Pisa, 30 of November 2023

Air Quality in the geotermical area of Tuscany

GEOTMX

Alessandro Bagnoli and Francesca Andreis (ARPAT - Geothermal Sector)

In Tuscany there are **34 active power plants (36 total production groups),** managed by ENEL Green Power Italia srl.
They are located in four territorial areas (Larderello, Radicondoli, Lago, Piancastagnaio).
The management of geothermal fluids in Tuscany produces a quantity of electricity equal to approximately 35% of the regional electricity needs.

ARPAT control activities in a geothermal power plant

ARPAT carries out the following sampling:

Gas manifold

- Gas composition (H_2S, CO_2, CH_4, N_2, CO, O_2, He, H_2)
- Determination of ammonia and hydrogen sulphide in condensate
- Flow measurements

Compressor discharge and AMIS outlet

- Gas composition (H_2S, CO_2, CH_4, N_2, CO, O_2, He, H_2) + humidity
- ammonia
- Determination of Hg e As (Se+Sb)
- Flow measurements
- H_2S e SO_2 with portable gas analyser (only at AMIS outlet)

Cooling tower

- Determination of Hg e As (Se+Sb)
- Determination of NH_3 e H_2S
- Drift analysis
- Flow measurements

Condensation water

- Cooling tower inlet, tower tank, column drain C2 AMIS, reinjection tank

ARPAT's air quality monitoring

1997: ARPAT begins to conduct the first monitoring, using a mobile laboratory located in various sites in the regional geothermal territory.

2000: the mobile laboratory (GEO1) is introduced, equipped with instrumentation for the continuous measurement of hydrogen sulphide (H_2S).

2003: the fixed location at Montecerboli, Pomarance (PI) becomes operational and starts continuous measurement of H_2S.

2012: the GEO2 (or GEOS) mobile vehicle is managed by the Geothermal Sector.

2014: both the GEO1 and GEO2 laboratories are equipped for the continuous measurement of gaseous mercury.

Today the monitoring of air quality in geothermal areas is done thanks to fixed and mobile automatic stations:

- 1 air quality station ARPAT, located at Montecerboli part of regional network
  [H_2S – PM_{10} – O_3 – NO – NO_2 – No_x]
- 2 mobile laboratories ARPAT
  GEO1 e GEO2 (or GEOS) [H_2S – Hg]
- 18 air quality monitoring network stations ENEL
  [H_2S – Radon (only 6)]

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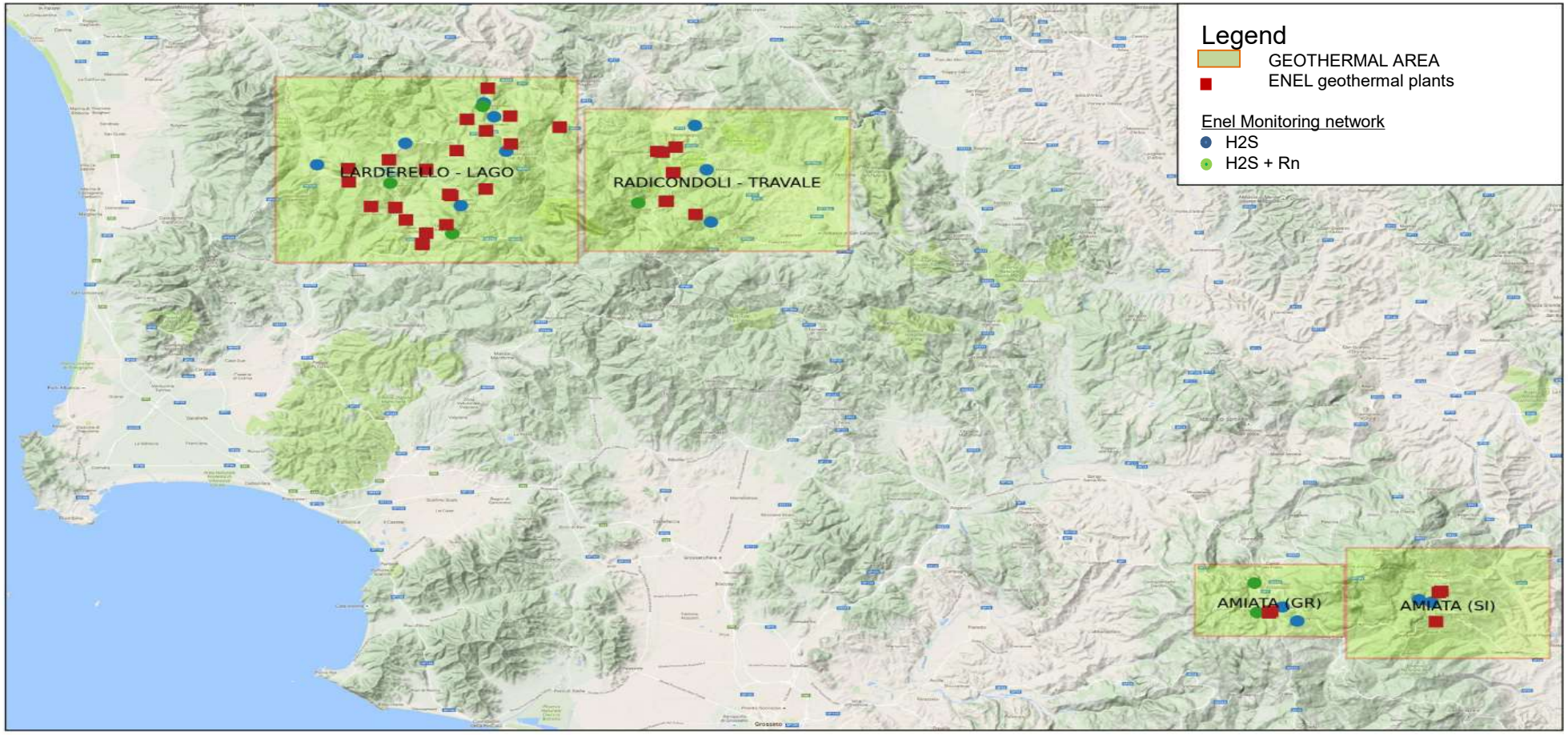
Overview of Tuscan geothermal power plants areas



Why does ARPAT use mobile laboratories?

ARPAT uses the Geo1 and Geo2 mobile laboratories for:

- verify the adequacy of the data relating to H_2S provided by the Air Quality Stations (SQA) managed by Enel;
- monitor areas too far from fixed stations;
- the detection of mercury (Hg).

In recent years the vehicles have been used mainly in the area of Amiata.

ARPAT's control of the data processed by ENEL's detection network is also implemented through VPN access to the database.

References an limit values adopted

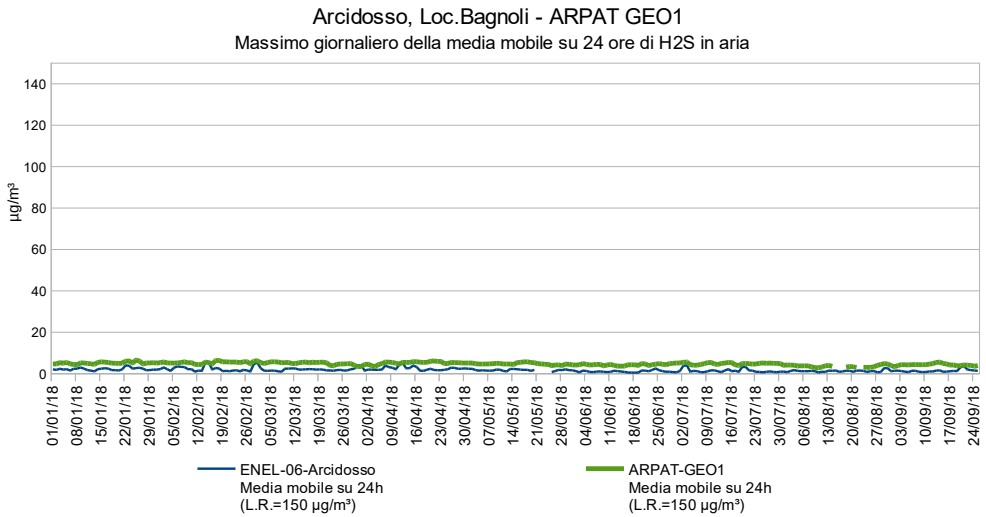
Substance	Concentration	Riference
Hydrogen sulphide (H_2S)	150 µg/m³ (average 24 hours)	WHO Guidelines ed. 2000
	100 µg/m³ (>1-14d – average)	WHO-IPCS
	20 µg/m³ (>90d – average)	WHO-IPCS
Arsenic (As)	6 ng/m³ (annual average)	The value indicated constitutes the target value of the Directive of the European Parliament and of the Council 2004/107/EC of Italian Legislative Decree 152 of 3/8/2007, transposing the aforementioned directive.
Mercury (Hg)	0,2 µg/m³ (annual average)	MRLs Minimal Risk level - Significant guideline levels for health developed by the US government agency ATSDR, in analogy to the EPA threshold values, for non-carcinogenic effects of chemical substances in the environment for use by the same ATSDR to evaluate contaminated sites (source list updated at November 2007). Value updated in 2001 http://www.atsdr.cdc.gov/
Boro (B)	20 µg/m³ (average 24 hours)	Adopting a confidence value of 100 compared to the value of 2mg/m³ referred to the TLV-TWA (Time Weighted Average) of the ACGIH (American Conference of Governmental Industrial Hygienists) ed. 2006 (inorganic borates).
	10 µg/m³ (>1-14d – average)	MRLs Minimal Risk level - Significant guideline levels for health, developed by the US government agency ATSDR, in analogy to the EPA threshold values, for non-carcinogenic effects of chemical substances in the environment for use by the same ATSDR to evaluate contaminated sites (source updated list in November 2007).
Ammonia (NH_3)	170 µg/m³ (average 24 hours)	Adopting a confidence value of 100 compared to the value of 17 mg/m³ referred to the TLV-TWA (Time Weighted Average) of the ACGIH (American Conference of Governmental Industrial Hygienists) ed.2006 (ammonia).
	70 µg/m³ (>1-14d – average)	MRLs Minimal Risk level - Significant guideline levels for health, developed by the US government agency ATSDR, in analogy to the EPA threshold values, for non-carcinogenic effects of chemical substances in the environment for use by the same ATSDR to evaluate contaminated sites (source updated list in November 2007). The value for ammonia is updated to 2004 http://www.atsdr.cdc.gov/
Antimony (Sb)	5 µg/m³ (average 24 hours)	Adopting a confidence value of 100 compared to the value of 0.5 mg/m³ referred to the TLV-TWA (Time Weighted Average) of the ACGIH (American Conference of Governmental Industrial Hygienists) ed. 2006 (antimony).
Radon (Rn)	200 Bq/m³ (annual average)	Recommendation 90/143/Euratom for new buildings (indoor)

