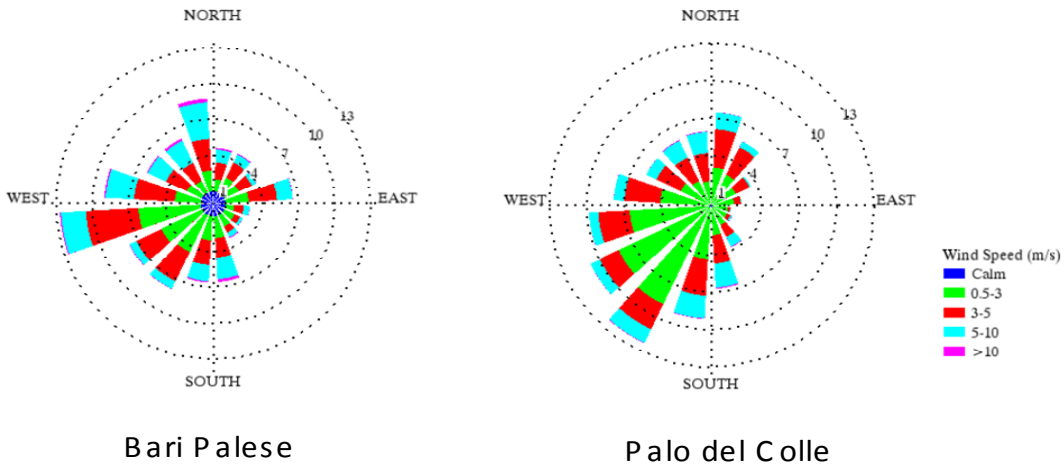

Figure S3. *Wind roses showing direction, distribution, and intensity at the weather stations of Bari Palese and Palo del colle.*

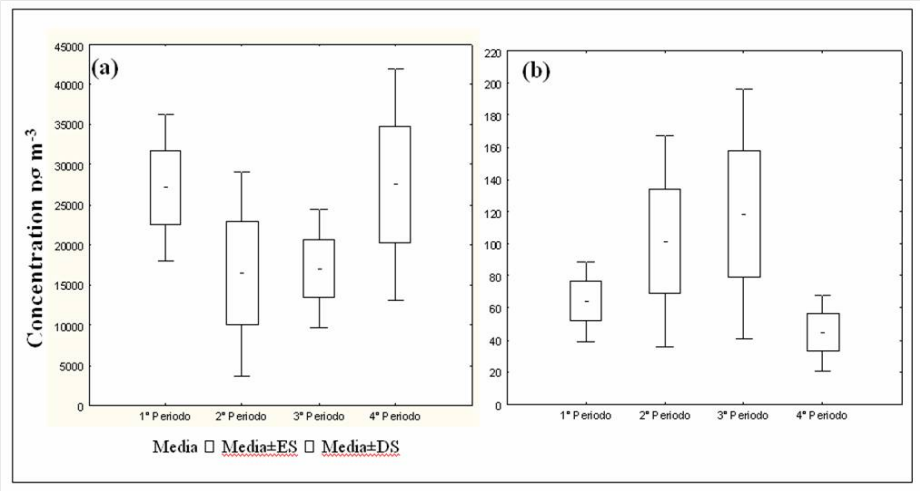

Figure S4. *Box and whisker plots of the concentrations in air (pg m^{-3}) of Bari and San Vito Taranto over 4 consecutive sampling periods;* ***(a)*** *total PAHs and* ***(b)*** *total PCBs.*

