Air Quality Impact of VOCs Emission from the Hazardous Waste Landfills Located in Giugliano (Na)

Sandro Finardi, Giuseppe Agrillo, Rita Baraldi, Giuseppe Brusasca, Luca Vitale, Giulia Carriero, Paolo Ciccioli, Sara Di Lonardo, Osvaldo Facini, Daniela Famulari, Daniele Gasbarra, Beniamino Gioli, Luisa Neri, Vincenzo Magliulo, Rossella Prandi, Gianni Tinarelli, Piero Toscano and Alessandro Zaldei

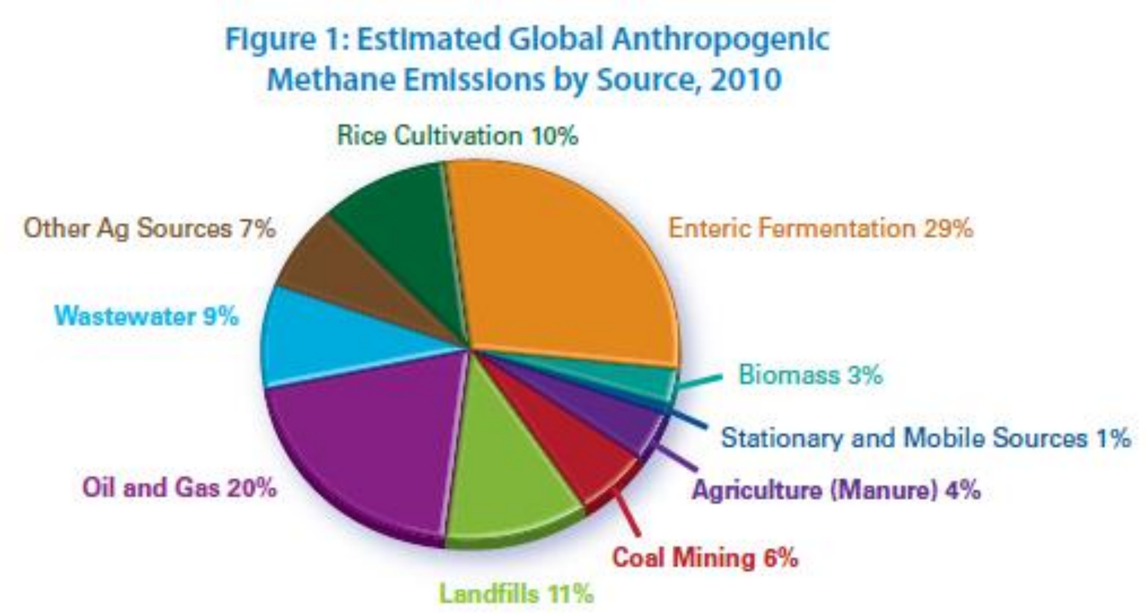
18th International Conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes *Bologna, 9-12 October 2017*

Landfill gas

- Landfill gas (LFG) is generated by the decomposition of biodegradable waste in landfills.
- LFG consists of 40÷60% CO_2, 45÷60% CH_4, 5% N_2, and up to 1% VOCs.
- LFG emissions may continue for 20 to 50 years after initial dumping of wastes.

ITALY (2015)
Solid waste disposal on land is responsible of 32.7% of CH_4 total national emissions (33.3% in 1990).

37.4% of urban waste disposed in landfills in 2015 (91.1% in 1990).



Co-disposal LFG is expected to include higher NM-VOC concentrations than Municipal Solid Waste LFG, that has not received significant quantity of toxic/hazardous compounds. (US-EPA, 2005).

VOCs in landfill gas

Biogas emission can increase the atmospheric levels of:

- benzene (carcinogenic);
- other aromatics (toluene, xylenes and styrene) affecting the human health;
- chlorinated VOCs such as trichloroethene and tetrachloroethene (carcinogenic).

EU Directive 1999/31/CE: biogas emitted from the uptake pipes of urban waste landfills must be conveyed to a purification unit, where the condensable components are removed by a chiller and a filter, to permit the safe use of gas for electricity generation.

Giugliano Landfills study area

Giugliano Landfills study area

Giugliano Landfills study area

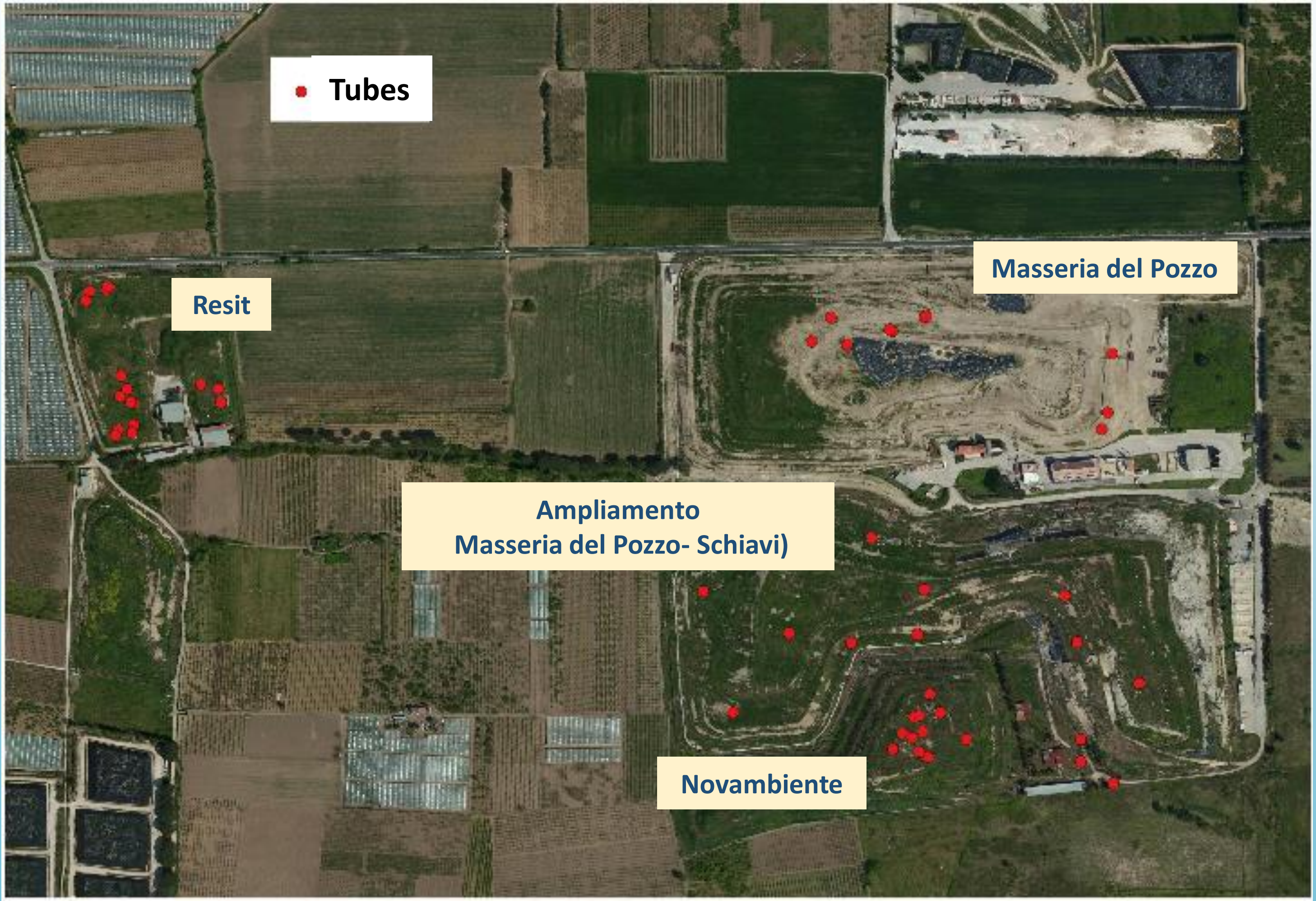
Hazardous waste landfills in Giugliano (NA)

Ten landfills located within Giugliano municipality

- used for illegal dumping of industrial and toxic wastes (together with urban waste);
- operational from the late 1980's to the early 2000's under the control of Camorra;
- closed and seized by court injunctions in 2003-2009;
- first phase of trials had led to convictions up to 20 years of jail;
- severe episodes of soil and water contamination reported (Balestri, 2010);
- arson episodes in 2007, 2010, 2013, 2015 and 2016;
- increasing fugitive emissions caused by:
  - the impairment of the biogas management system,
  - the formation of large fractures in the waste sealing,
  - damages caused by arsons.