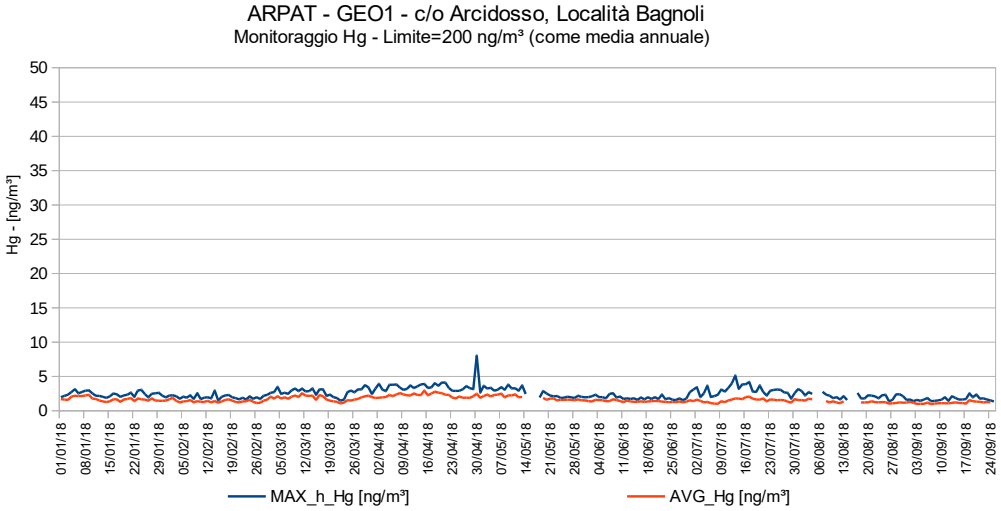
GEO 1: Monitoring 2013-2018

At the request of the Municipality of **Arcidosso**, from 8 May 2013, until 25 September 2018, the GEO1 mobile laboratory was located at "**Bagnoli**" (Arcidosso) to check the **H_2S** and **Hg** levels in this location.

The results were published in a bulletin, first monthly, then quarterly.

http://www.arpat.toscana.it/datiemappe/bollettini/bollettino-della-qualita-dellaria-nella-zona-geotermica-del-monte-amiata/resolveuid/9624005ffe193dc792025e1086e6a762





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MONITORAGGIO DELLE EMISSIONI DI H_2S (IDROGENO SOLFORATO) DELLA CENTRALE GEOTERMOELETTRICA BAGNORE 4 (GR)

DATI DELLE STAZIONI DI MONITORAGGIO NELL'AREA AMIATINA (ARCIDOSSO, SANTA FIORA, BAGNORE, MERIGAR, PIANCASTAGNAIO E PIANCASTAGNAIO2)

Periodo: Ottobre 2016

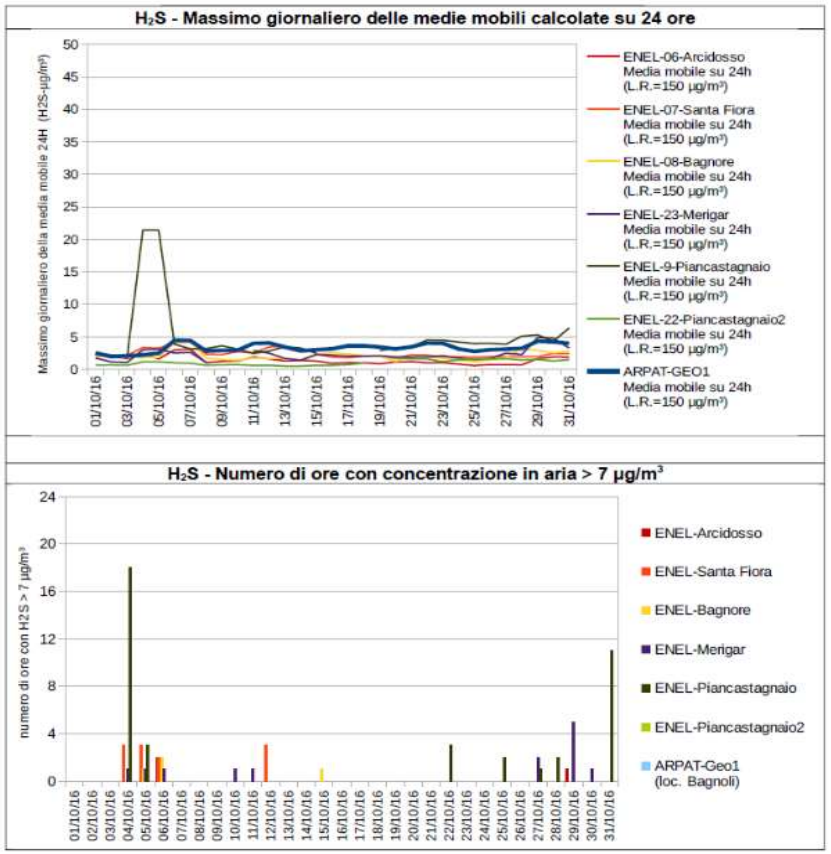
The bulletin had the function of making accessible the concentration of hydrogen sulphide in the air during the construction of the "Bagnore 4" power plant.

The ARPAT mobile vehicles present in the area were used integrated with the data provided by the ENEL GP survey network (Arcidosso, Bagnore, Santa Fiora, Merigar, Piancastagnaio, Piancastagnaio2).

Overall, at least 7 detection stations were therefore always used, located around the Bagnore and Piancastagnaio power plants, thus being able to detect emission phenomena at low altitude as the different wind conditions varied.

The bulletins were available at ARPAT website.

http://www.arpat.toscana.it/datiemappe/bollettini/bollettino-della-qualita-dellaria-nella-zona-geotermica-del-monte-amiata/resolveuid/9624005ffe193dc792025e1086e6a762



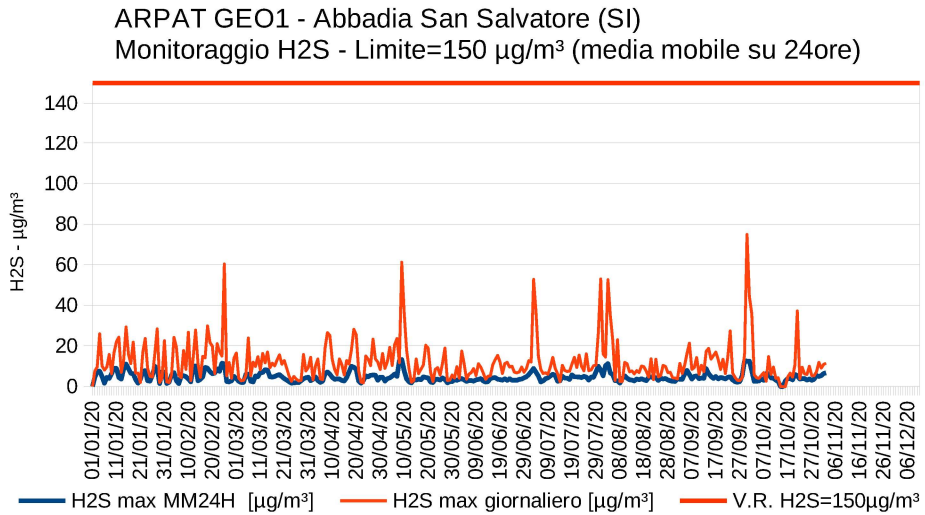
Nel mese di Ottobre 2016, nelle stazioni monitorate e dai dati in nostro possesso, il limite di riferimento indicato dalle Linee Guida del WHO (150 µg/m³) è stato sempre rispettato.
Potrebbero essersi verificate molestie olfattive, a causa del superamento della soglia di percezione dell'H_2S, ad Arcidosso i giorni 6 e 29; a Santa Fiora nei giorni 4, 5, 6 e 12; a Bagnore i giorni 5, 6 e 15; a Merigar nei giorni 4, 5, 6, 10, 11, 27, 29 e 30; a Piancastagnaio nei giorni 4, 5, 22 25, 27, 29 e 30.
Tali superamenti possono essere correlati alla manutenzione programmata al gruppo 2 di Bagnore 4 e ai ripetuti blocchi AMIS di Piancastagnaio 5.
Per approfondimenti: consultare la pagina del sito Web di ARPAT relativo alla geotermia.

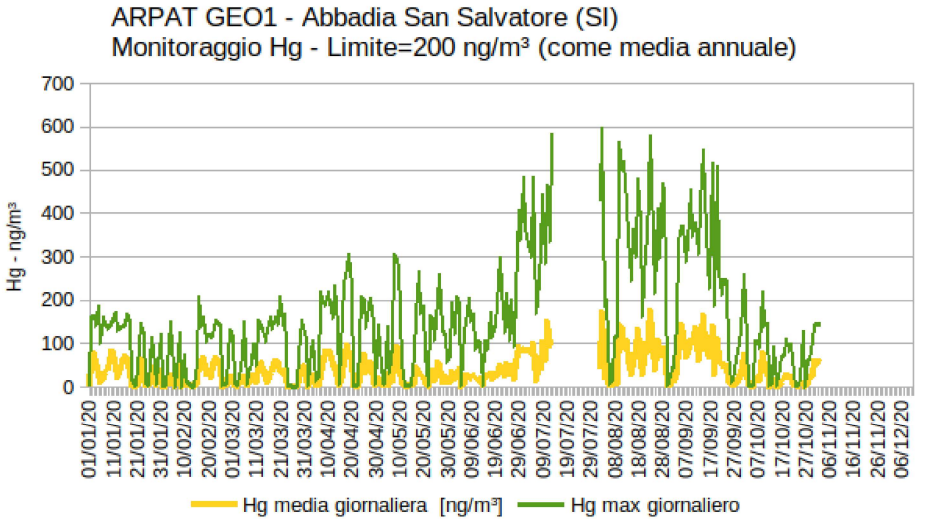
GEO 1: Monitoring 2019-2020

Afterwards, the GEO1 vehicle was positioned in **Abbadia San Salvatore** for two campaigns (9/18-3/2019 and 10/19-10/2020).