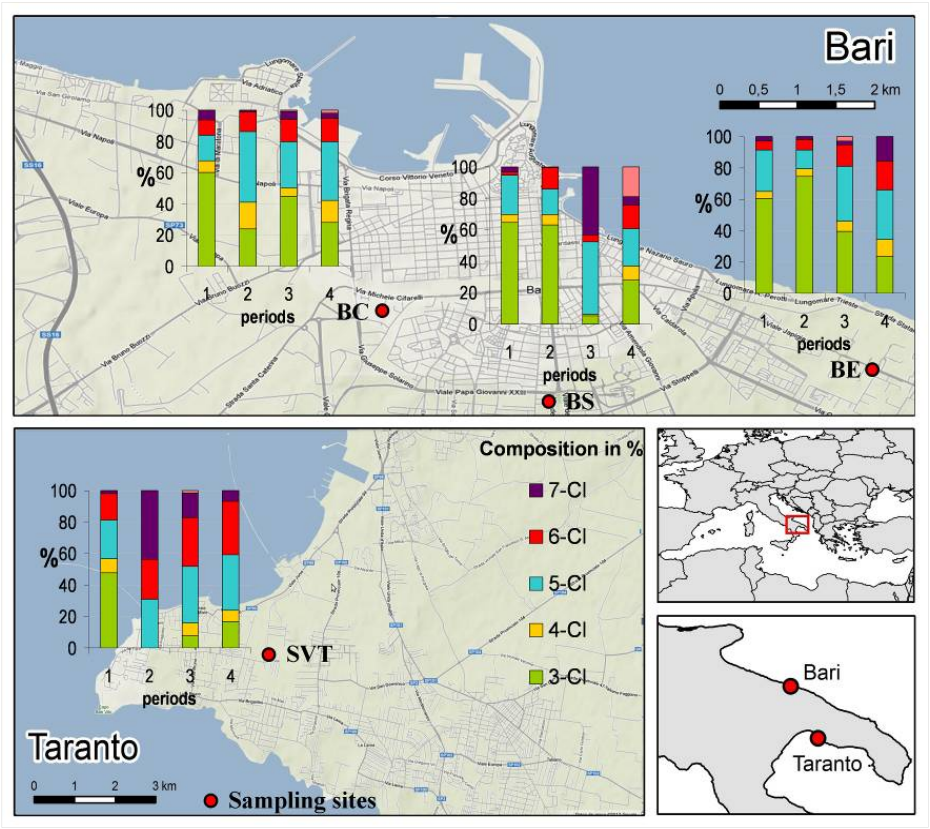

Figure S5. *PCBs congeners composition (%) during 4 periods in two cities of Puglia region in Southern Italy.*

