Monitoring of PHAs deposition in the most important petrolifer area in Italy, the Agri Valley (Southern Italy, Basilicata Region)

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INTRODUCTION

The Val d'Agri Oil Center (COVA) is located in the Basilicata Region in southern Italy in the industrial area of the Municipality of Viggiano (PZ). The COVA came into operation in 2001 and refines the oil extracted from one of the largest onshore deposits in Europe which supplies over 10% of Italy's oil needs. Environmental monitoring activities are conducted on different environmental matrices: air, water, soil and ecosystems. Air quality monitoring involves the measurement of dry and humid deposition of atmospheric contaminants such as PAHs, PCBs and metals and the volatile component of hydrocarbons in ambient air (BTEX). This work reports the evaluation of PAHs and metals from January 2019 to September 2024.

MATERIAL AND METHOD

Total atmospheric deposition, which was defined as sum of wet and dry deposition, can be estimated by depobulk. Bulk deposition was collected at ten stations during four years period. Every depobulk have been exposed for about 30 ± 2 days samples. We have had two type of depobulk, one for studying microorganic depositions like polycyclic aromatic hydrocarbons (PAH) and another type for studying inorganic deposition like metals.

The first depobulk in PEHD for metals and the second one in Pyrex for determination of PAH were showed in the figure 1, while an example of installation depobulk in the field was in Figure 2. The geographical location of the sampling sites of deposition measurements in Val D'Agri were showed in Figure 3.

PAH

Deposition samples for the determination of PAH compounds have been taken in Pyrex funnel-bottle bulk collector and the samples have been prepared using solid phase extraction with organic solvent (Figure 4). Identification and quantification of the substances have performed by GC/MS triple quad (Figure5), using Method UN EN 15980:2011.

Metals

Deposition samples for the determination of metals have been taken in PHDE funnel-bottle bulk collector and the metals were brought into solution by digestion techniques (Figure 6) and analyzed by ICP-MS(Figure 7), using Method UN EN 15841:2010.

Figure 2 Example of installation Depobulk in the field

Figure 1 Material of depobulks, to the left in PHDE and to the right in Pyrex

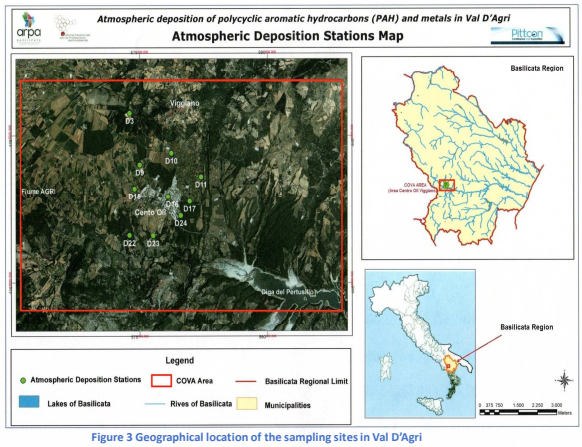

Figure 3 Geographical location of the sampling sites in Val D'Agri

Figure 4. SPE extractor

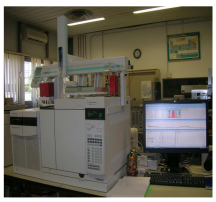

Figure 5. Triple quadrupole GC/MS

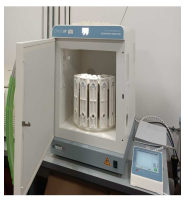

Figure 6 Microwave digestion system

Figure 7. ICP-MS

RESULTS AND DISCUSSION

The aim of this work was to evaluate the temporal trend of metals and PAH, especially benzo(a)pyrene. We used the analytical concentration in bulk deposition to evaluate the amount of deposition for a day in ug/(m2*die) for metals and ng/(m2*die) for PAH.

We have evaluated the possible temporal trends in time series of data grouped by sites and seasons. Looking the plots of stations, we can observe for all sites the similar time trend, as metals as PAH. In some particular periods we can observe the highest peaks, the highest peak almost always were in the first quarter of the year (Figure 8). We have observed the highest ever peak in the period from January to March 2024. Considering the annual averages of benzo(a)pyrene (Figure 9 and Table 1), it can be seen that the highest concentrations always occurs at sites 16 and 17 for all years, and these are the closest sites to the oil center.

Among metals we investigated the temporal trend of arsenic, cadmium, nickel and lead. Arsenic is almost always below the limit of quantification. For cadmium nickel and lead we also observe higher concentrations in station 16. The histograms of nickel and lead are shown in the Figures 10 and 11, whereas data set in Table 2 and 3.