Comparing the results obtained in the two sites we can notice:

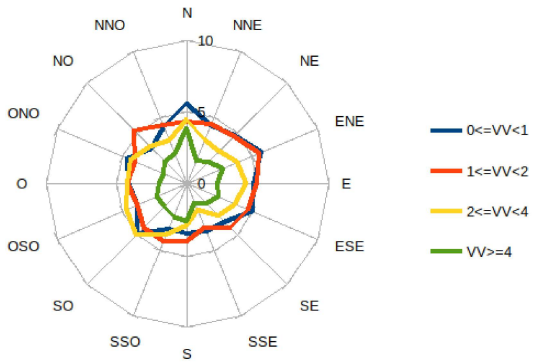
- H_2S concentrations within sanitary limits for both monitoring sites;
- Relevant Hg concentrations;
- Hg concentrations not attributable to geothermal activity (wind direction), increasing during the warmer seasons (temperature).



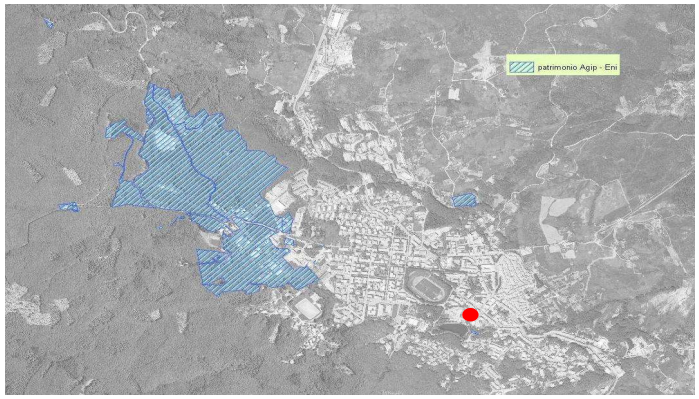


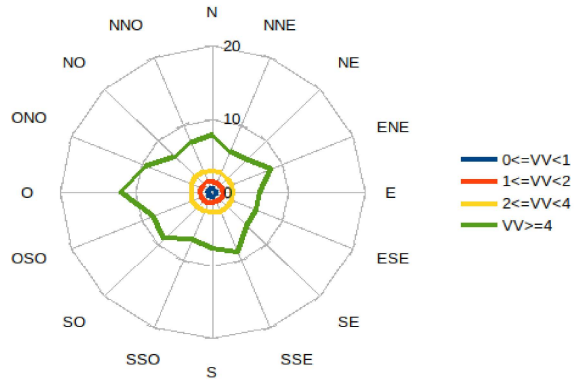
Hg in Abbadia San Salvatore

- The values assumed by the average concentration indicator for the period are significantly lower than the MRLs reference value of the ATSDR (equal to 200 ng/m^3 on the annual average).
- The values detected are also significantly lower than the WHO guideline value (1000 ng/m³).



Hydrogen sulphide: average value (H_2S, µg/m³), determined by sector of origin and by wind intensity class (VV).

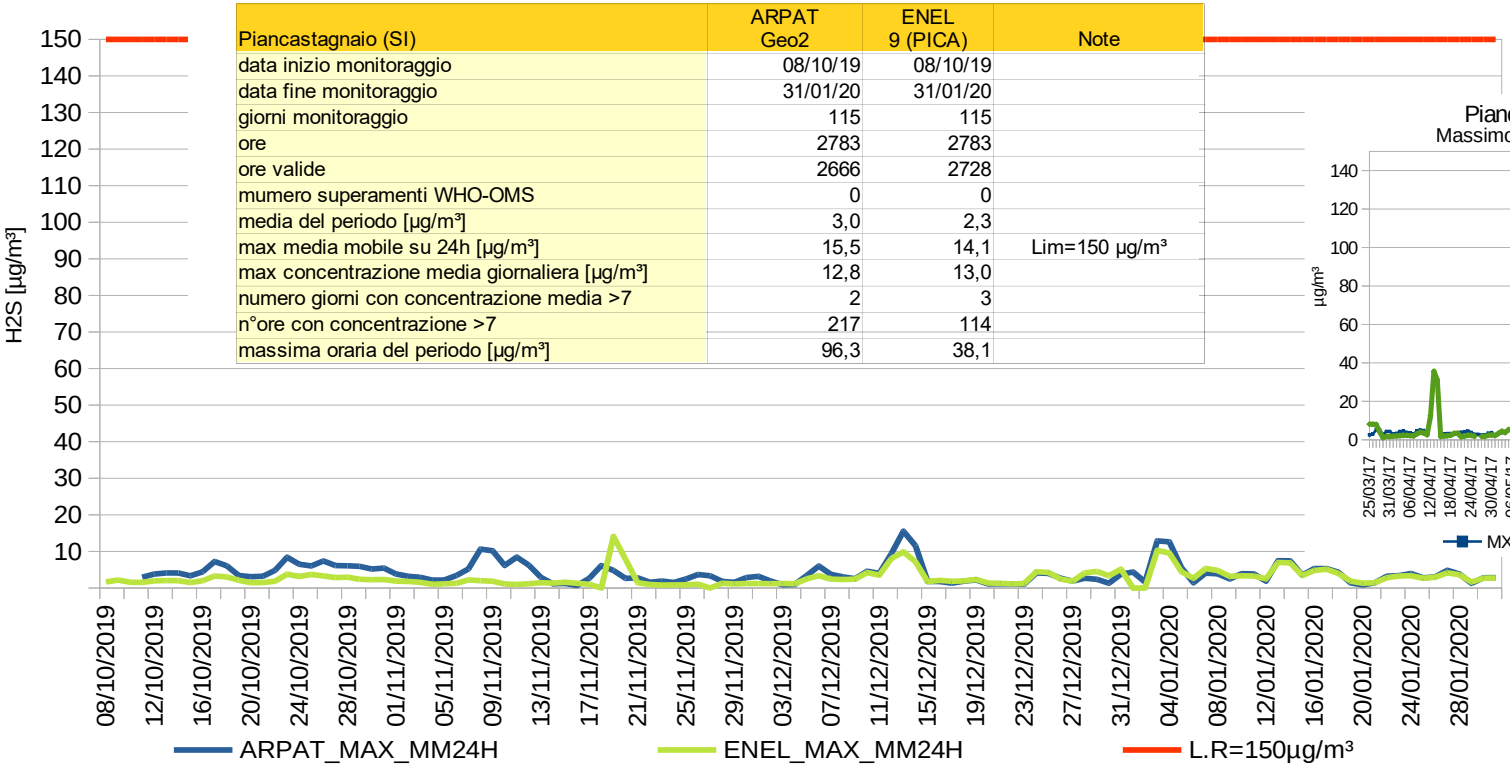


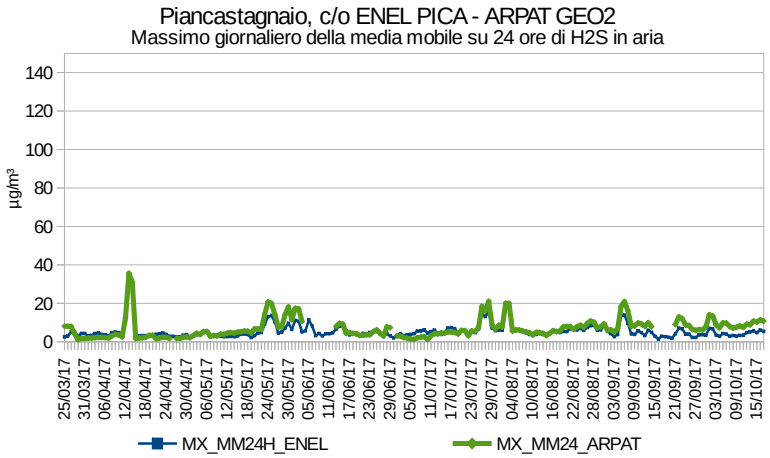


Gaseous mercury [ng/m³]: average value (Hg, ng/m³) determined by sector of origin and by wind intensity class (VV).

Piancastagnaio (SI), GEO 2 vs SQA ENEL PICA
08/10/2019 – 05/02/2020 --- H_2S

Piancastagnaio (SI)	ARPAT Geo2	ENEL 9 (PICA)	Note
data inizio monitoraggio	08/10/19	08/10/19	
data fine monitoraggio	31/01/20	31/01/20	
giorni monitoraggio	115	115	
ore	2783	2783	
ore valide	2666	2728	
mumero superamenti WHO-OMS	0	0	
media del periodo [µg/m³]	3,0	2,3	
max media mobile su 24h [µg/m³]	15,5	14,1	Lim=150 µg/m³
max concentrazione media giornaliera [µg/m³]	12,8	13,0	
numero giorni con concentrazione media >7	2	3	
n°ore con concentrazione >7	217	114	
massima oraria del periodo [µg/m³]	96,3	38,1	