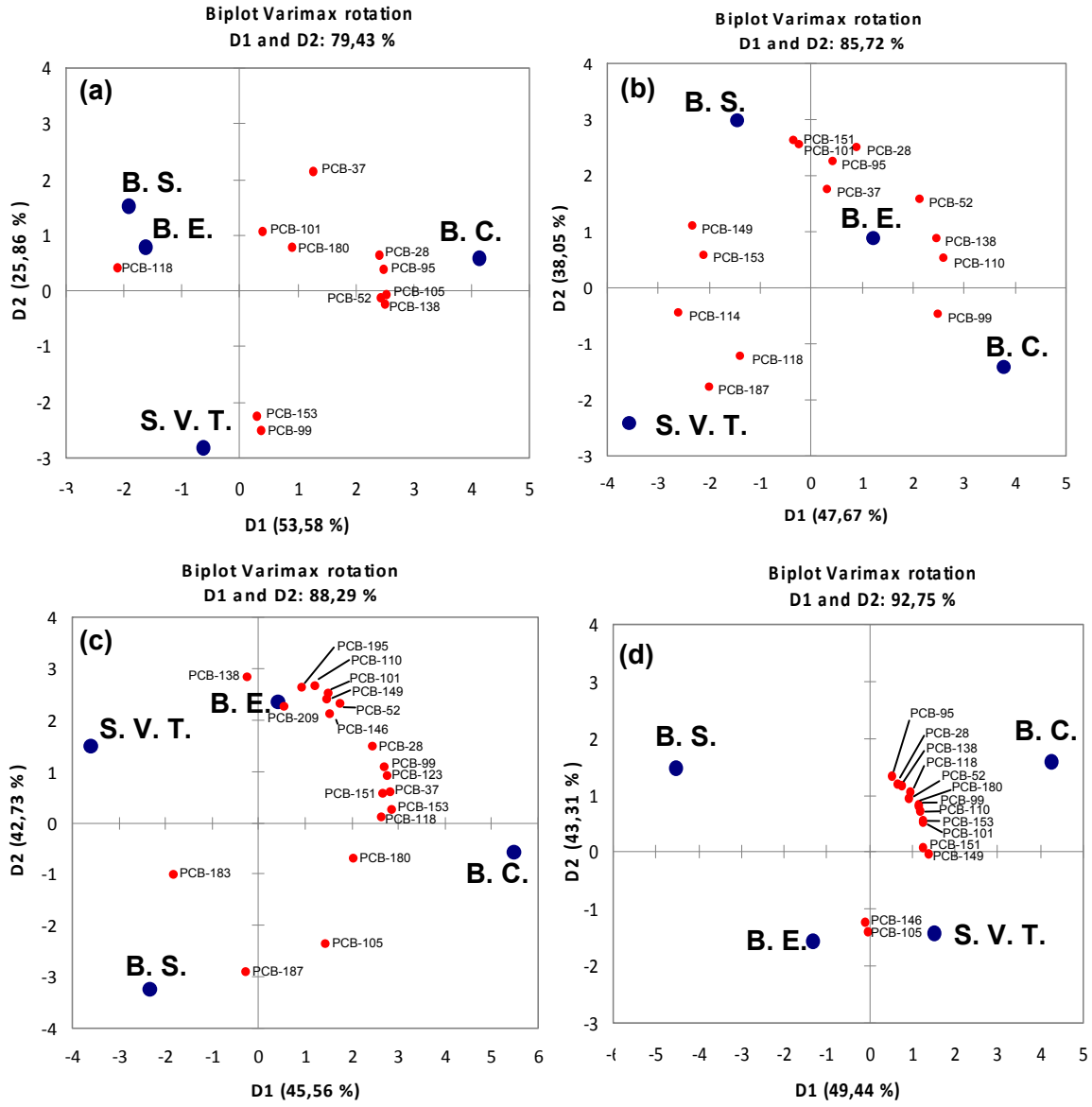

Figure S6. *Score plot for principal component analysis (PCA) applied to PCBs congeners across four sampling sites in Puglia Region.* ***(a)*** *PCA analysis of the period 1 of PCBs (n=11),* ***(b)*** *period 2 of PCBs (n=14),* ***(c)*** *period 3 of PCBs (n=19) and* ***(d)*** *period 4 of PCBs (n=14). B.S. = Bari South, B.E. = Bari East, B.C. = Bari Centre, and S.V.T. = San Vito Taranto.*

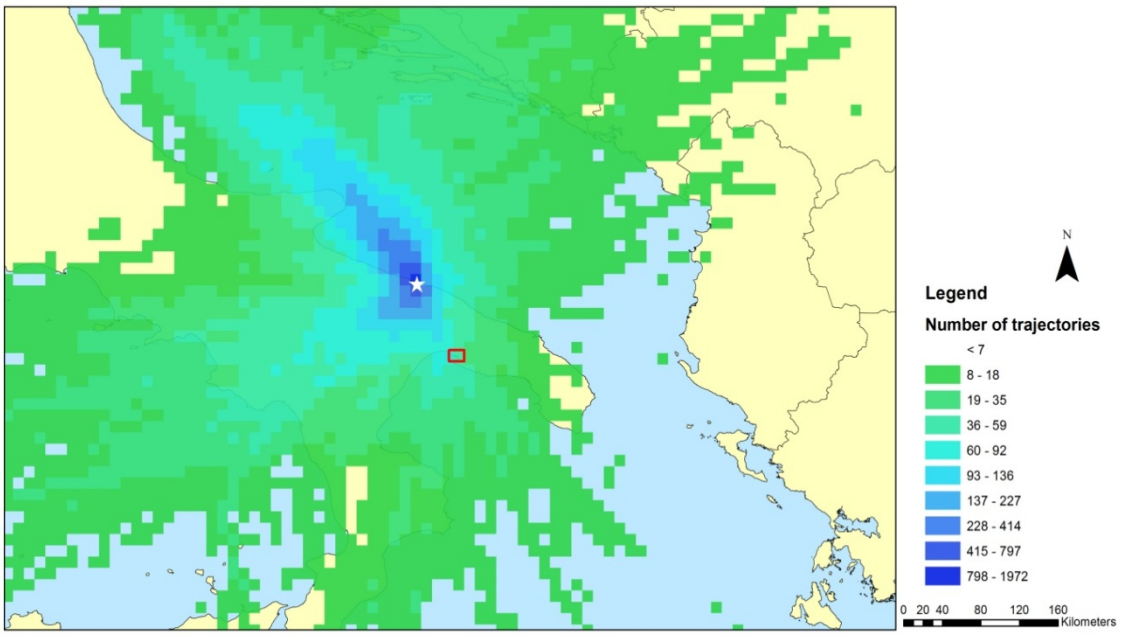

Figure S7. *Sum of 24-hour backward trajectories obtained from HYSPLIT model for all four periods reaching the city of Bari at 3, 9, 15, and 21 UTC. The star indicates the location of the city of Bari and the rectangle the greater industrial area of the city of Taranto.*