Landfill emissions have been estimated integrating different techniques to sample and analyse CH_4 and VOCs fluxes

Captation tube sampling for VOCs detection

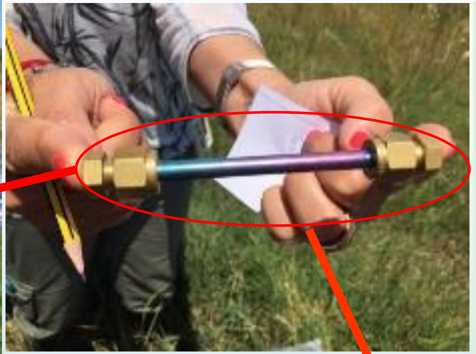


Landfill VOC sampling

ARIANET

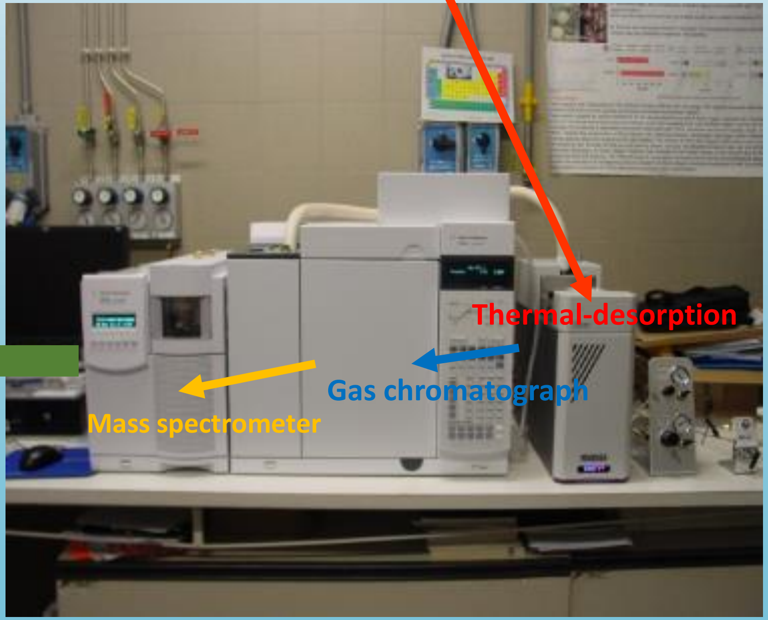
VOCs chemical analysis

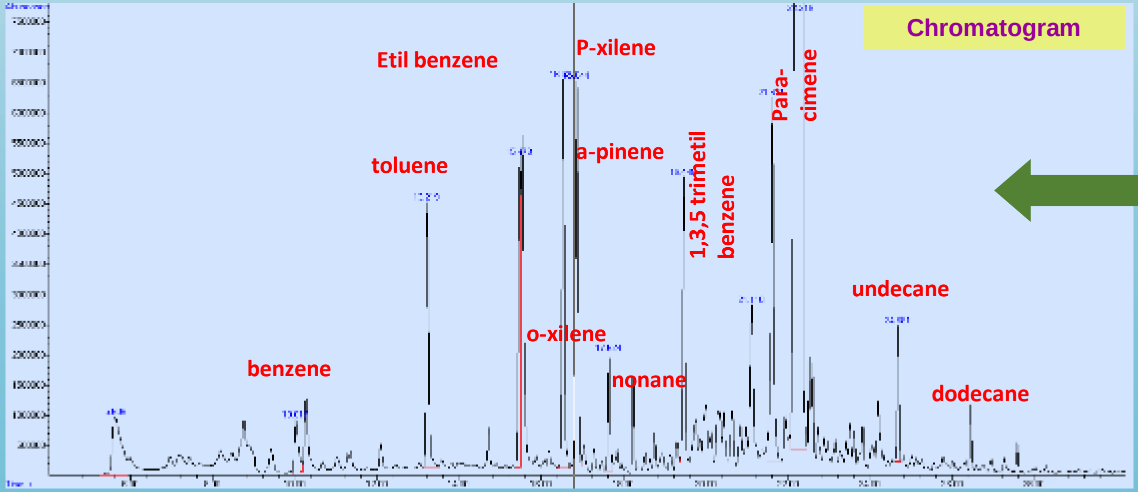
biogas captation tubes



Metal adsorption trap containing Tenax substrate to retain VOCs

Lab chemical analysis





Volatile Organic Compounds identified by GC-MS:

More than 160 compounds were identified and quantified in the biogas of the various landfills.

No unique tracer of toxic waste dumping can be clearly identified

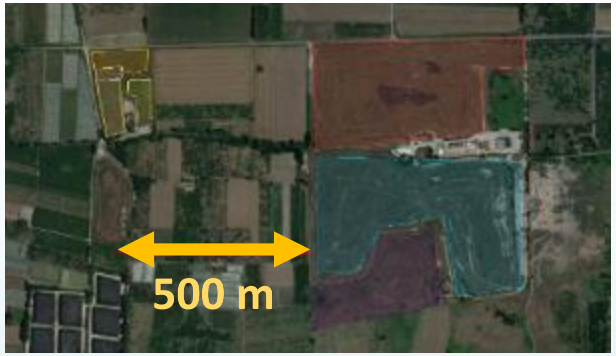
To simplify the analysis of the differences among the landfill emissions, VOCs were grouped according to the following chemical classes:

- arenes,
- alkenes,
- alkanes,
- carbonyls,
- alcohols,
- heterocyclic,
- chlorinated,
- other compounds.

	Compounds	RT	Ions	MW	Formula
Acids	formic aci				
Acids	acetic aci				
Acids	nonanoic				
Acids	decanoic				
Alcohols	1 octanol				
Aldehydes	methacro				
Aldehydes	hexanal				
Aldehydes	heptanal				
Aldehydes	OCTANAL				
Aldehydes	NONANA				
Aldehydes	DECANAL				
Aldehydes	benzaldeh				
Alkanes	pentane				
Alkanes	pentane,				
Alkanes	pentane,				
Alkanes	hexane				
Alkanes	hexane, 2				
Alkanes	hexane, 3				
Alkanes	pentane, trimethyl				
Alkanes	heptane				
Alkanes	3 methyl				
Alkanes	octane				
Alkanes	nonane				
Alkanes	undecane				
Alkanes	dodecane	27 351	57-43-71	170.33	C12H16
Alkanes	tetradecane	32 384		198.39	C14H30
Alkenes	1-octene	14 204	55-41-83-70	112.22	C8H16

	Compounds	RT	Ions	MW	Formula
				84.95	CH2Cl2
				78.11	C6H6
				92.14	C7H8
				106.17	C8H10
				106.17	C8H10
				106.17	C8H10
				104.15	C8H8
				120.20	C9H12
				120.20	C9H12
				120.20	C9H12
				120.20	C9H12
				128.17	C10H8
				72.11	C4H8O
				120.15	C8H8O
				70.09	C4H6O
				81.12	C5H7N
				154.21	C12H10
				94.11	C6H6O
				154.25	C10H10O
				68.12	C5H8
				136.24	C10H16
				136.24	C10H16
Terpenes	beta pinene	20 711	93-69-41-91	136.24	C10H16
Terpenes	para cimene	21 340	119-91-134	134.21	C10H14
Terpenes	limonene	22 300	68-93-67-79	136.24	C10H16