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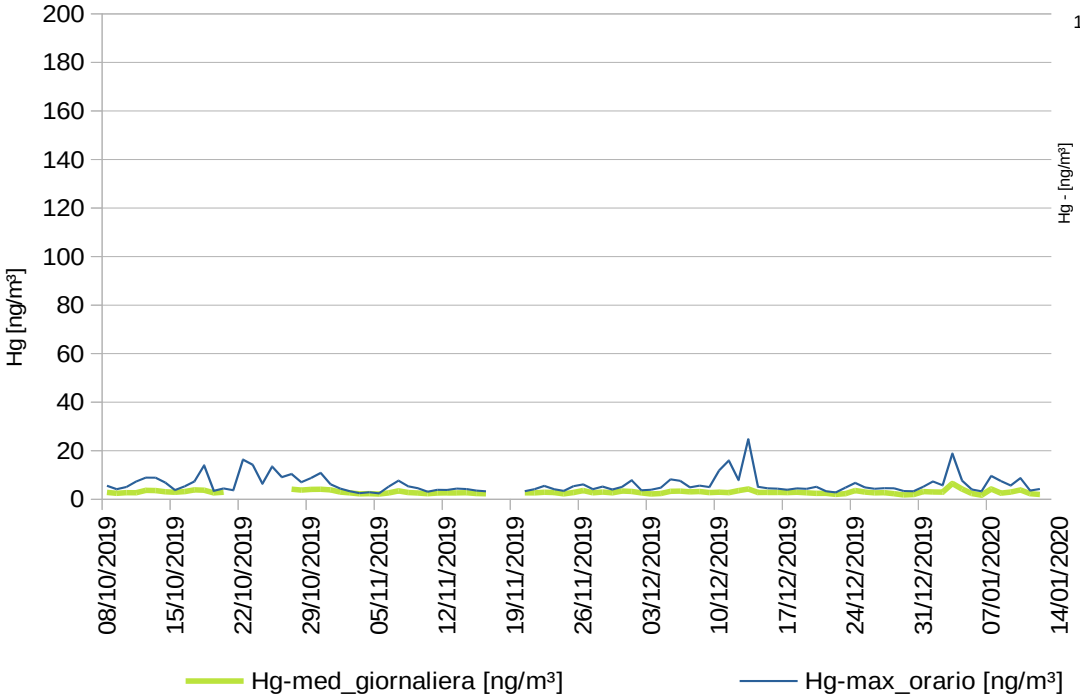
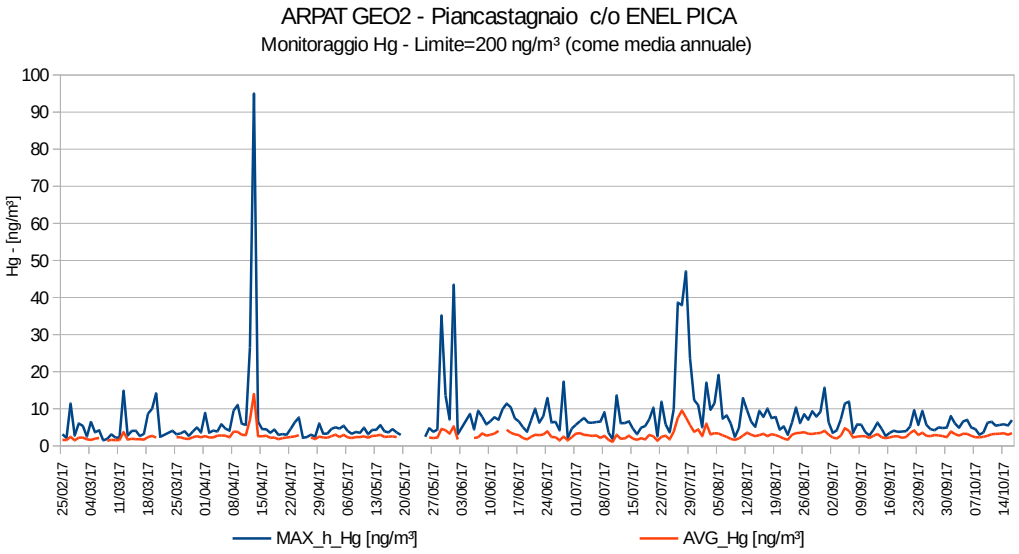
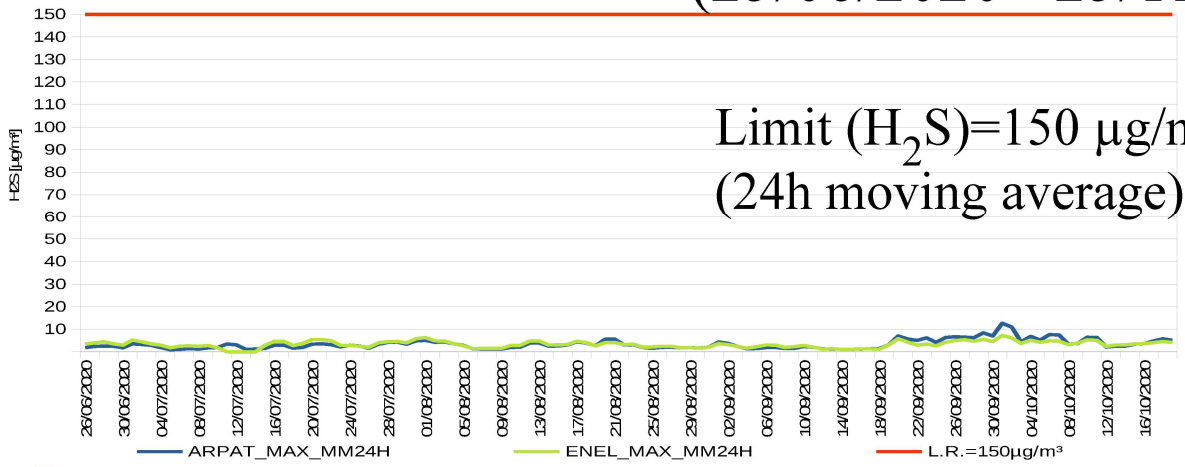
Piancastagnaio (SI): GEO 2
08/10/2019 - 05/02/2020
Hg monitoring - Limit=200 ng/m³ (as annual average)



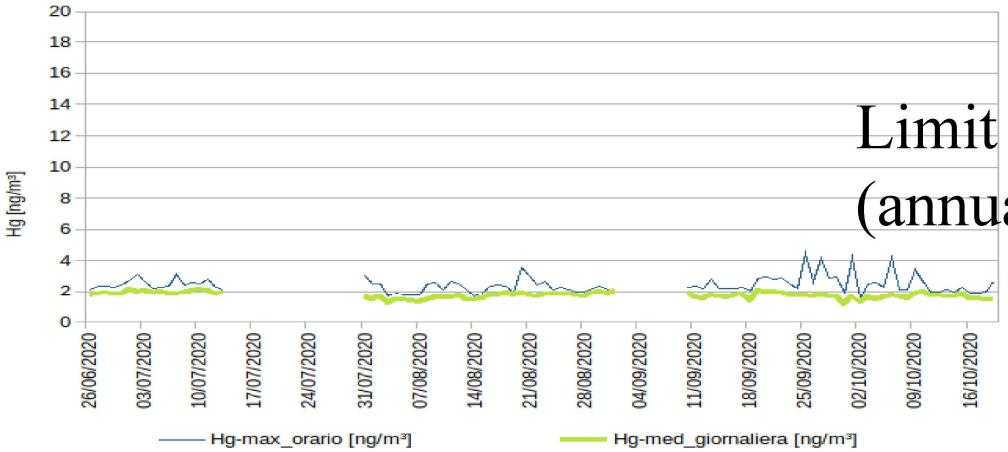


Belforte, Radicondoli (SI): GEO2 monitoring vs ENEL (25/06/2020 - 25/11/2020)



Limit (H_2S)=150 µg/m³
(24h moving average)

Belforte, Radicondoli (SI)	ARPAT Geo2	ENEL 18 (BEFO)	Note
data inizio monitoraggio	26/06/20	26/06/20	
data fine monitoraggio	24/11/20	24/11/20	
giorni monitoraggio	151	151	
ore	3647	3647	
ore valide	2791	2775	
mumero superamenti WHO-OMS	0	0	
media del periodo [µg/m³]	2,7	2,9	
max media mobile su 24h [µg/m³]	12,6	7,2	Lim=150 µg/m³
max concentrazione media giornaliera [µg/m³]	11,1	6,3	
numero giorni con concentrazione media >7	4	0	
n°ore con concentrazione >7	210	156	
massima oraria del periodo [µg/m³]	50,3	26,4	



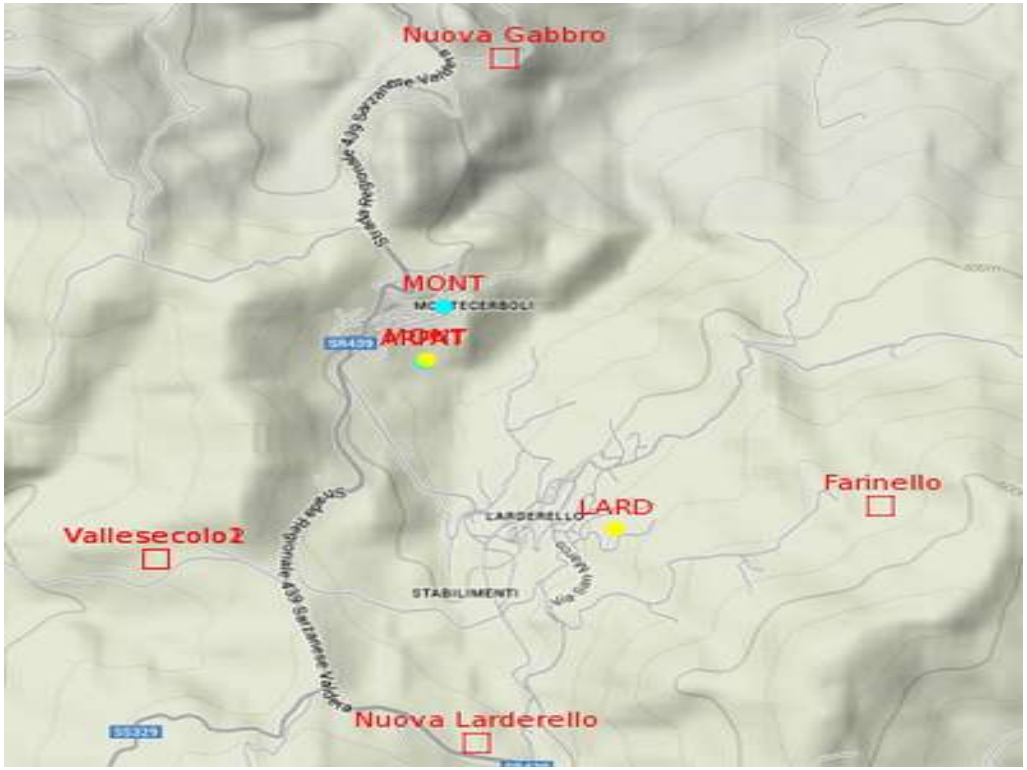
Limit (Hg)=200 ng/m³
(annual average)

Fixed air quality station in Montecerboli

The fixed station of **Montecerboli**, is part of the regional Air Quality monitoring network and is managed, on behalf of the Toscany Region, by ARPAT (DGRT n° 1025 of 06/ 12/2010).