Averages Benzo(a)pirene ng/(m2*die)	2019	2020	2021	2022	2023	2024
Station 03	2,44	0,40	0,50	0,96	1,12	3,42
Station 09	3,37	0,40	0,50	0,97	2,06	3,93
Station 10	3,35	0,40	0,50	0,52	2,02	0,77
Station 11	2,73	2,52	0,50	0,60	1,34	0,77
Station 15	1,42	1,93	0,50	0,70	1,89	6,20
Station 16	4,05	2,40	0,48	2,96	6,67	15,40
Station 17	2,02	0,40	0,48	1,58	2,17	17,28
Station 22	2,57	0,40	0,48	0,98	2,16	7,60
Station 23	1,22	0,40	0,48	0,60	1,52	2,87
Station 24	4,11	0,40	0,48	0,63	1,54	6,97

Table 1. Annual averages benzo(a)pyrene

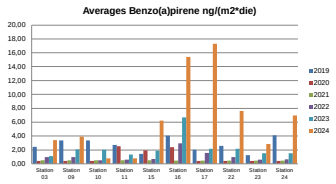

Figure 9. Annual averages of benzo(a)pyrene

Averages Nickel ug/(m2*die)	2019	2020	2021	2022	2023	2024
Station 03	1,4	2,3	2,6	2,0	1,9	3,7
Station 09	2,2	3,2	3,9	2,5	2,2	4,9
Station 10	1,4	3,0	3,7	1,9	1,4	1,9
Station 11	1,5	2,7	3,6	1,7	1,7	2,5
Station 15	2,7	4,6	3,0	1,9	2,7	2,8
Station 16	4,3	5,1	6,2	3,9	5,1	2,4
Station 17	2,3	3,0	2,9	1,7	1,5	1,2
Station 22	1,9	3,1	3,2	2,0	1,0	1,5
Station 23	1,4	2,5	2,6	1,8	0,5	2,0
Station 24	2,0	4,9	4,5	1,8	0,8	1,6

Table 2. Annual averages nickel

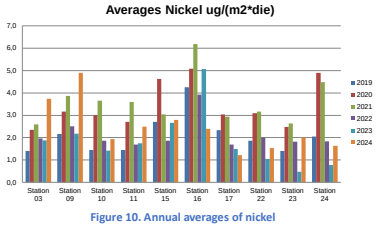

Figure 10. Annual averages of nickel

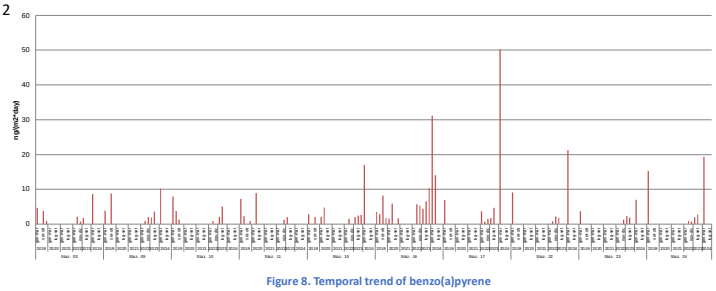

Figure 8. Temporal trend of benzo(a)pyrene

CONCLUSIONS

In Italian regulations there are no threshold value for atmospheric depositions but Legislative Decree 155/2010 in outdoor air provides target value for arsenic, cadmium, nickel and benzo(a)pyrene. In no case we have found values that exceed these indications, but we have observed higher concentrations of these pollutants in the closest sites to the oil center, especially in station 16.

Averages Lead ug/(m2*die)	2019	2020	2021	2022	2023	2024
Station 03	2,0	1,3	3,8	3,0	3,3	7,0
Station 09	2,7	1,6	2,0	4,4	3,2	15,4
Station 10	1,5	1,2	1,6	3,3	2,6	8,0
Station 11	1,9	1,5	2,3	2,2	3,0	8,5
Station 15	3,3	2,1	1,9	3,3	2,5	14,0
Station 16	5,8	6,4	6,6	10,5	6,2	10,9
Station 17	2,4	1,4	2,3	3,3	4,1	8,2
Station 22	1,9	1,2	2,0	3,0	3,8	5,5
Station 23	1,9	1,5	1,3	2,3	3,6	7,6
Station 24	2,6	2,5	2,4	3,0	3,1	6,3

Table 3. Annual averages Lead

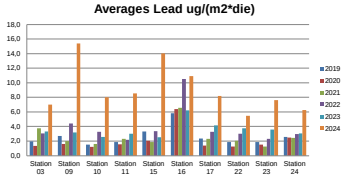

Figure 11. Annual averages of Lead

REFERENCES

- UN EN 15841:2010
- UN EN 5980:2011
- ISSN 1123-3117 Rapporti ISTISAN 06/38
- Legislative Decree 155/2010
- European Directive 2004/107/CE

ACKNOWLEDGMENTS

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