Giugliano landfill VOCs emissions



compared with

Malagrotta landfill emissions

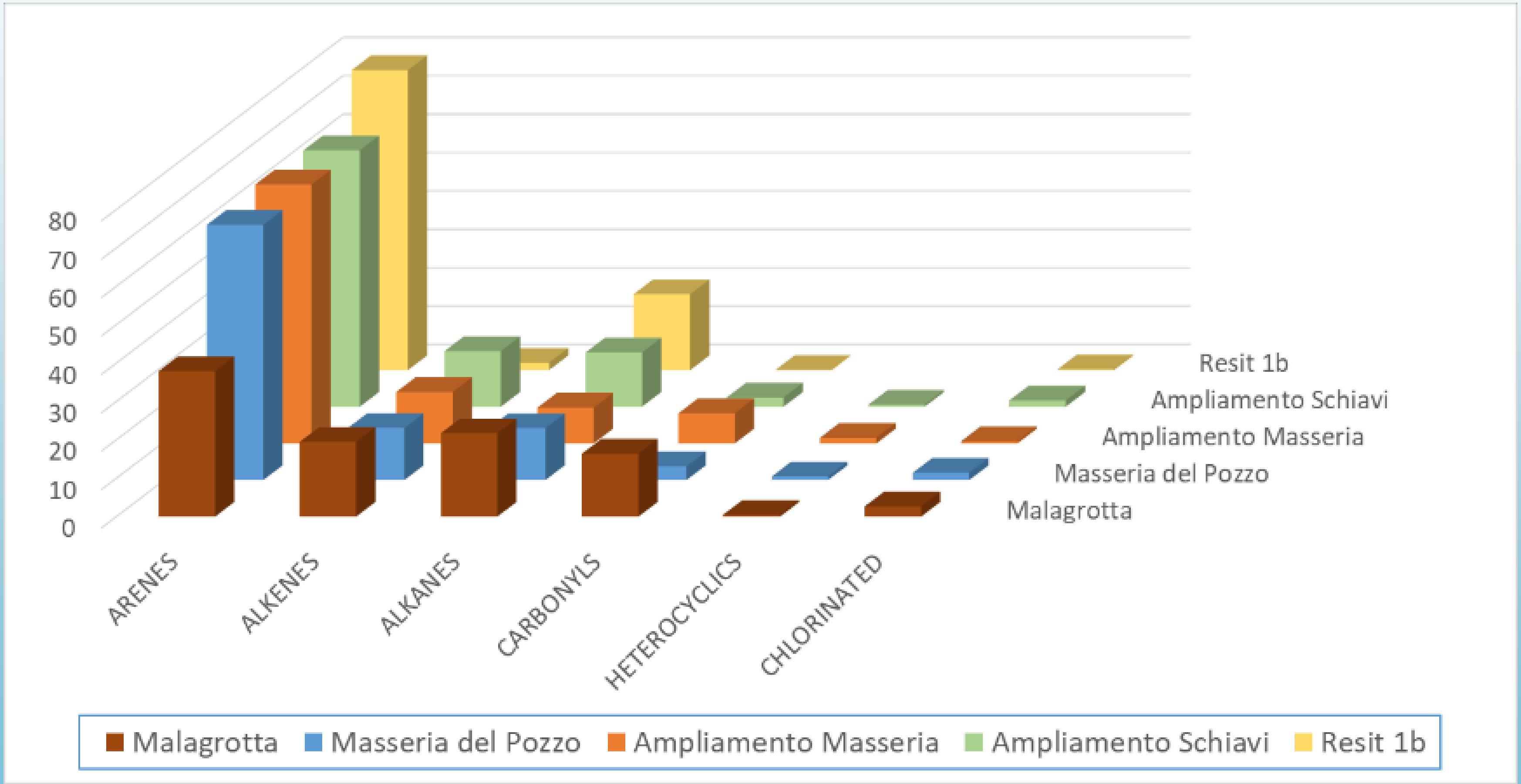
- SW outskirts of Rome,
- the largest landfill in Europe until it was closed down in 2013,
- biogas sampled in the late 1990's from the main ducts at the inlet of the filtration unit of two aged pits,
- sampling and analytical meth. were the same as in Giugliano,
- located about 180 km NW of Giugliano.

Mean percent composition of the classes of VOCs detected in the biogas of the Giugliano Landfills (Naples) compared to Malagrotta landfill (Rome)

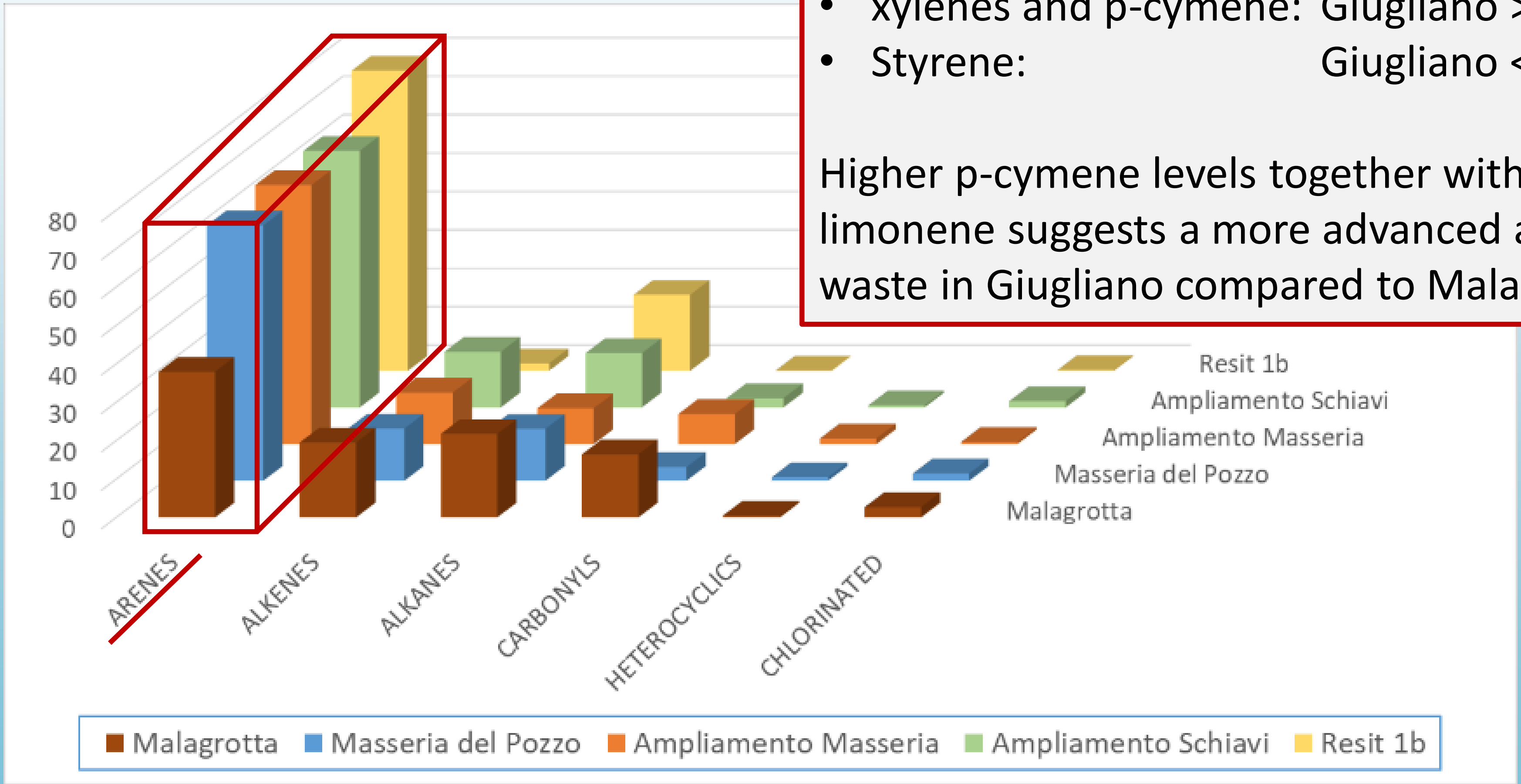
Geographic area	Giugliano							Roma
Landfill name	Masseria del Pozzo	Amplia-mento Masseria	Amplia-mento Schiavi	Novambiente	Resit 1b	Resit 2b	Resit X	Malagrotta
Landfill surface (m^2)	125,153	63,581	83,027	50,135	5,041	7,915	7,408	2,400,000
Biogas VOC composition (%)								
ARENES	**66.49**	**67.42**	**66.78**	37.21	**78.13**	34.21	45.67	*37.92*
ALKENES	13.59	13.39	14.47	5.38	1.92	1.63	15.83	19.50
ALKANES	13.52	9.30	14.13	**56.34**	19.78	**63.96**	**37.67**	21.73
CARBONYLS	**3.58**	**7.85**	**2.41**	**0.27**	**0.01**	**0.02**	**0.54**	16.42
ALCOHOLS	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.24
HETEROCYCLICS	0.92	1.47	0.51	0.52	b.d.l.	0.03	b.d.l.	0.49
CHLORINATED	1.90	0.56	1.64	0.05	0.19	0.06	0.09	2.66
OTHERS	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.03