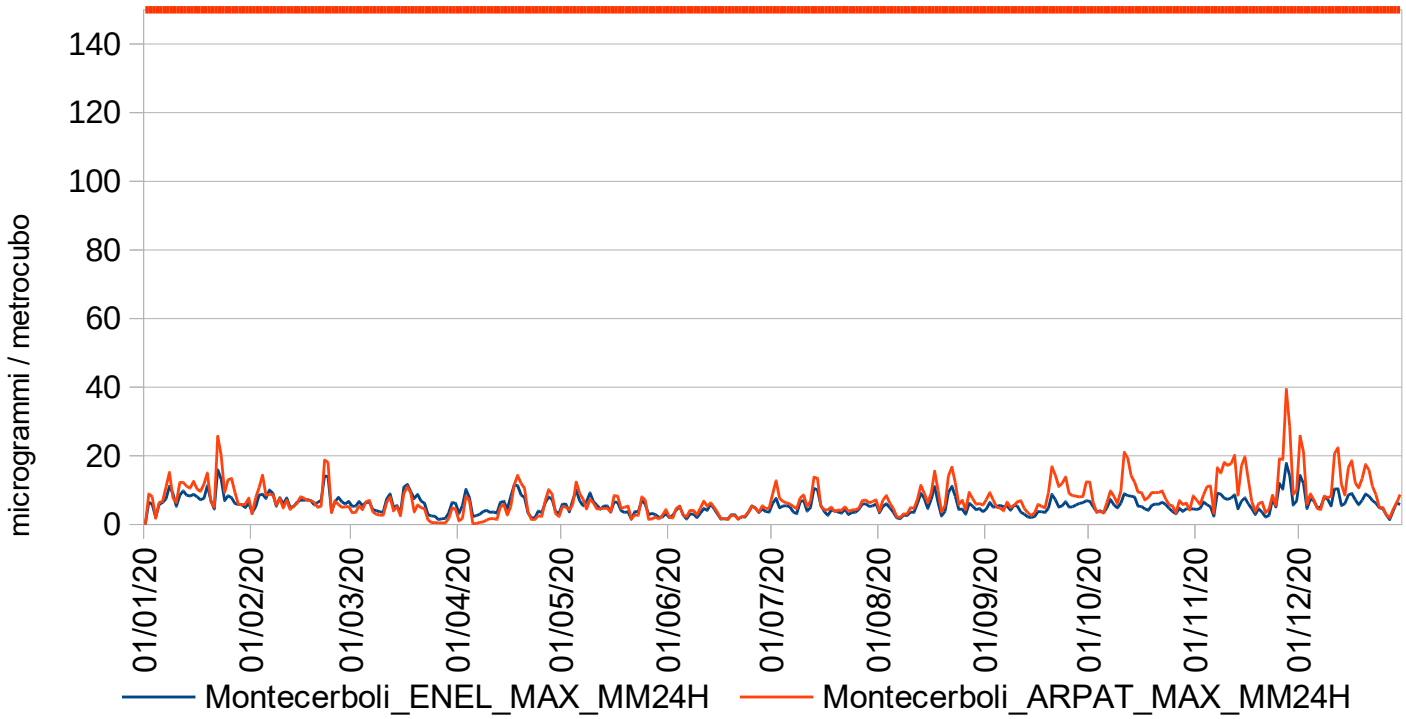
H_2S data collected by ARPAT confirm compliance with the 3 moving averages limits and the consistency with the ENEL GP data.

At Montecerboli we collect data about:
H_2S–PM_{10} –O_3 –NO –NO_2 –NO_x



Fixed location in Montecerboli

Daily maximum of the 24-hour moving average of H_2S concentration (µg/m³).
Comparison between ENEL data and ARPAT data in 2020



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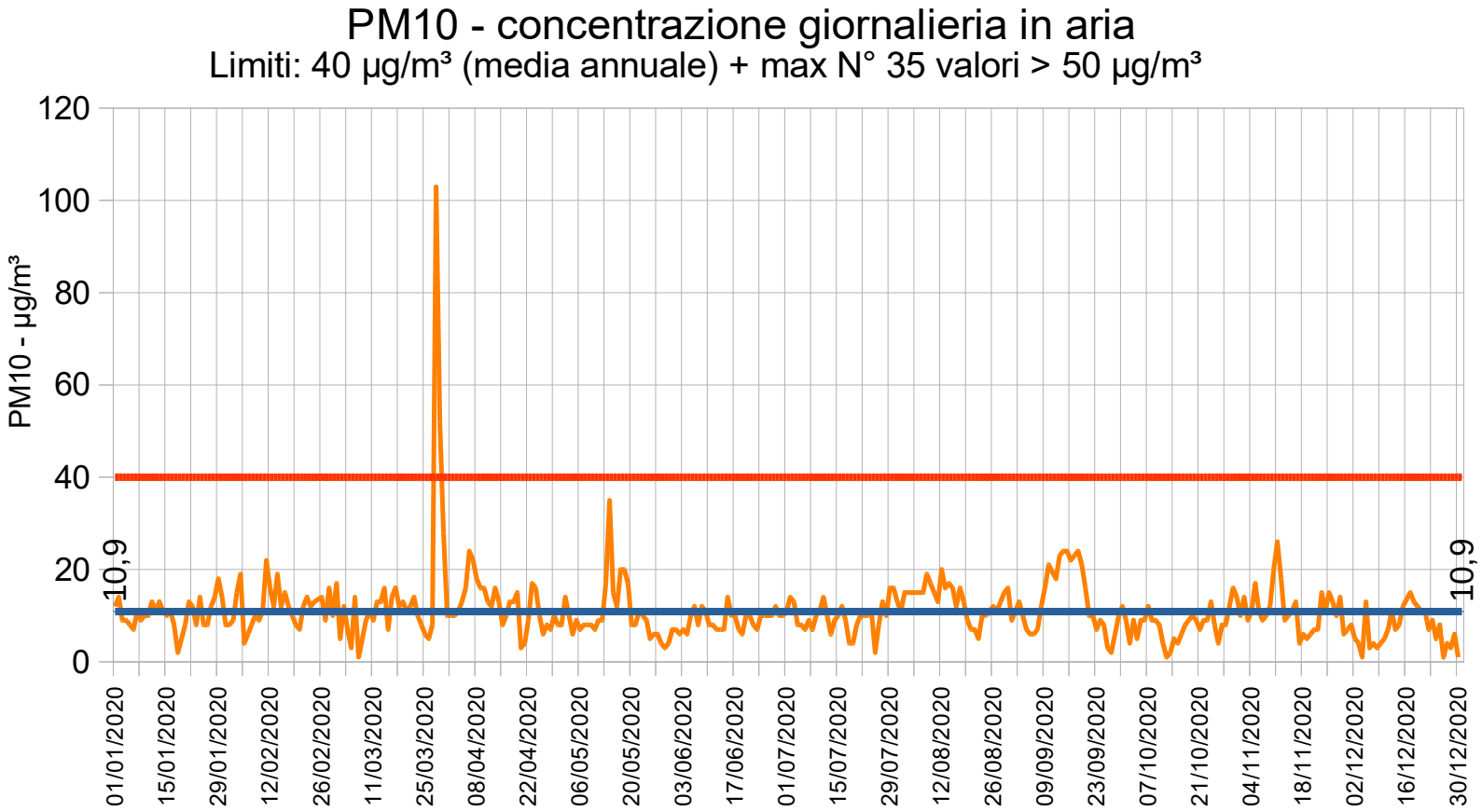
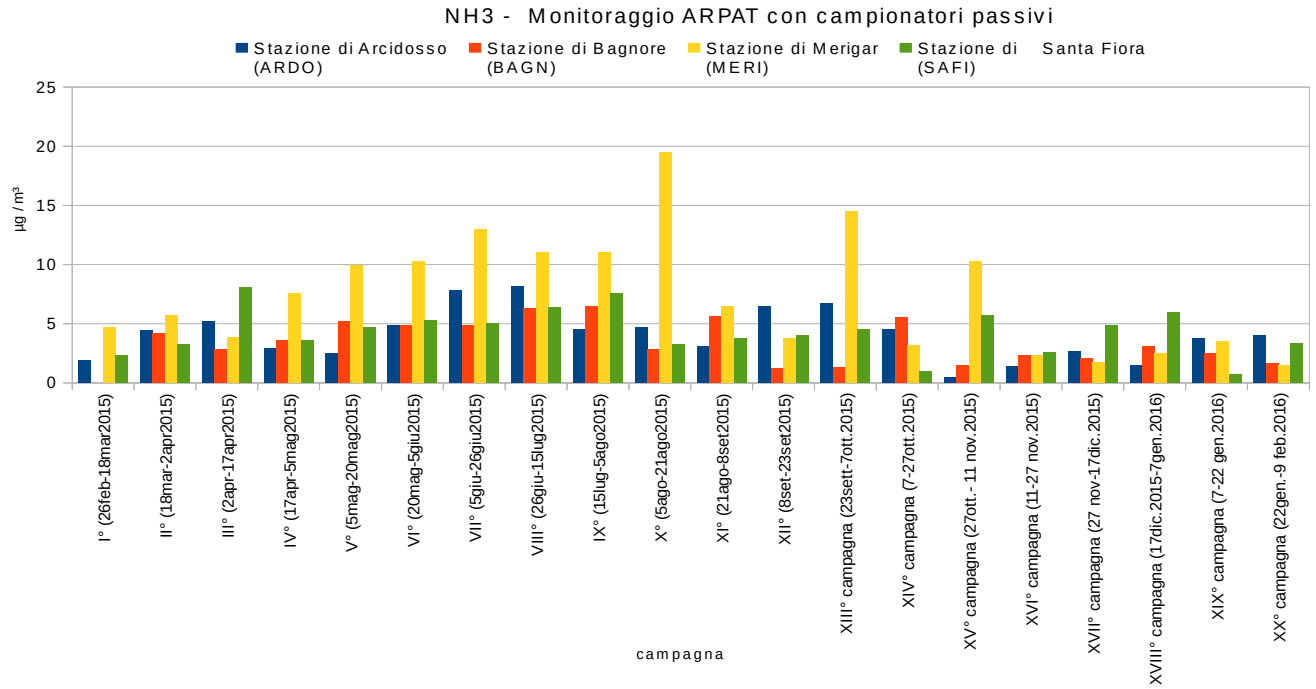
Fixed location in Montecerboli