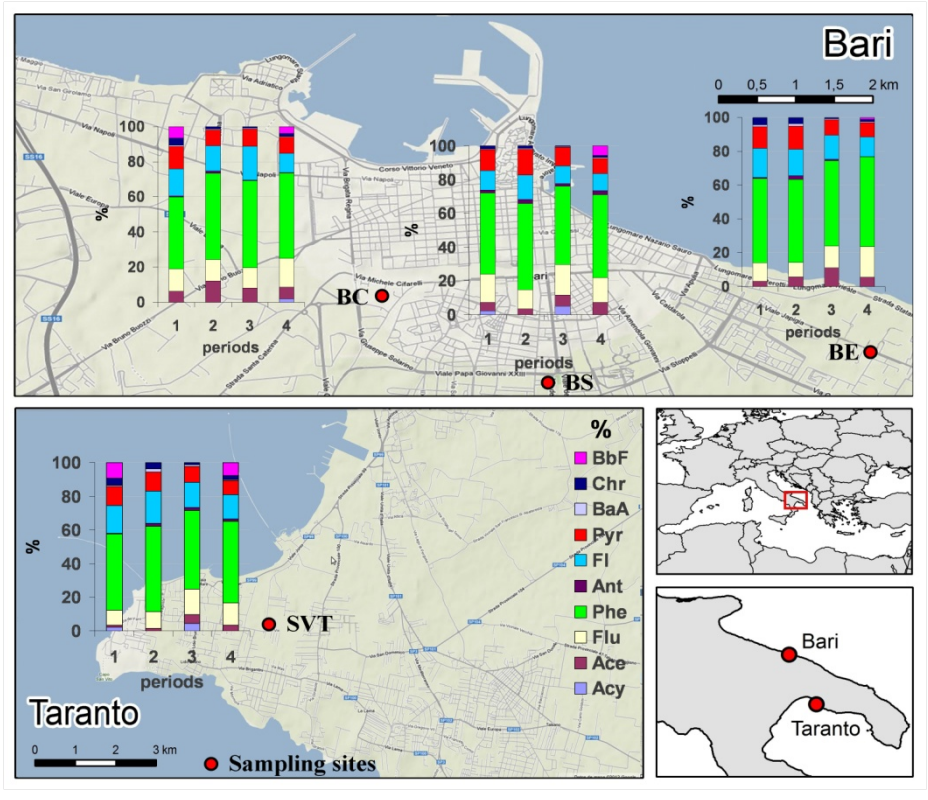

Figure S8. *PAHs compounds composition (%) during 4 periods in two cities of Puglia region in Southern Italy.*