b. d. l. = below detection limit

Percent composition of VOCs (in classes) - group 1



Percent composition of VOCs (in classes) - group 1

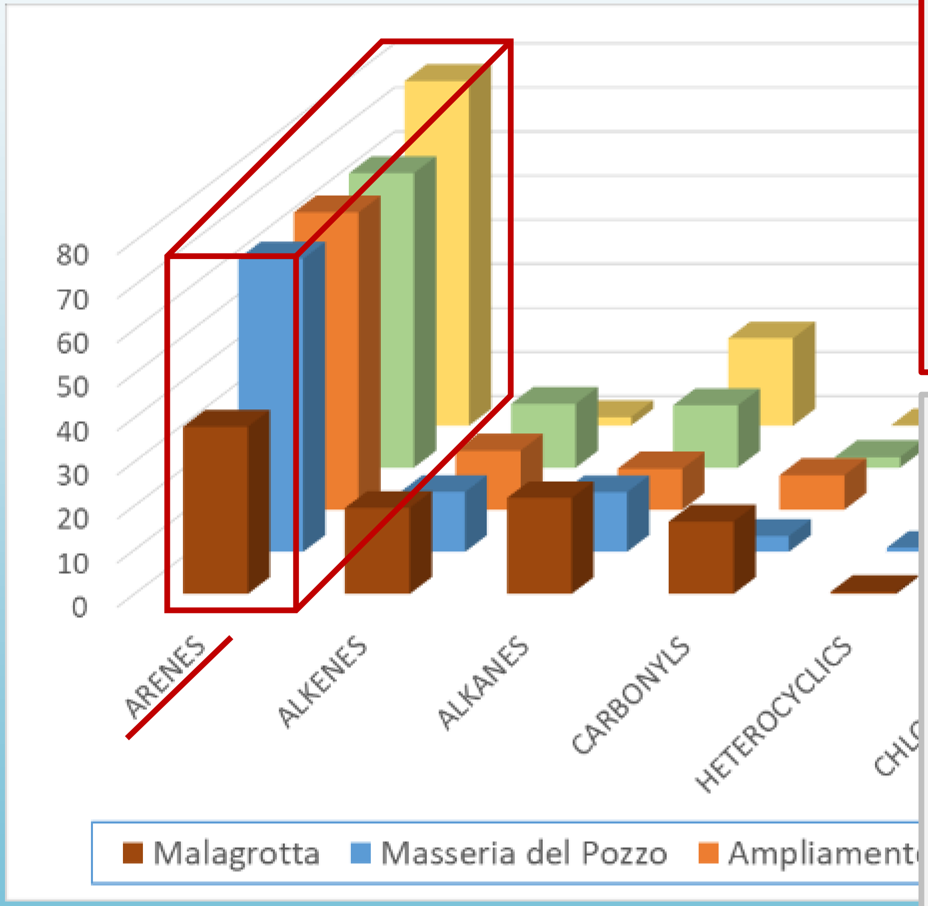


ARENES: 2-3 times higher in Giugliano than in Malagrotta

- benzene: Giugliano ~ Malagrotta;
- xylenes and p-cymene: Giugliano >> Malagrotta;
- Styrene: Giugliano << Malagrotta;

Higher p-cymene levels together with the lower content of limonene suggests a more advanced aging process of waste in Giugliano compared to Malagrotta.

Percent composition of VOCs (in classes) - group 1



ARENES: 2-3 times higher in Giugliano than in Malagrotta

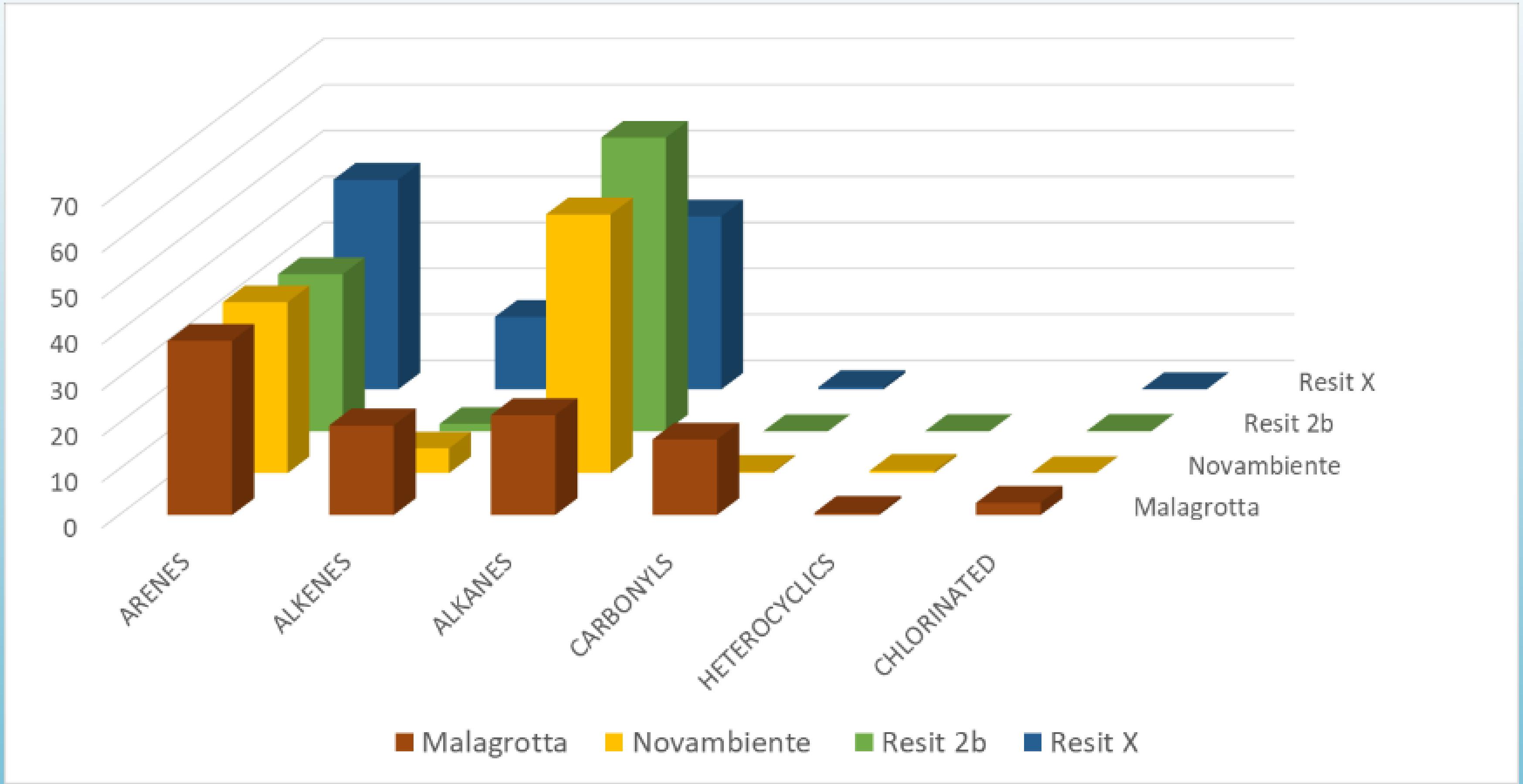
- benzene: Giugliano ~ Malagrotta;
- xylenes and p-cymene: Giugliano >> Malagrotta;
- Styrene: Giugliano << Malagrotta;

Higher p-cymene levels together with the lower content of limonene suggests a more advanced aging process of waste in Giugliano compared to Malagrotta.

CHLORINATED: 1,1-di-, tri-, tetrachlorethenes with the lower homolog as the dominant component, at variance with Malagrotta, where tri- and tetrachloroethenes, together with 1,2-dichloroethene were dominant.

Higher xylene levels together with the presence of 1,1-dichloroethene, and MEK among CARBONYLS, can be attributed to the dumping of solvents of industrial origin.

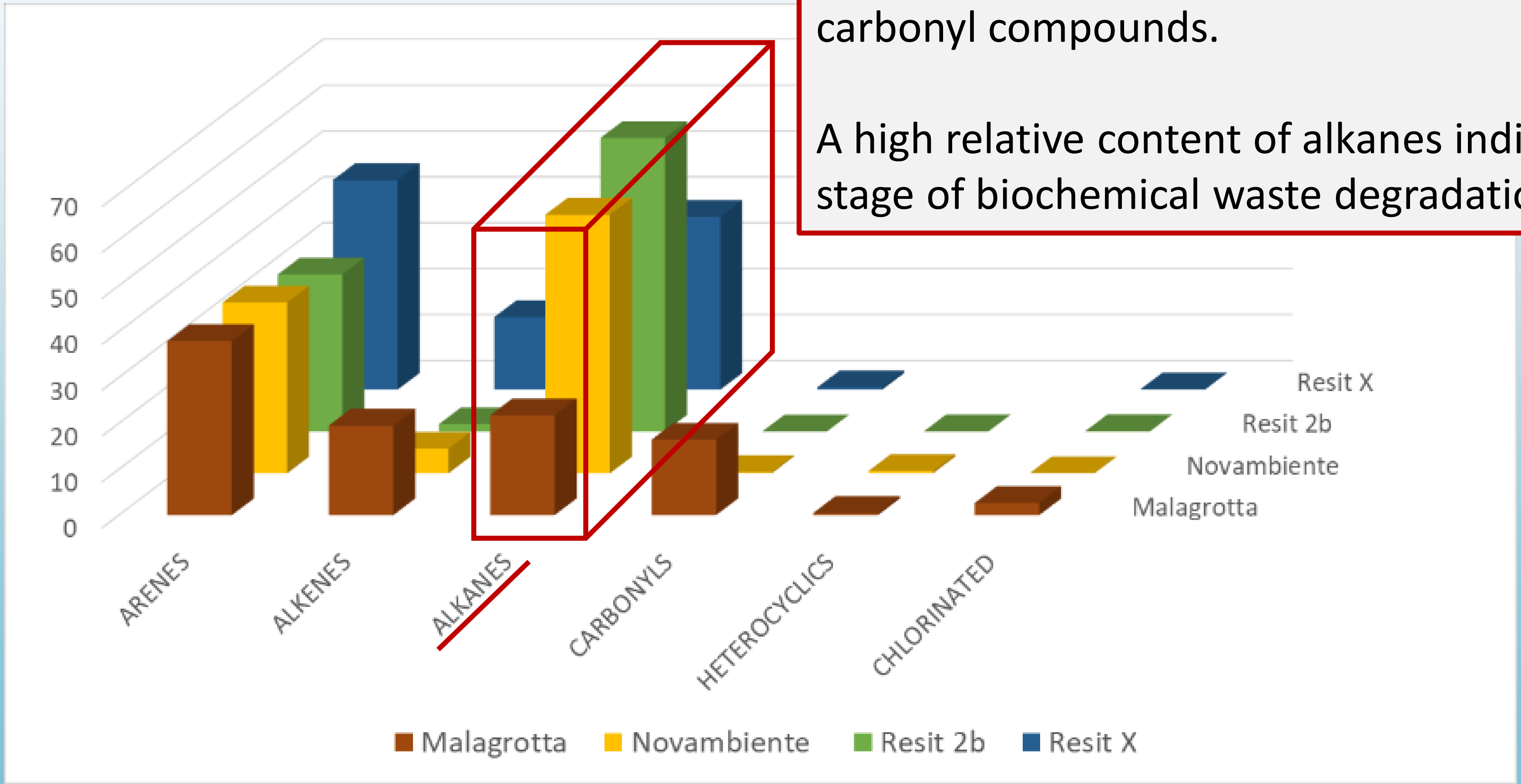
Percent composition of VOCs (in classes) - group 2