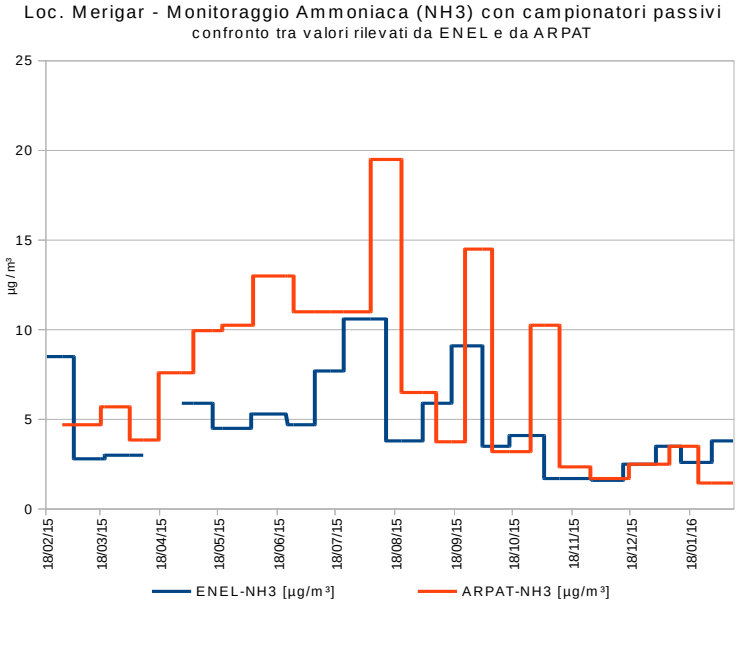


NH_3 monitoring

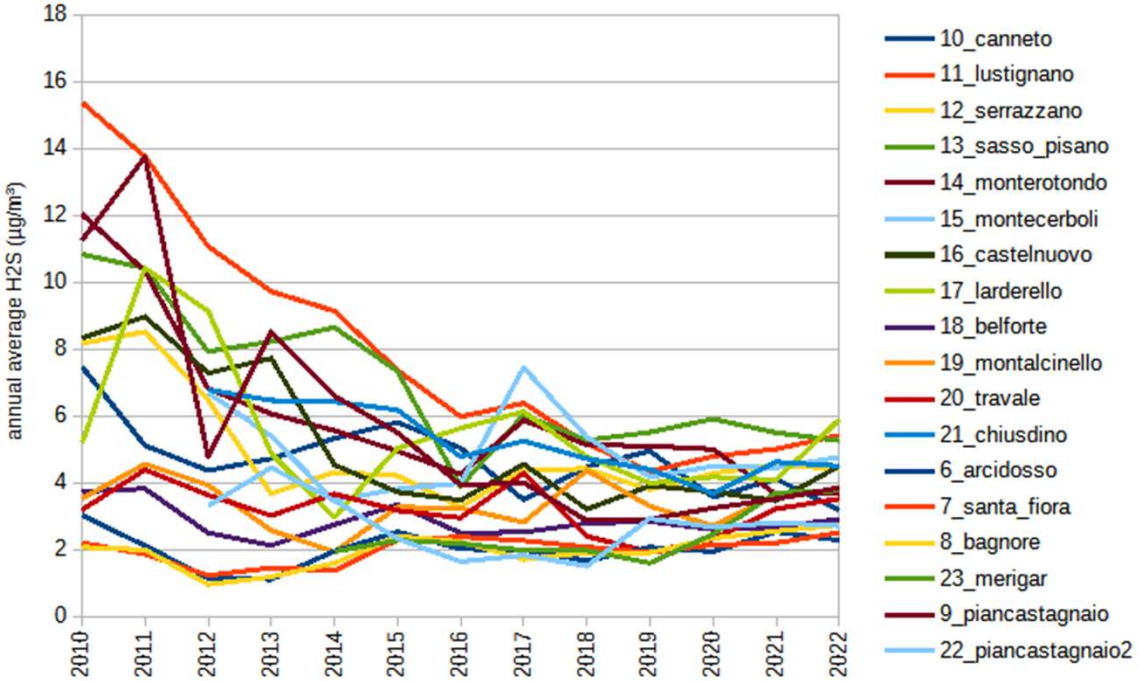
In 2015-2016 ARPAT carried out monitoring for NH3 with passive samplers in the area surrounding the Bagnore power plant.
Below is the comparison between the data collected by ENEL and ARPAT:

Reference Values (MRLs by ATSDR, USA): 70 µg/m³ (1-14 days average period)





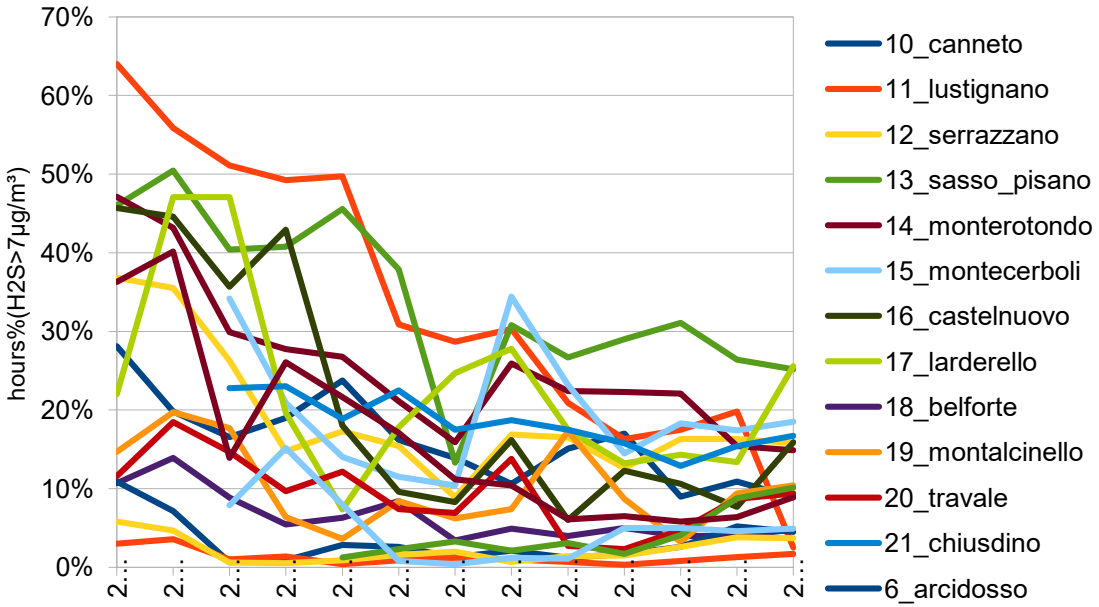
Hydrogen sulphide ENEL GP data (H_2S)
Historical trend of annual averages



H_2S	H_2S – Annual average [µg/m³]												
	2010	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**	**2022**
canneto	7,47	5,11	4,37	4,72	5,33	5,81	5,04	3,49	4,48	4,95	3,57	4,11	3,18
lustignano	15,38	13,76	11,07	9,72	9,14	7,37	5,98	6,38	5,17	4,34	4,79	5,01	5,42
serrazzano	8,17	8,52	6,48	3,67	4,31	4,21	3,28	4,38	4,42	3,79	4,28	4,54	4,41
sasso_pisano	10,84	10,42	7,93	8,22	8,65	7,34	3,89	6,03	5,27	5,51	5,91	5,50	5,26
monterotondo	12,04	10,33	6,81	6,06	5,56	4,95	4,26	5,87	5,13	5,10	5,00	3,65	3,69
montecerboli	ND	ND	*6,69*	5,39	3,46	3,82	3,98	7,45	5,37	4,17	4,50	4,45	4,77
castelnuovo	8,33	8,97	7,28	7,72	4,54	3,72	3,48	4,56	3,21	3,91	3,73	3,46	4,50
larderello	5,19	10,43	9,14	4,88	2,97	5,03	5,63	6,13	4,78	3,99	4,17	4,09	5,89
belforte	3,74	3,82	2,50	2,13	2,75	3,34	2,50	2,52	2,79	2,84	2,61	2,67	2,91
montalcinello	3,53	4,56	3,93	2,58	1,93	3,27	3,24	2,82	4,37	3,30	2,71	3,63	3,80
travale	3,19	4,39	3,63	3,02	3,67	3,17	2,95	4,28	2,40	1,93	2,32	3,22	3,52
chiusdino	ND	ND	*6,78*	6,46	6,43	6,18	4,78	5,25	4,72	4,40	3,68	4,62	4,50
rcidosso	3,03	2,11	1,16	1,11	1,95	2,53	2,02	1,99	1,67	2,07	1,94	2,53	2,28
anta_fiora	2,20	1,87	1,23	1,46	1,37	2,29	2,38	2,27	2,08	1,92	2,14	2,20	2,51
agnore	2,07	1,99	0,96	1,19	1,59	2,4	2,24	1,71	1,91	1,91	2,34	2,55	2,73
merigar	ND	ND	ND	NS	1,94	2,28	2,18	1,98	1,97	1,60	2,46	3,70	3,77
iancastagnaio	11,25	13,75	4,78	8,52	6,60	5,5	3,93	4,00	2,87	2,91	3,24	3,52	3,85
piancastagnaio2	ND	NS	3,31	4,45	3,47	2,33	1,64	1,83	1,51	2,93	2,67	2,81	2,71

ND =	Dati non disponibili
NS =	Dati non significativi, in quanto la data di messa in servizio della centralina, non permette di avere una distribuzione uniforme sull'anno.
nnn	Valori ricavati su una frazione ritenuta significativa dell'intero anno (21_chiusdino: 1/3/2012; 15_montecerboli: 19/04/2012)

Hydrogen sulphide ENEL GP data (H_2S)
Historical trend of H_2S concentration > 7 µg/m³