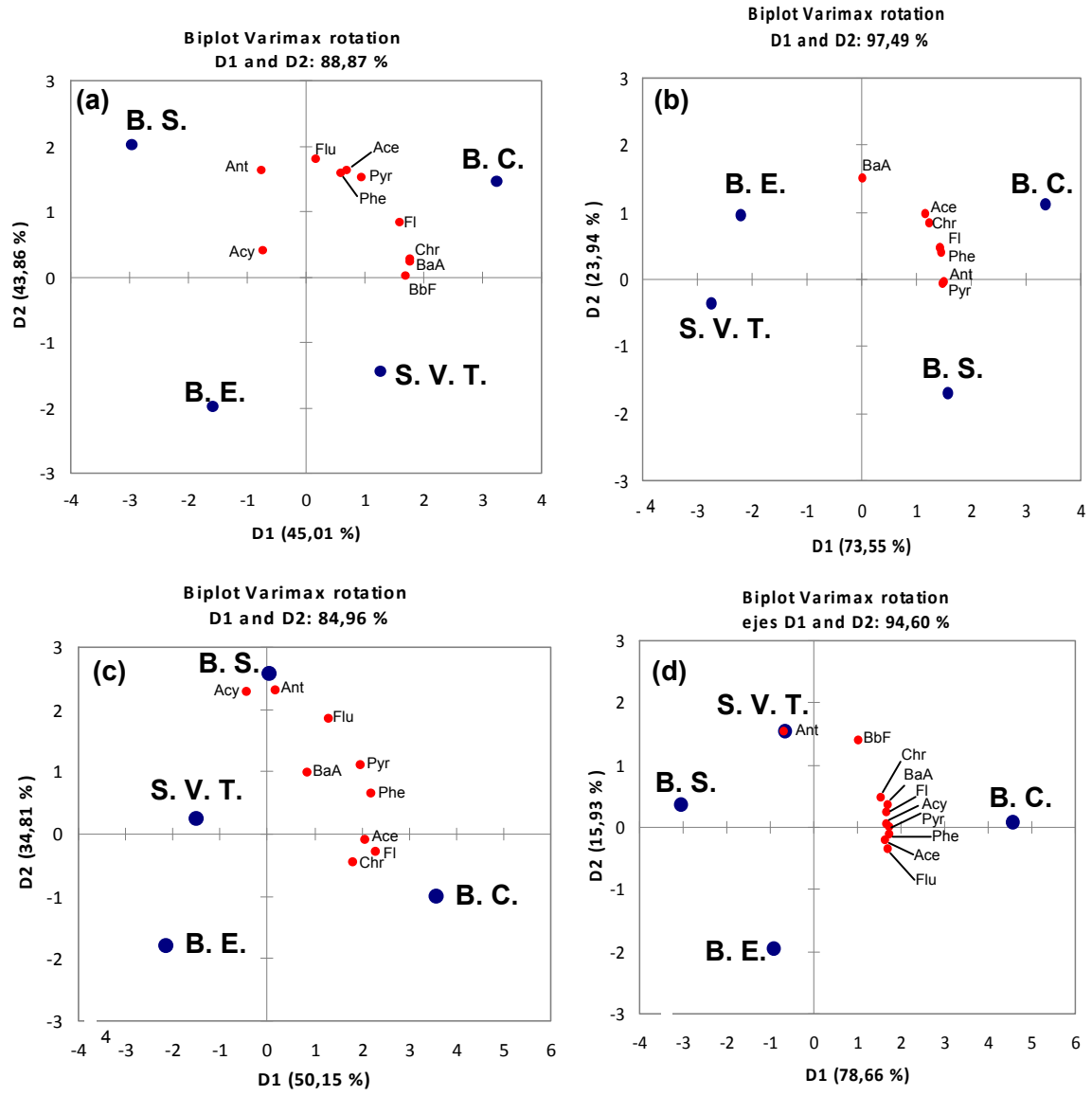

Figure S9. *Plot for principal component analysis (PCA) applied to PAHs across four sampling sites in Puglia Region.* ***(a)*** *PCA analysis of the period 1 of PAHs (n=10),* ***(b)*** *period 2 of PAHs (n=8),* ***(c)*** *period 3 of PAHs (n=9) and* ***(d)*** *period 4 of PAHs (n=10). B.S. = Bari South, B.E. = Bari East, B.C. = Bari Centre, and S.V.T. = San Vito Taranto.*

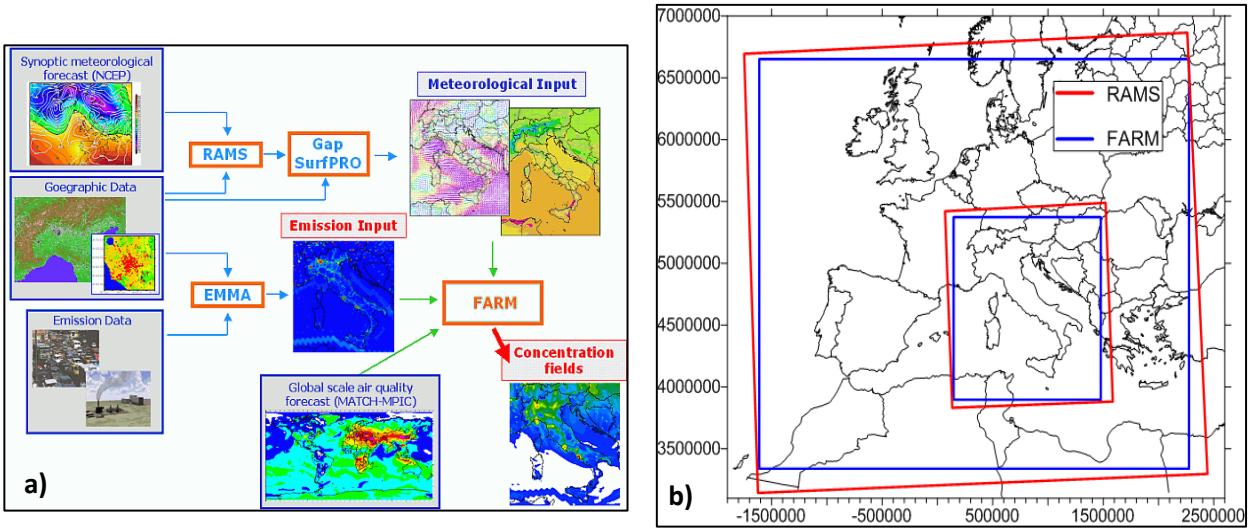

Figure S10. (a) *QualeAria data flux diagram, and* ***(b)*** *QualeAria background and national domains (http://www.aria-net.eu/QualeAria/index_en.html).*