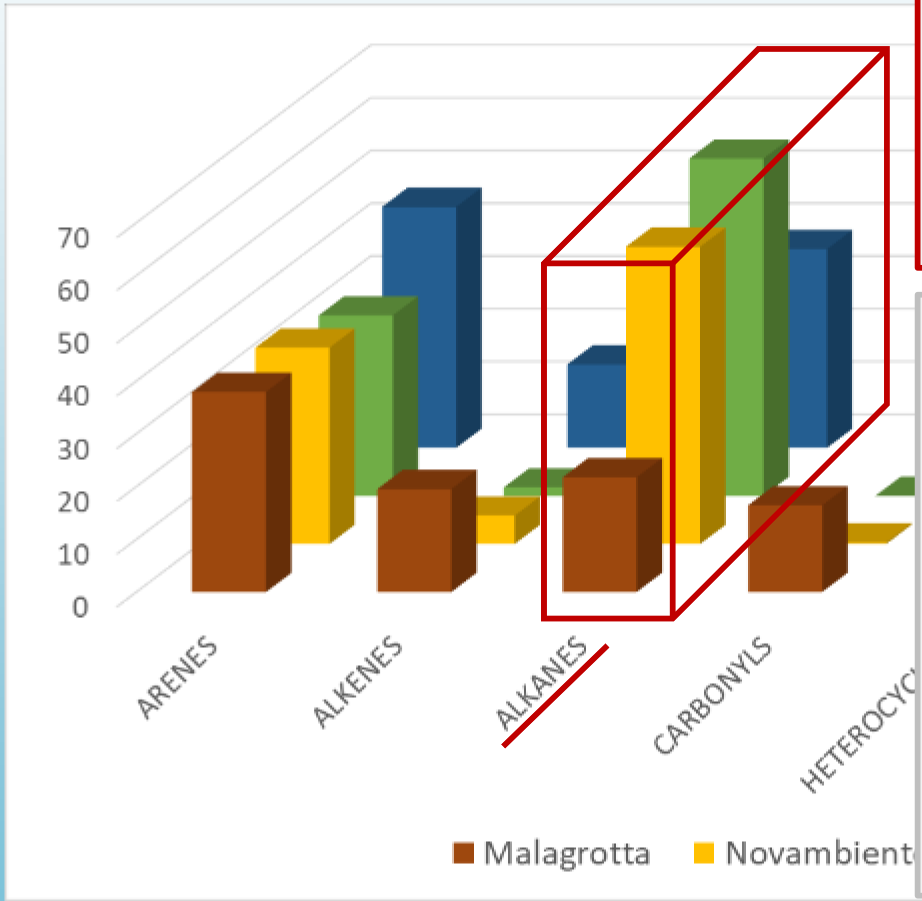
Percent composition of VOCs (in classes) - group 2

ALKANES: 2-3 times higher in Giugliano than in Malagrotta, associated to a drop in the relative content of alkenes and carbonyl compounds.

A high relative content of alkanes indicates an advanced stage of biochemical waste degradation.



Percent composition of VOCs (in classes) - group 2



ALKANES: 2-3 times higher in Giugliano than in Malagrotta, associated to a drop in the relative content of alkenes and carbonyl compounds.

A high relative content of alkanes indicates an advanced stage of biochemical waste degradation.

ARENES: even if the overall content is similar to that detected in Malagrotta, the BTEX fraction is larger for Resit and Novambiente landfills indicating the possible dumping of petroleum derived products.

CHLORINATED: only 1,2-dichlorobenzene is detected in fraction larger than in Malagrotta indicating the possible dumping of agrochemical and insecticide production waste.

Air quality impact assessment of toxic compounds

	Cancer risk		Toxic risk	WHO Guideline values
	IUR [µg/m^3]$^{-1}$	SL TR=1.0E-6 [µg/m^3]	RfC [µg/m^3]	[µg/m^3]
benzene	7.80E-06	0.36	30	no safe level
toluene			5000	260 *
ethylbenzene	2.50E-06	1.12	1000	
p-xylene			100	
o-xylene			100	
styrene			1000	260 *
1,1-dichloro ethylene			200	
tetrachloro ethylene	2.60E-07	10.80	40	250
trichloro ethylene	4.10E-06	0.48	2	no safe level
1,2-dichloro benzene			200	
Methyl Ethyl Ketone			5000	

***(weekly average)**

IUR: Inhalation Unit Risk

SL TR=1.0E-6: Screening level Target Risk 10-6

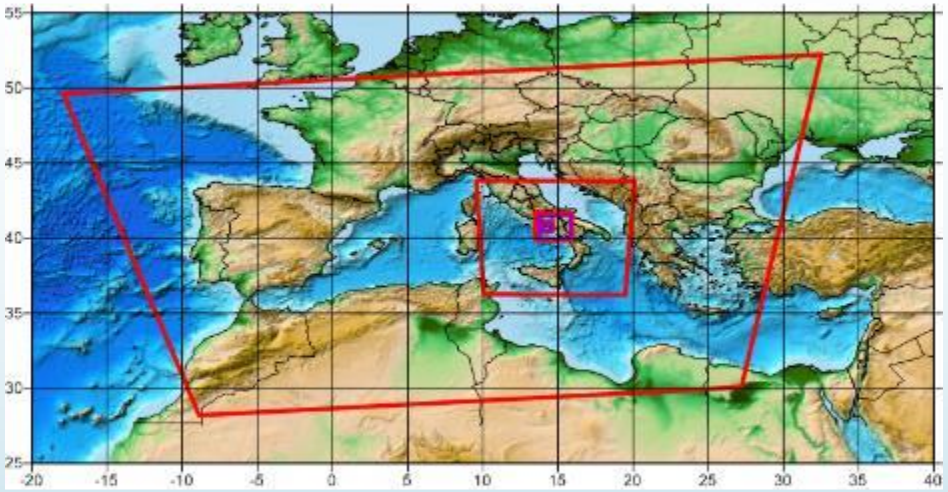
RfC: Reference Concentration

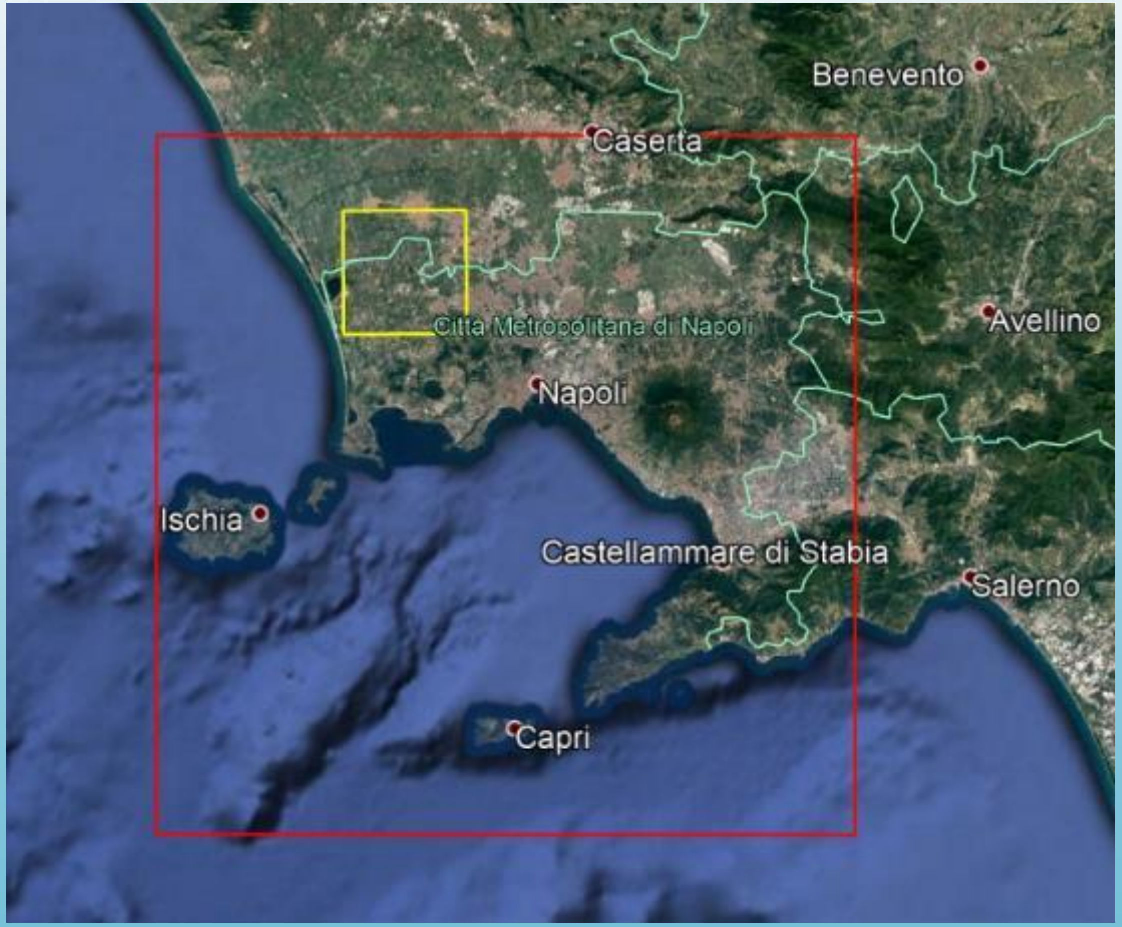
Carcinogenic and chronic non-carcinogenic risk factors