H_2S	hours% (H2S>7 µg/m³)												
	2010	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**	**2022**
10_canneto	28,1%	19,8%	16,5%	19,0%	23,7%	16,2%	13,9%	10,6%	15,1%	17,0%	9,0%	10,9%	8,9%
11_lustignano	64,0%	55,9%	51,1%	49,2%	49,7%	30,9%	28,7%	30,3%	20,9%	16,3%	17,5%	19,8%	2,5%
12_serrazzano	36,8%	35,5%	26,3%	14,8%	17,3%	15,4%	8,9%	16,9%	16,5%	12,6%	16,3%	16,3%	15,8%
13_sasso_pisano	46,0%	50,5%	40,4%	40,8%	45,6%	37,9%	13,3%	30,8%	26,7%	29,0%	31,1%	26,4%	25,2%
14_monterotondo	47,1%	43,2%	29,9%	27,7%	26,8%	21,1%	15,9%	25,9%	22,4%	22,3%	22,1%	15,4%	14,9%
15_montecerboli	ND	ND	*34,2%*	20,9%	14,0%	11,5%	10,4%	34,4%	23,2%	14,5%	18,3%	17,4%	18,5%
16_castelnuovo	45,7%	44,6%	35,7%	42,9%	18,0%	9,6%	8,3%	16,2%	6,0%	12,3%	10,6%	7,7%	15,9%
17_larderello	22,0%	47,1%	47,1%	19,7%	7,3%	17,8%	24,7%	27,8%	17,5%	13,2%	14,3%	13,4%	25,6%
18_belforte	10,7%	13,9%	8,9%	5,5%	6,3%	8,4%	3,4%	4,9%	4,0%	5,0%	4,0%	4,0%	4,8%
19_montalcinello	14,7%	19,7%	17,7%	6,4%	3,6%	8,4%	6,2%	7,4%	17,3%	8,7%	3,2%	9,4%	10,4%
20_travale	11,6%	18,5%	14,7%	9,7%	12,2%	7,4%	6,9%	13,8%	2,7%	2,3%	4,7%	8,7%	9,4%
21_chiusdino	ND	ND	*22,8%*	23,0%	18,9%	22,5%	17,5%	18,7%	17,5%	15,8%	12,9%	15,4%	16,7%
6_arcidosso	10,9%	7,2%	0,6%	0,9%	2,9%	2,6%	1,3%	2,1%	1,2%	1,7%	2,6%	5,2%	4,5%
7_santa_fiora	3,0%	3,6%	1,0%	1,4%	0,4%	0,9%	1,2%	1,0%	0,7%	0,3%	0,8%	1,3%	1,7%
8_bagnore	5,8%	4,7%	0,6%	0,5%	0,9%	1,6%	2,0%	0,7%	1,4%	1,5%	2,6%	3,8%	3,7%
23_merigar	ND	ND	ND	NS	1,3%	2,3%	3,3%	2,1%	3,1%	1,7%	4,1%	8,8%	10,1%
9_piancastagnaio	36,3%	40,2%	13,9%	26,1%	21,7%	17,1%	11,2%	10,4%	6,1%	6,5%	5,8%	6,4%	8,9%
22_piancastagnaio2	ND	NS	7,9%	15,2%	8,0%	0,8%	0,4%	1,2%	1,1%	5,0%	5,0%	4,6%	4,9%

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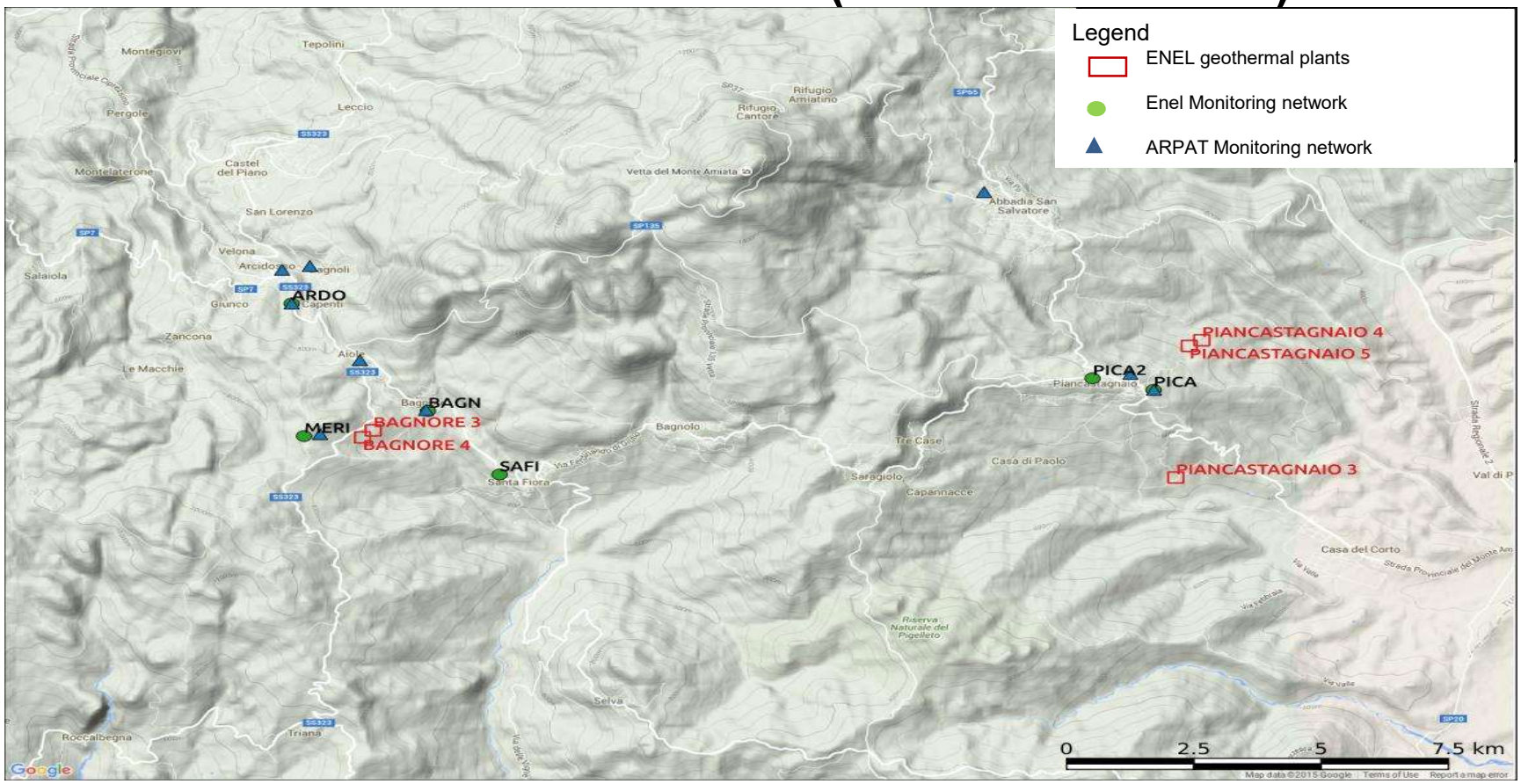
MOUNT AMIATA AREA (Grosseto & Siena)



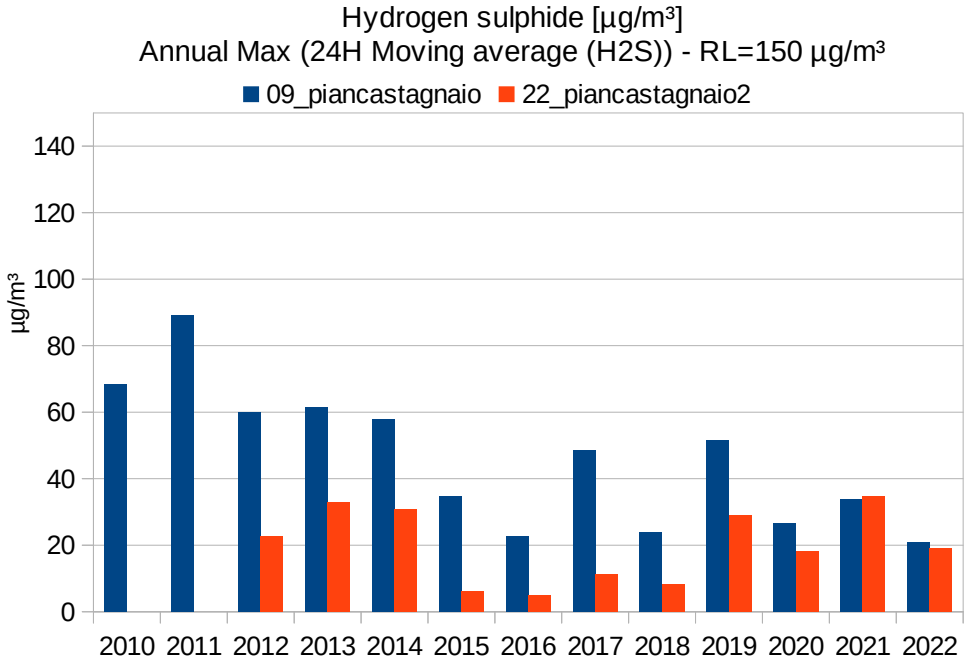
AMIATA AREA (SIENA)

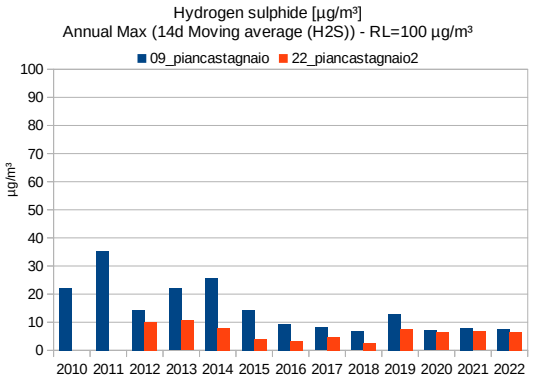
H_2S Annual max of:	Moving average 24 hors (µg/m³)													Moving average 14 days (µg/m³)												Moving average 90 days (µg/m³)											
	L.R. = 150 µg/m³													L.R. = 100 µg/m³												L.R. = 20 µg/m³											
location:	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
09_piancastagnaio (PICA)	68,4	89,3	59,9	61,5	57,9	34,6	22,6	48,5	23,8	51,6	26,7	33,9	20,8	22,1	35,2	14,2	22,0	25,6	14,5	9,3	8,2	6,7	13,0	7,1	7,8	7,6	14,7	17,4	11,5	15,1	11,3	8,0	8,5	5,0	3,9	5,5	3,9	4,1	4,6
22_piancastagnaio2 (PICA2)	ND	NS	22,6	32,8	30,8	6,3	5,0	11,4	8,4	29,0	18,0	34,6	19,0	ND	NS	10,1	10,7	7,8	4,1	3,3	4,7	2,7	7,6	6,4	6,7	6,5	ND	NS	5,3	7,1	4,4	3,6	2,6	2,6	2,4	3,5	3,3	3,3	4,2

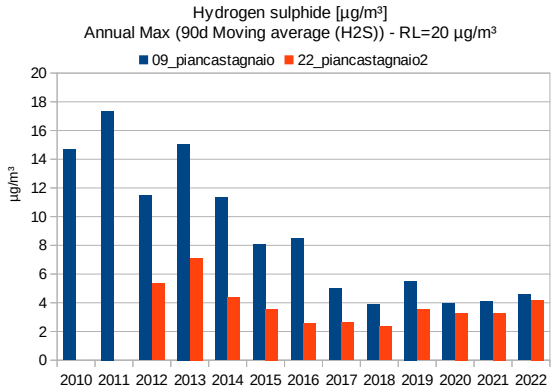
* = Maximum determinated from avaible a October 2016