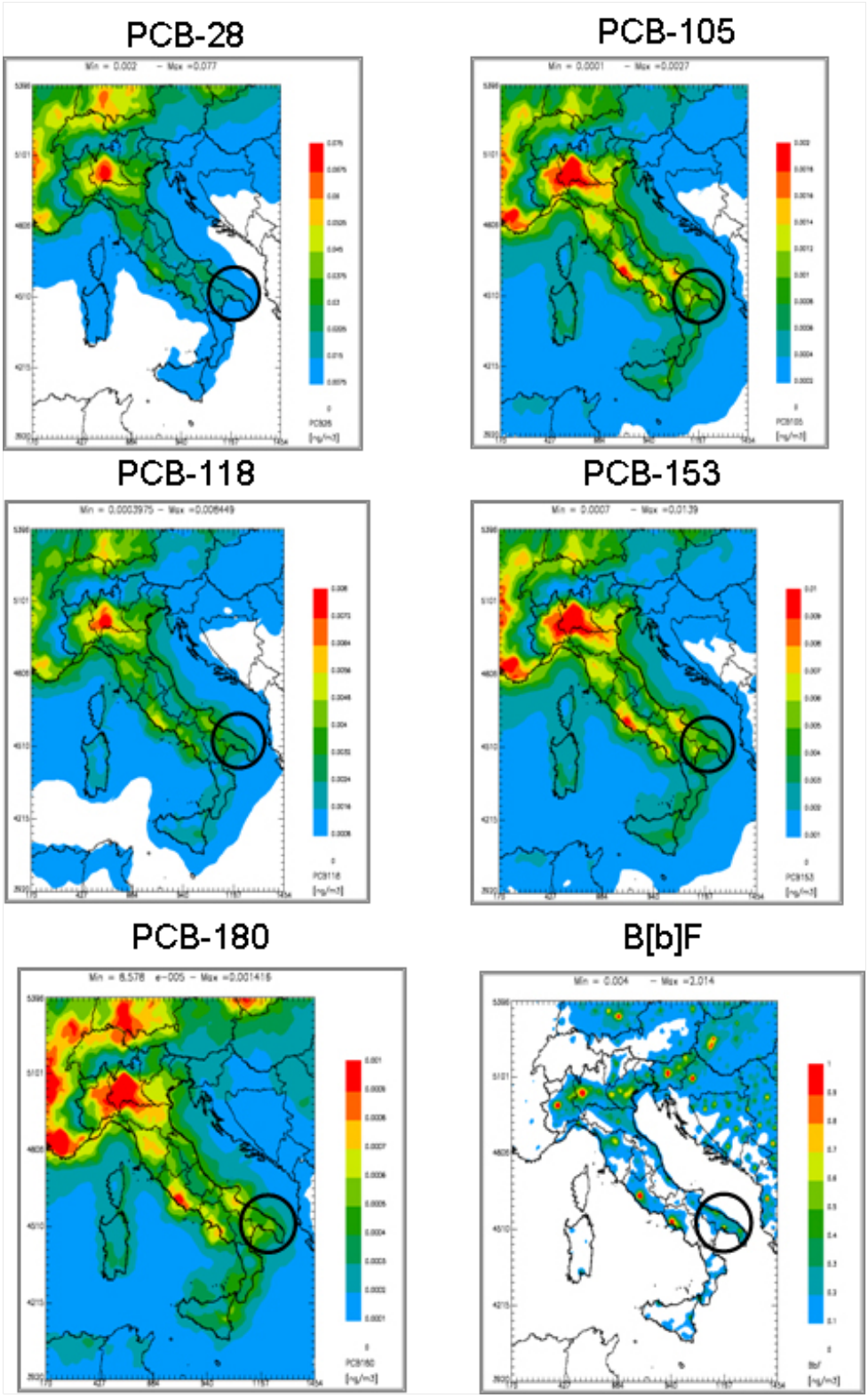

Figure S11. Average concentrations of PCBs congeners (28, 105, 118, 153 and 180) and benzo(b)fluoranthene (from January 1st to March 28th, 2010) computed by QualeAria over Italy.