(ISS/INAIL, 2014; US/EPA,2017; WHO, 2000)

Simulation set-up: WRF + SPRAY

WRF V3.5.1
Grid spacing: 45, 9, 3, 1 km
Vertical grid: 35 levs (up to 50 hPa)
BCs: GFS
Land Cover: CORINE 2006





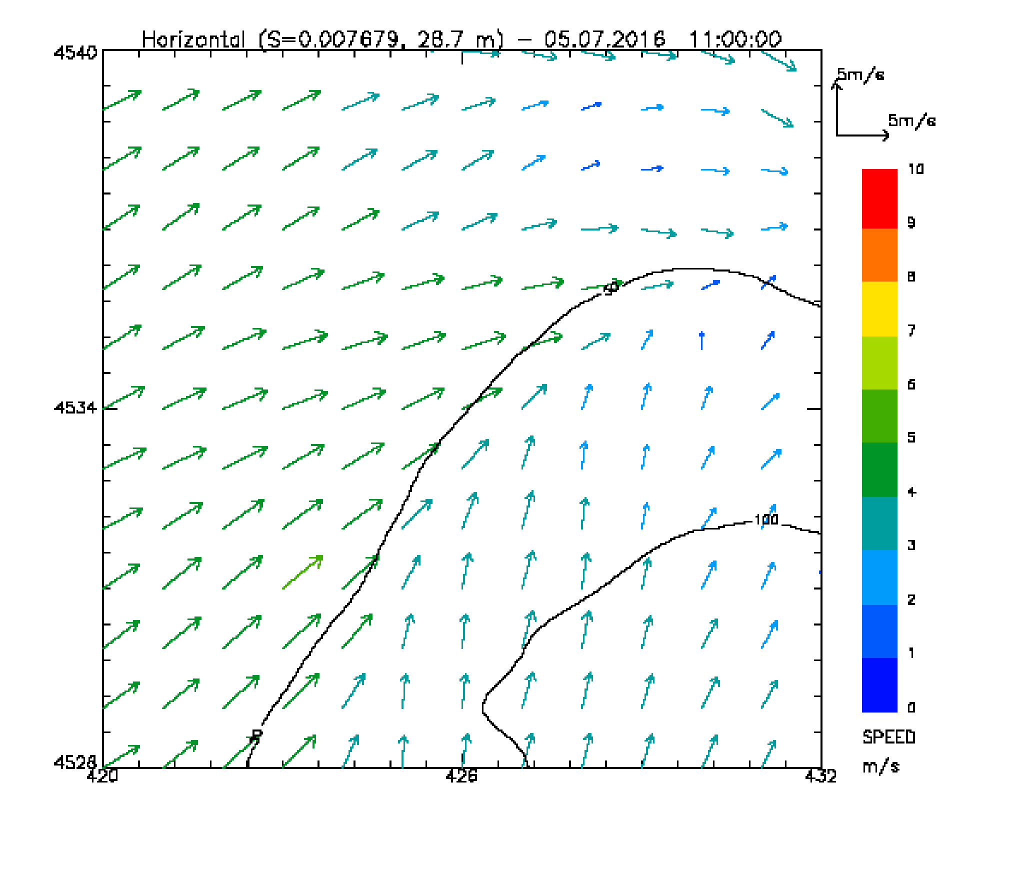
SPRAY
Computational domain: 12x12 km^2
Grid spacing: 100m
Wind adjustment: mass-consistent model SWIFT
Sources: individual landfill contribution
Emissions: hourly frequency
Pollutants: non-reactive

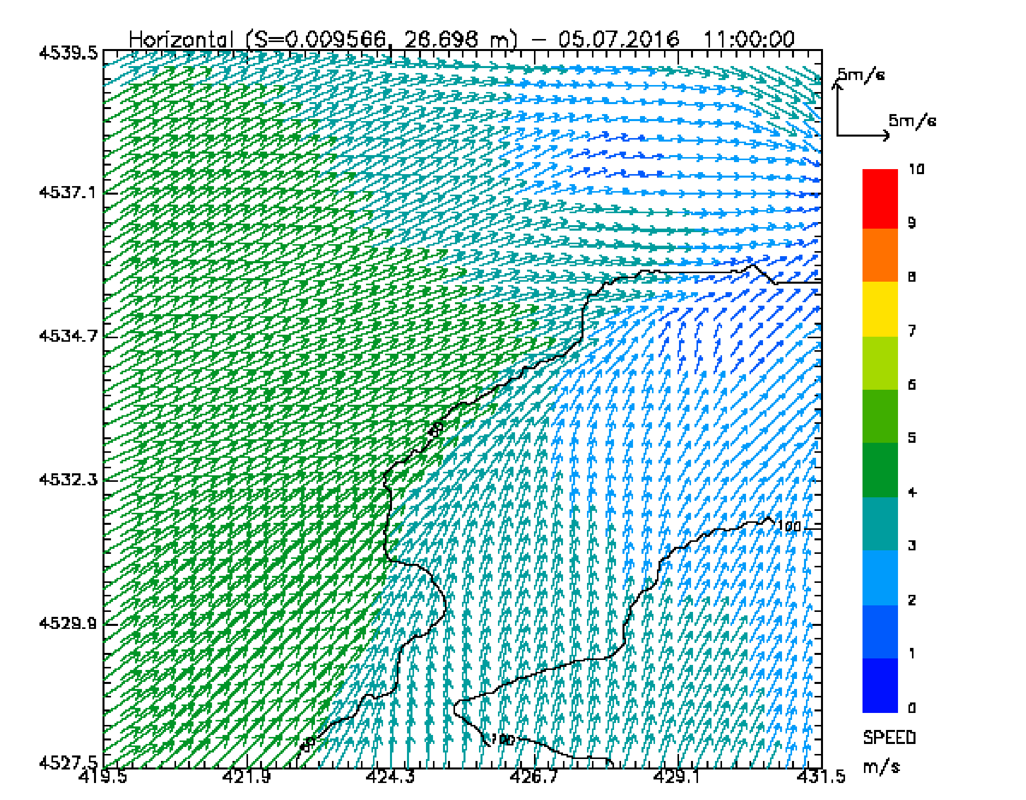
year-long simulation (01/11/2015 - 31/10/2016)

Wind field adjustment: mass-consistent model SWIFT

WRF (Δx=1 km)

SWIFT (Δx=100m)