ND = Data not avaible

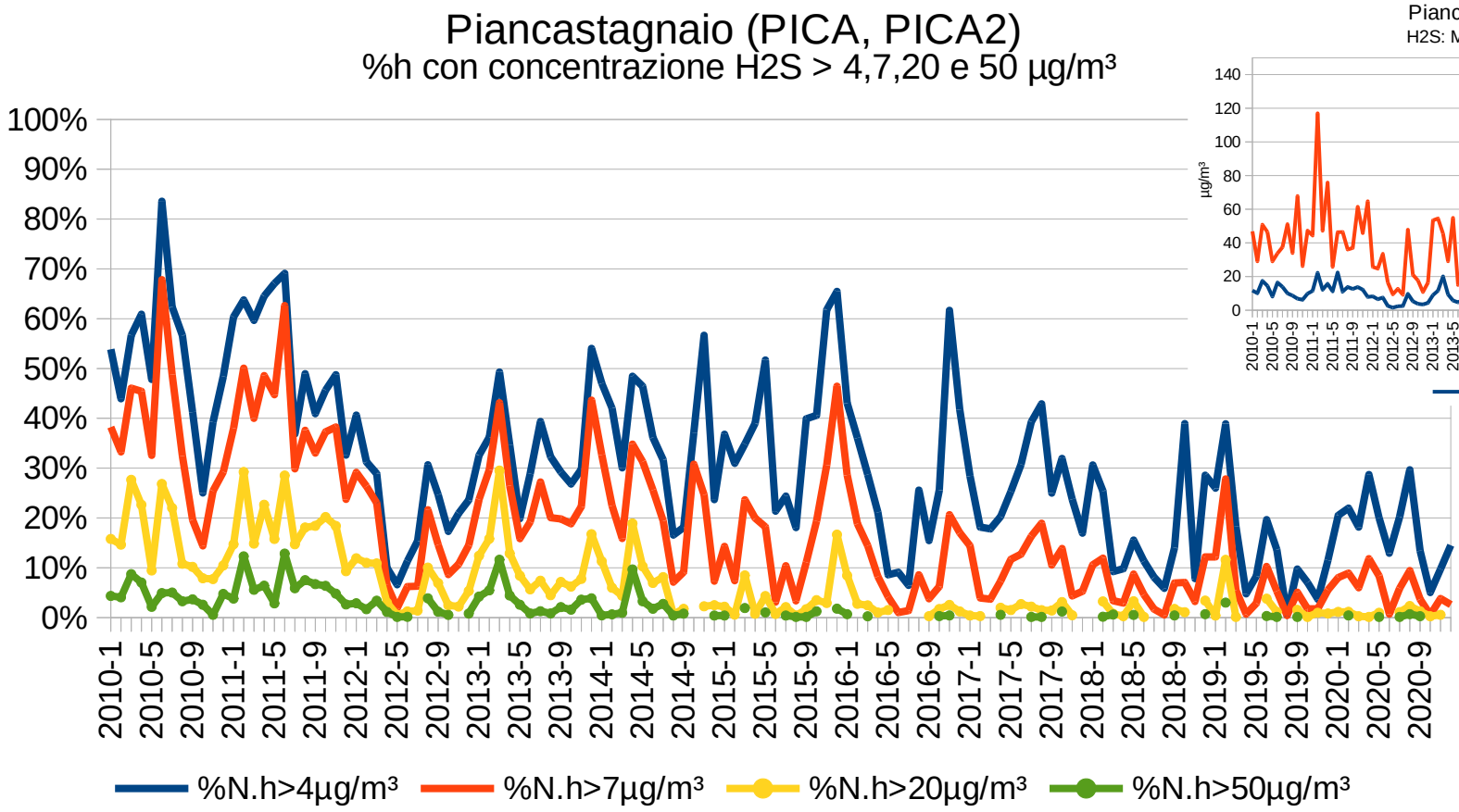
NS = Data not rappresentative, because distribuition is not uniform over the year.

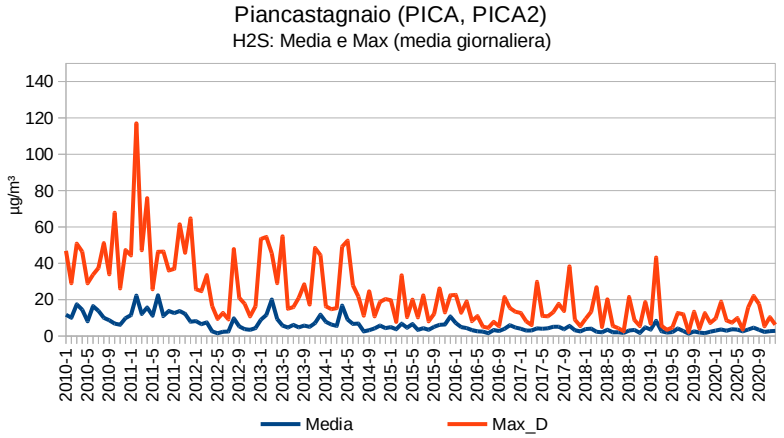






PIANCASTAGNAIO (SI)





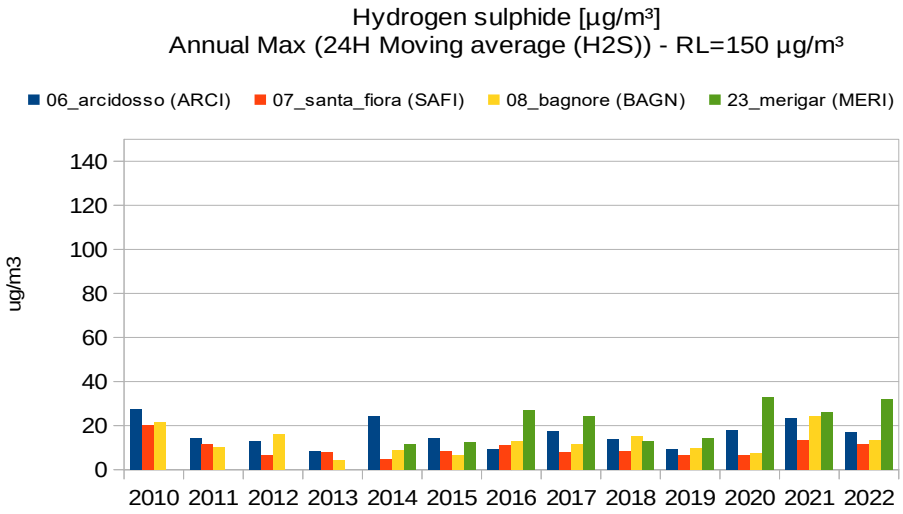
AMIATA AREA (GROSSETO)

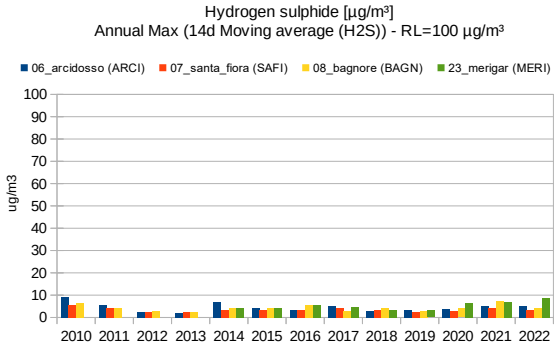
H_2S Annual max of:	Moving average 24 hors (µg/m³)													Moving average 14 days (µg/m³)												Moving average 90 days (µg/m³)											
	L.R. = 150 µg/m³													L.R. = 100 µg/m³												L.R. = 20 µg/m³											
location:	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
06_arcidosso (ARCI)	27,5	14,4	13,1	8,4	24,3	14,2	9,2	17,3	13,8	9,3	18,1	23,2	17,1	9,1	5,7	2,6	2,0	7,0	4,3	3,3	5,2	3,1	3,5	3,6	5,2	5,0	4,2	3,3	2,7	1,6	3,5	3,3	3,0	2,6	2,2	2,7	2,6	3,3	2,8
07_santa_fiora (SAFI)	20,4	11,4	6,5	7,9	4,8	8,3	11,0	7,7	8,6	6,7	6,8	13,3	11,5	5,8	4,4	2,6	2,5	3,2	3,2	3,5	4,5	3,4	2,5	2,8	4,2	3,5	4,1	2,6	2,2	2,0	2,3	2,6	2,8	3,1	2,8	2,2	2,4	2,6	3,0
08_bagnore (BAGN)	21,5	10,3	16,3	4,1	8,7	6,7	13,0	11,6	15,4	9,8	7,6	24,3	13,6	6,4	4,2	2,9	2,5	4,3	4,2	5,4	3,0	4,2	3,1	4,0	7,3	4,3	3,2	2,7	2,2	2,0	3,1	3,3	3,8	2,4	2,5	2,7	2,7	3,3	3,4
23_merigar (MERI)	ND	ND	ND	NS	11,6	12,5	27,1	24,4	13,1	14,4	32,7	25,9	32,1	ND	ND	ND	NS	4,0	4,1	5,6	4,6	3,2	3,1	6,3	7,0	8,7	ND	ND	ND	NS	2,5	2,9	2,9	2,7	2,4	2,0	3,1	4,5	5,5

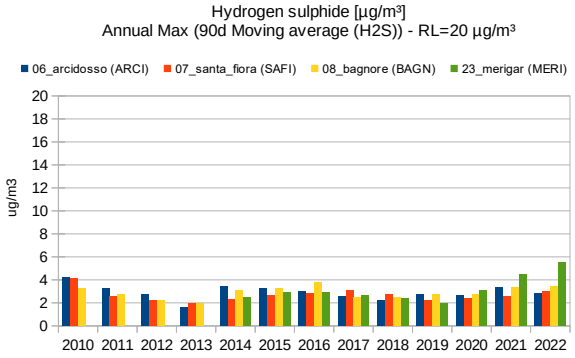
* = Maximum determinated from avaible a October 2016

ND = Data not avaible

NS = Data not rappresentative, because distribuition is not uniform over the year.







IMPROVEMENT OBJECTIVES

- Reduce olfactory disturbance caused by H_2S;
- Reduce periods of central blocking and AMIS shutdown;
- Adopt interconnection strategies between the power plants (and when possible between the AMIS plants) that allow avoiding, in the event of a central block, the overflow of untreated geothermal fluids into the atmosphere;
- Reduce AMIS maintenance intervention times;
- Reduction of "drift" emitted by the cooling tower.

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THANKS FOR YOUR ATTENTION