Table S1. *Sampling sites information at Bari and San Vito Taranto stations, temperature (°C), deployment time and coordinates*

Period	Sampling Sites	Latitude N	Longitude X	T (°C)	days	Start	Final
1	BC	41°06'58.86''	16°51'42.09''	9.5	94	10/1/2009	14/04/09
	BE	41°06'26.94''	16°54'32.45''	9.5	90	4/1/2009	4/4/2009
	BS	41°06'22.99''	16°52'24.80''	9.5	104	1/1/2009	15/04/09
	SVT	40°24'58.73''	17°14'12.38''	10.6	109	27/12/09	15/04/09
2	BC	41°06'58.86''	16°51'42.09''	18.8	70	14/04/09	23/06/09
	BE	41°06'26.94''	16°54'32.45''	18.8	83	4/4/2009	28/06/09
	BS	41°06'22.99''	16°52'24.80''	18.8	72	15/04/09	28/06/09
	SVT	40°24'58.73''	17°14'12.38''	22.9	72	15/04/09	28/06/09
3	BC	41°06'58.86''	16°51'42.09''	23.9	97	23/06/09	28/09/09
	BE	41°06'26.94''	16°54'32.45''	23.9	92	28/06/09	28/09/09
	BS	41°06'22.99''	16°52'24.80''	23.9	122	28/06/09	28/10/09
	SVT	40°24'58.73''	17°14'12.38''	27.3	92	28/06/09	28/09/09
4	BC	41°06'58.86''	16°51'42.09''	11.4	142	28/09/09	17/02/10
	BE	41°06'26.94''	16°54'32.45''	11.4	145	28/09/09	20/02/10
	BS	41°06'22.99''	16°52'24.80''	11.4	151	28/10/09	28/03/10
	SVT	40°24'58.73''	17°14'12.38''	12.9	145	28/09/09	20/02/10

Abbreviations, BC= Bari center, BE= Bari east, BS= Bari south, SVT= San Vito Taranto

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Table S2. *Concentrations (pg m^{-3}) of PCBs congeners at each sampling site, method detection limit (MDL), and air volumes (V_{AIR}, m^3)*

	Periods	28	37	52	95	99	101	105	110	114	118	123	138	146	149	151	153	156	157	167	170	177	180	183	187	189	209	Total
1	Bari Center	30	30	8	6	2	4	4	<0.5	<2	<0.5	<1	4	<2	<2	<1	1	<2	2	2	2	<2	1	<1	1	2	<1	100
	Bari East	6	20	2	3	1	2	3	2	<2	2	<1	1	1	<2	<1	1	<2	<2	<2	<2	<2	1	<1	<0.5	<1	<1	45
	Bari South	10	30	3	3	<1	6	3	<0.5	<2	4	<1	<2	<2	<2	<1	1	<2	<2	<2	1	<2	1	<1	<0.5	<1	<1	60
	San Vito T.	7	14	4	3	<1	3	3	<0.5	<2	2	<1	2	1	2	<1	3	<2	<2	<2	<2	<2	1	<1	<0.5	<1	<1	45
2	Bari Center	14	<2	10	4	3	<1.5	10	5	<2	<0.5	3	3	<2	<2	<1	3	2	<2	<2	<2	<2	<2	<1	1	<1	<1	6
	Bari East	20	120	10	3	2	4	<2.5	4	1	7	<1	2	<2	3	2	2	<2	<2	3	<2	<2	<2	<1	1	3	<1	190
	Bari South	30	50	10	8	<1	5	<2.5	3	4	<0.5	<1	2	<2	4	2	4	<2	5	<2	<2	<2	<2	<1	1	<1	<1	130
	San Vito T.	<2	<2	<0.5	<1	<1	<1.5	<2.5	<0.5	7	9	<1	<2	3	4	<1	4	<2	<2	2	14	<2	<2	<1	2	6	<1	50
3	Bari Center	30	60	10	8	6	10	4	10	<2	10	10	4	7	8	4	5	<2	<2	1	3	<2	4	1	2	<1	2	200
	Bari East	30	30	10	13	4	10	2	10	<2	8	8	7	5	7	2	2	<2	<2	<2	<2	<2	1	1	2	<1	5	156
	Bari South	<2	2	0	3	<1	2	5	2	<2	6	<1	1	<2	1	<1	<0.5	<2	<2	<2	<2	<2	2	2	3	10	<1	40
	San Vito T.	7	<2	8	8	2	10	1	8	<2	3	2	7	6	7	1	1	5	2	<2	8	<2	2	2	2	<1	1	90
4	Bari Center	20	<2	10	7	4	10	<2.5	6	<2	3	<1	3	1	3	1	5	<2	<2	<2	<2	<2	2	<1	<0.5	<1	2	76
	Bari East	8	<2	4	2	1	4	2	2	<2	<0.5	<1	1	1	2	0	1	<2	<2	<2	2	1	1	1	<0.5	1	<1	34
	Bari South	10	<2	4	5	1	1	<2.5	2	<2	1	<1	2	0	2	0	2	<2	<2	<2	<2	1	1	<1	0	1	8	42
	San Vito T.	6	<2	2	3	1	4	1	3	<2	1	<1	2	1	3	1	3	<2	2	<2	<2	<2	1	1	1	<1	<1	36
MDL pg m^{-3}		2	2	0.5	1	1	1.5	2.5	0.5	2	0.5	1	2	2	2	1	0.5	2	2	2	2	2	2	1	0.5	1	1	
V_{air}, m^3 (60 d.)		189	194	204	220	224	224	232	227	231	231	232	231	230	229	228	230	233	233	233	233	233	233	232	232	234	234	
V_{air}, m^3 (150 d.)		353	373	421	505	528	524	570	545	567	564	571	569	561	555	551	563	579	577	577	580	576	578	573	572	582	584	