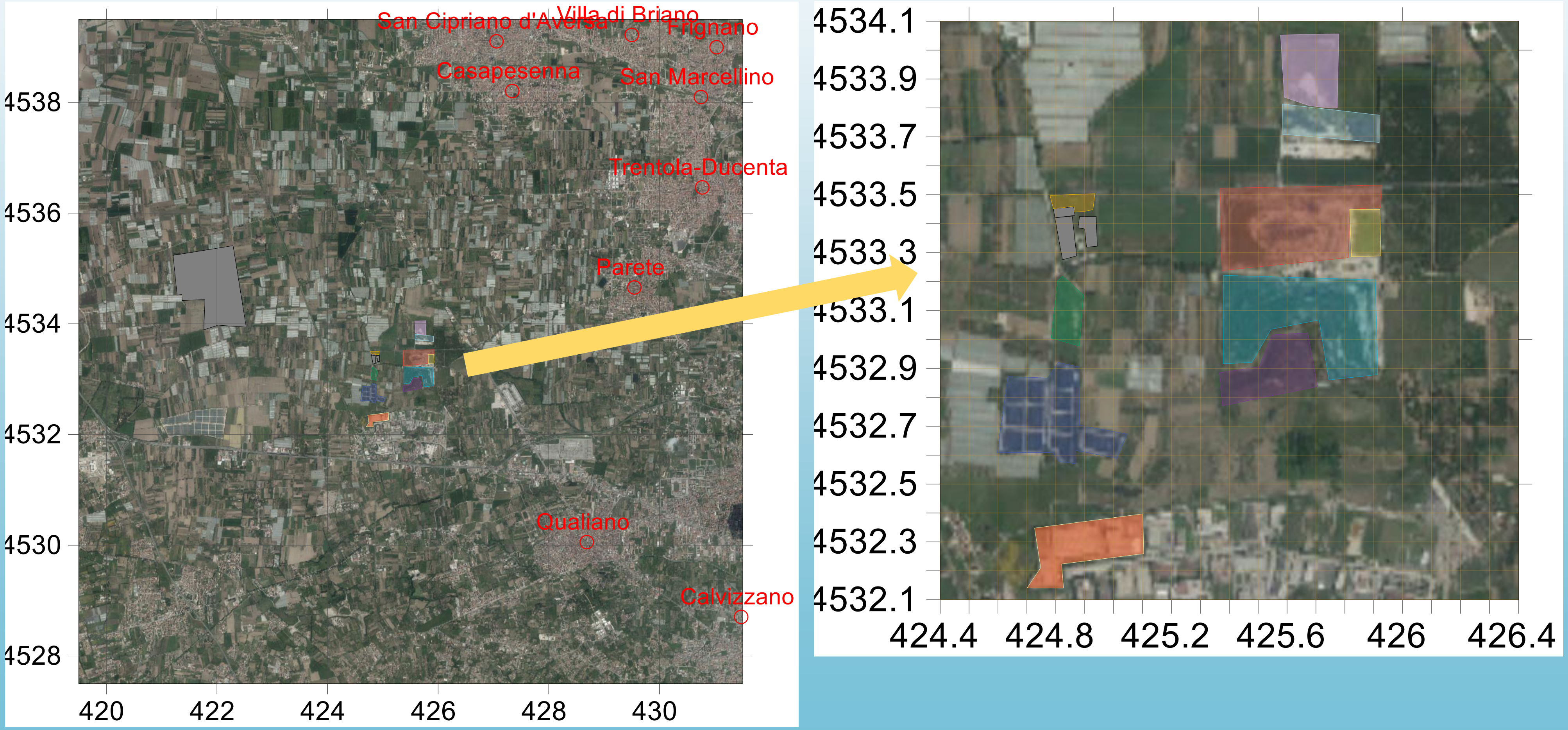
Plot: 1 arrow every 300m

Atmospheric turbulence similatity scaling parameters estimated by met. pre-processor SURFPRO

SPRAY model computational domain

Computational domain:

- extension: 12x12 km^2
- grid spacing: 100m
- includes the nearest inhabited areas and provides high resolution needed nearby the landfill area



Hourly emissions

CH_4 hourly emission estimate for each individual landfill from:
- Continuous eddy correlation flux measurements
- Airborne measurements
- Surface sampling

Yearly average emission: Masseria: 0.312 g m^{-2} h^{-1}
Resit: 0.390 g m^{-2} h^{-1}

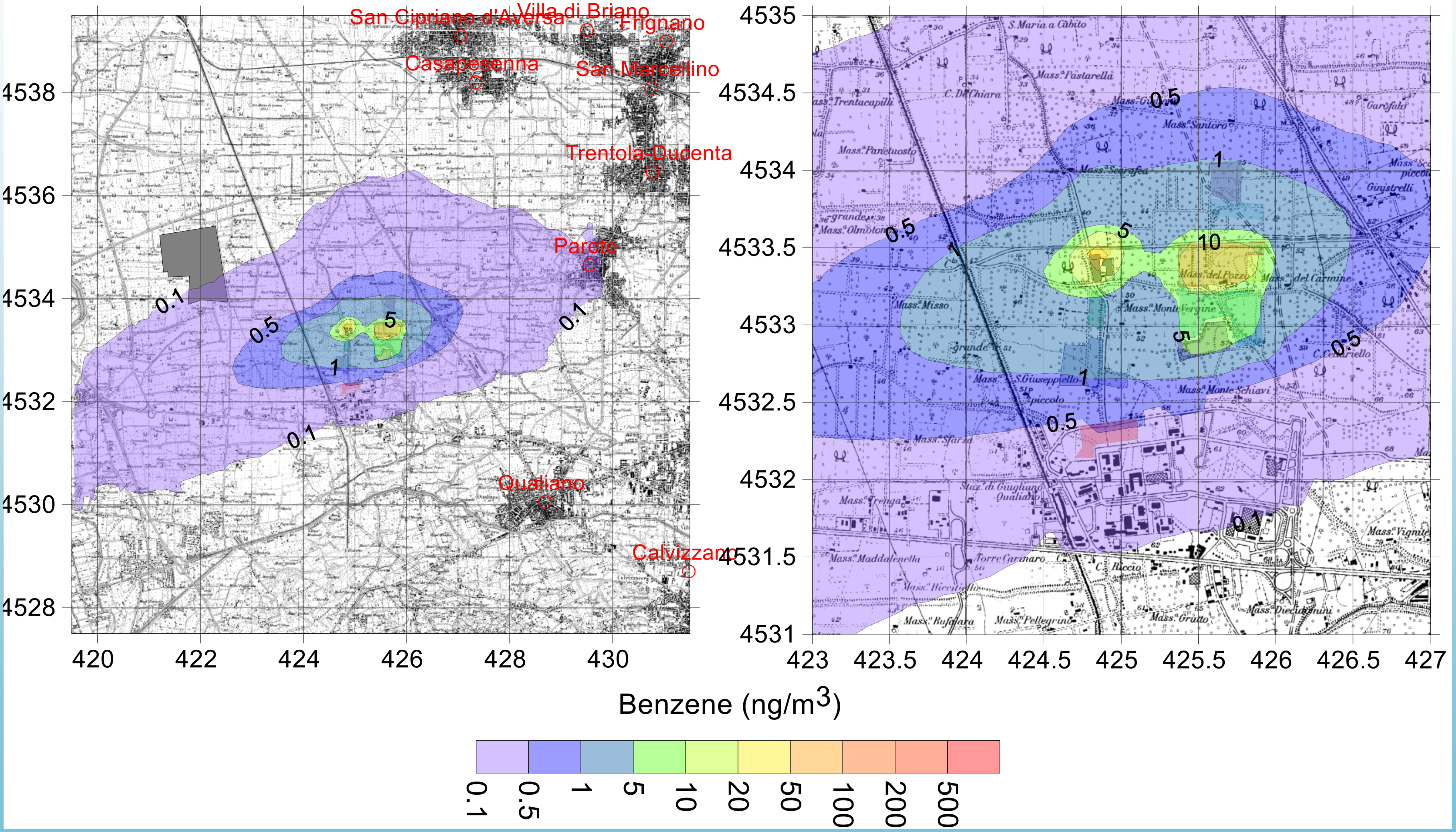
VOC/CH_4 ratio estimated for each compound from surface sampling and GC-MS analyses

Landfill	Surface m^2	CH_4	benzene	toluene	ethyl benzene	p-xylene	o-xylene	styrene	1,1-dichloro ethylene	tetrachloro ethylene	trichloro ethylene	1,2-dichloro benzene	MEK
Masseria del Pozzo	125153	393.2	6.45	68.52	68.35	125.41	32.45	0.479	4.092	2.093	0.144	0.023	36.04
Ampliamento Masseria del Pozzo + Schiavi	146608	431.9	3.14	64.63	19.35	87.81	33.07	0.073	2.098	2.069	0.075	0.033	92.17
Novambiente	50135	157.5	1.66	3.41	14.09	3.53	0.74	0.020	0.024			0.024	
Resit categoria 1b	5041	27.6	0.41	21.19	26.85	36.86	6.87					0.022	
Resit categoria 2b	7915	43.3	3.37	13.25	11.48	7.42	0.98						
Resit X	7408	40.5	3.06	13.11	11.83	8.73	1.27					0.001	

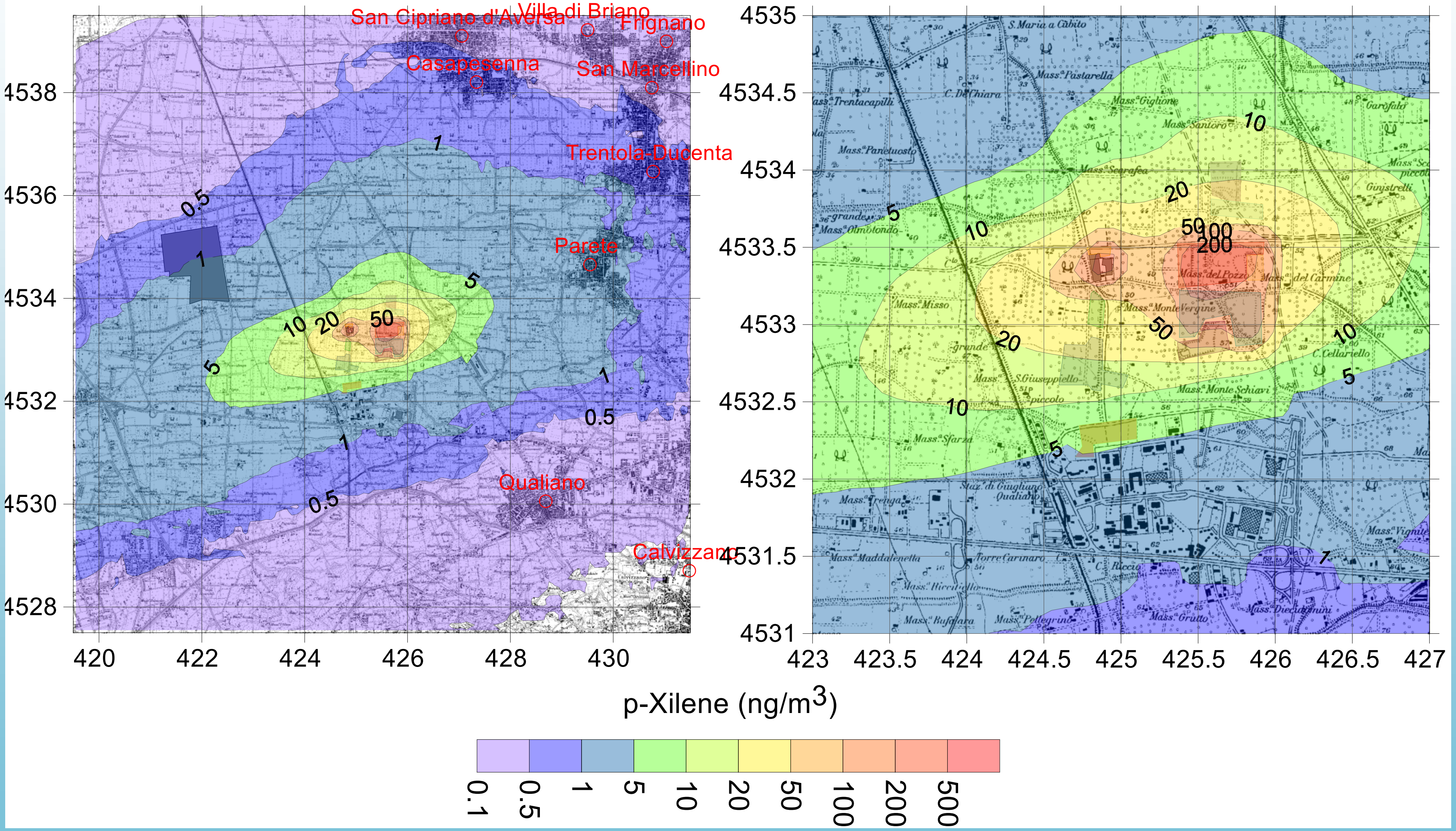
Annual total emissions CH_4 (ton/year); VOCs (kg/year)

ARIANET

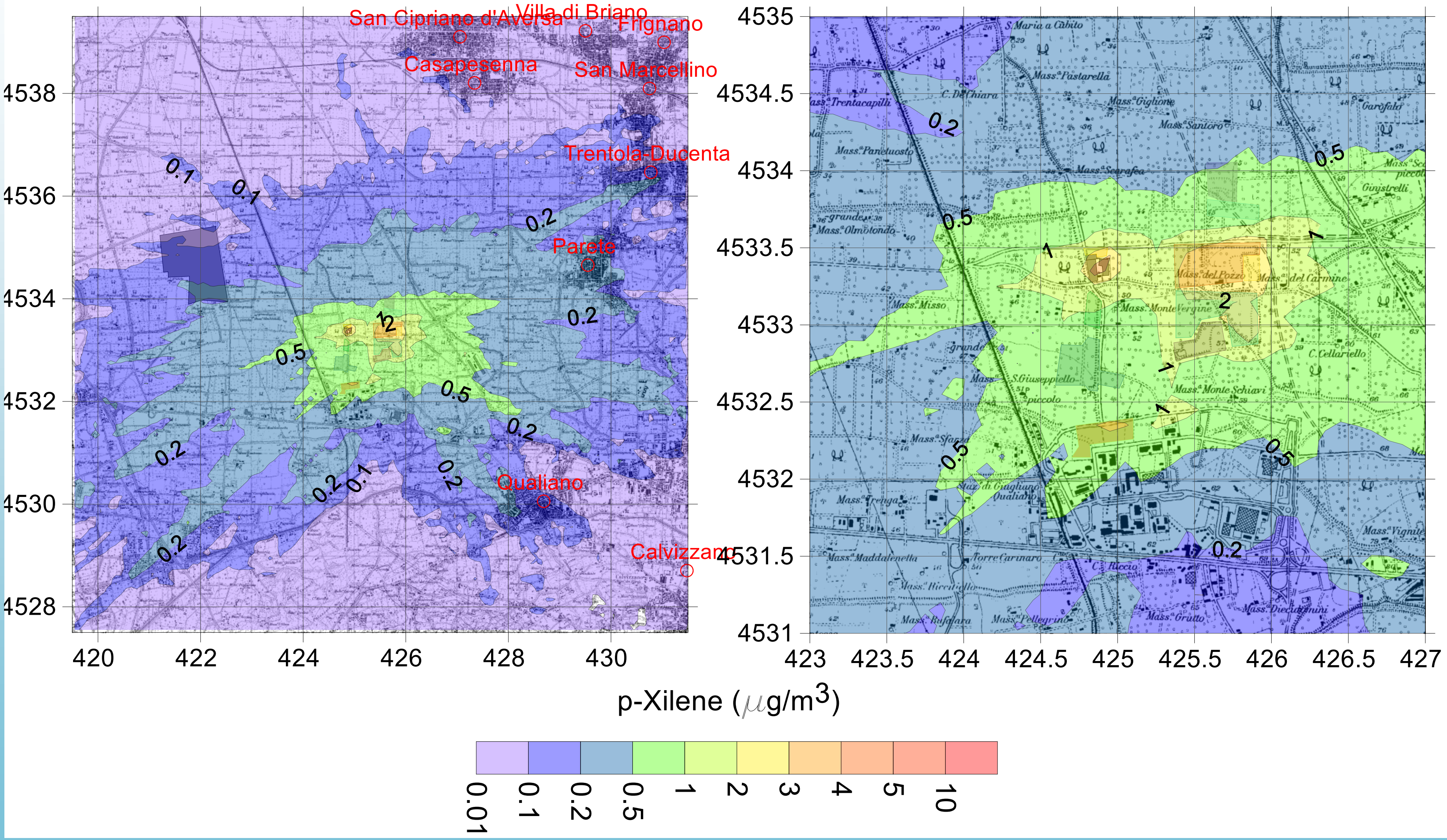
Benzene annual average concentration (ng m^{-3})



p-xilene annual average concentration (ng m^{-3})



p-xilene hourly maximum concentration ($\mu g\ m^{-3}$)



Maximum computed concentrations vs ref. toxicity values

	Computed atmospheric concentration (grid maximum)		Reference values	
	Annual average ng/m^3	Hourly maximum $\mu g/m^3$	Screening Level $\mu g/m^3$	Cancer(ca)/ non-cancer(nc) risk
benzene	26	0.3	0.36	ca
toluene	186	2.7	5210	nc
ethylbenzene	198	3.0	1.12	ca
p-xylene	311	3.5	104	nc
o-xylene	83	0.7	104	nc
styrene	1.1	0.01	1040	nc
1,1-dichloro ethene	9.7	0.09	209	nc
tetrachloro ethene	5.2	0.05	10.8	ca
trichloro ethene	0.34	0.003	0.48	ca
1,2-dichloro benzene	0.11	0.002	209	nc
Methyl Ethyl Ketone	360	1.9	5210	nc

Screening levels: **Cancer risk: Target Risk 10-6**

Noncancer risk: Target Hazard Quotient (THQ) = 1

Conclusions

- ✓ Toxic compounds are present in the emission of the Giugliano landfills, possibly due to the past damping of toxic wastes.

- ✓ The air quality impact assessment showed that present emission rates are not sufficient to induce acute or chronic diseases to the local population.

- ✓ Closed landfills must be kept under control to avoid increase in VOC emissions due to fracturing of the sealing system, risk of fires and explosions.

- ✓ VOCs can worsen local air quality contributing to ozone and particle formation when mixed with other VOC, NOx and particles emitted from sources active within the Naples-Caserta conurbation (ship traffic, biomass burning for domestic heating, illegal open burning of wastes and forest fires).

Thank you

BioQuAr project has been funded by Government Commissioner for Remediation and coordinated by the Institute for Mediterranean Agriculture and Forest Systems (ISAFOM) of the National Research Council.