Abbreviations: MDL: method detection limit (pg m^{-3}), an average air volume of 240 m^3 was used to calculate MDL. d:days.

***Table S3**. Concentrations (pg m^{-3}) of PAHs at each sampling site, method detection limit (MDL) and air volumes (V_{AIR}, m^3)*

Periods	pg m^{-3}	Acy	Ace	Flu	Phe	Ant	3-r	Fl	Pyr	BaA	Chr	4-r	BbF	$Total_{10}$ PAH
1°	**Bari center**	< 2	2 360	4 800	15 600	300	23 000	5 900	4 900	260	1 500	13 000	410	36 000
	Bari east	< 2	490	1 700	7 800	140	10 000	2 700	2 000	160	680	5 500	< 1	15 700
	Bari south	660	1 500	4 850	14 200	510	22 000	3 400	3 700	150	520	7 700	< 1	29 000
	San Vito T.	580	300	2 250	11 600	70	15 000	4 200	2 900	230	1 020	8 300	400	23 500
2°	**Bari center**	< 2	4 100	4 200	16 600	440	25 000	4 800	3 100	130	500	8 500	< 1	34 000
	Bari east	< 2	520	770	4 400	190	5 900	1 400	1 200	130	330	3 100	< 1	9 000
	Bari south	< 2	650	1 930	9 000	400	12 000	2 560	2 600	90	280	5 600	< 1	17 500
	San Vito T.	< 2	80	530	2 680	80	3 400	1 030	600	110	190	1 900	< 1	5 300
3	**Bari center**	< 2	2 020	2 840	12 300	150	17 000	4 700	2 500	90	240	7 500	< 1	25 000
	Bari east	< 2	1 100	1 200	4 800	70	7 200	1 400	900	40	70	2 400	< 1	9 600
	Bari south	1100	1 440	3 820	9 900	360	17 000	2 200	2 400	80	90	4 800	< 1	21 400
	San Vito T.	540	610	1 840	5 600	220	9 000	1 800	1 200	110	170	3 200	< 1	12 100
4°	**Bari center**	940	3 200	7 850	23 200	150	35 000	5 200	4 500	150	740	10 600	370	46 300
	Bari east	< 2	1 300	4 330	12 500	30	18 000	2 800	2 000	80	370	5 200	40	23 400
	Bari south	< 2	1 000	2 030	6 840	340	10 000	1 400	1 250	70	180	2 900	150	13 300
	San Vito T.	< 2	880	3 250	12 000	310	16 000	3 600	2 050	100	600	6 300	370	24 200
MDL		2	1	2	2	2		4	2	1	1		1	
V_{air}, m^3 (60 days)		50	50	110	170	170		230	230	240	240		240	
V_{air}, m^3 (150 days)		50	50	130	280	280		530	560	630	630		650	

Abbreviations: Acenaphthylene (Ac), Acenaphthene (Ace), Fluorene (Fl), Phenanthene (Phe), Antracene (An), Fluoranthene (Flu), Pyrene (Pyr), Banzo(a)antracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF).

Table S4. Contributions of different activities to Italian PAHs emission (ton/year)

Activity	ton/yr PAHs	ton/yr PCBs
Energy Production	5 649	70
Combustion in Residential	78 357	46
Combustion in Industry	1 952	14
Production Processes	33 332	93
Solvent Use	11	
Road Transport	2 740	
Other Transport & Mobile Machinery	322	
Waste Treatment	30 304	2
Nature	1 966	
Total	154 634	224

References

EEA, 2009. EMEP/EEA Air Pollutant Emission Inventory Guidebook-2009, Technical Report No. 9/2009, http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009, accessed in October 2013.

ISPRA, 2009. Provincial Levels of the National Emissions Inventory for the Years 1990-1995-2000-2005, Report 92/2009, Rome, 200 pages.