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# Air Quality in Portal Areas: An Index for VOCs Pollution Assessment

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Additional information is available at the end of the chapter

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### 1. Introduction

Air quality in portal areas is usually compromised by local emissions related to many different typologies of commercial, industrial and touristic activities.

Therefore, in order to reduce the consequences on the environment and human health due to exhausted gas released near the water surface and the ground, the air quality of portal areas should be monitored in all the different subareas of a harbour, by dividing it according with the different intended use areas.

Thus, it will be possible to pinpoint the most critical zones of each considered port and consequentially to plan specific actions for improving air quality in those areas.

In particular, this chapter deals with the emissions of VOCs (Volatile Organic Compounds) which play a key role in the short term chemical composition of the troposphere, as well as in climate changes (Murrells & Derwent, 2007).

Are classified as VOCs, in fact, both hydrocarbons containing carbon and hydrogen as the only elements (alkenes and aromatic compounds) and compounds containing also oxygen, chlorine or other elements, such as aldehydes, ethers, alcohols, esters, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). According with the Italian regulation (article 268 of the 152/2006 Legislative Decree) VOCs are those organic substances which have at 293.15 K (20°C) a vapour pressure greater then or equal to 0.01 kPa.

The contents of this chapter have been developed considering the Italian and European regulations, which applications will improve the environmental quality in portal areas.

Among these, the Marine Environmental Protection Committee (MEPC) of the International Maritime Organization (IMO) has developed a protocol of an International Convention for



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the Prevention of Pollution from Shipping (IMO/MARPOL 73/78) establishing a monitoring program for reducing emissions (IMO, 2008).

In the light of these considerations, the main goals of our chapter are:

- To elaborate an air quality index weighed on the atmospheric concentrations of all VOCs, in order to obtain a single number that expresses the overall VOCs pollution of an area.
- To validate this index through its application in some case studies areas
- To pinpoint the most critical areas of the analysed harbours in order to select BAT (Best Available Technologies) and best practices for mitigating VOCs concentrations and improving local air quality.

#### 2. AQIvoc index elaboration

In order to elaborate an Air Quality Index for VOCs, called AQI<sub>voc</sub>, weighed on the atmospheric concentrations of all VOCs as well as on dangerousness and impact of each substance in atmosphere, we assigned to each VOC an environmental impact coefficient ( $\alpha$ ) interrelated with its emission limit value according with the Italian regulations

$$\alpha_i = \frac{V_{\text{max}}}{V_i} \tag{1}$$

Where:

 $\alpha_i$  = environmental impact coefficient for the i-th VOC

 $V_{max}$  = highest emission limit value among all VOCs

V<sub>i</sub> = emission limit value for the i-th VOC

The values of the environmental impact coefficient were assigned in proportion to the emission limit value specified for each ith class, giving a coefficient of greater environmental impact where the regulatory limit value of emission in atmosphere is lower.

In particular, considering the Italian regulation, the Annex III of the fifth part of the 152/2006 Legislative Decree shows a classification of volatile organic compounds divided into five classes according to their impact on the environment; consequentially the same Decree assigns to each of the five classes a maximum value of emission in atmosphere (Table 1).

Pollutants classification	Emission limit in atmosphere	environmental impact				
(152/2006 Legislative Decree)	(152/2006 Legislative Decree)	coefficient $\alpha$				
Class I	5 mg/Nm <sup>3</sup>	120				
Class II	20 mg/Nm <sup>3</sup>	30				
Class III	150 mg/Nm <sup>3</sup>	4				
Class IV	300 mg/Nm <sup>3</sup>	2				
Class V	600 mg/Nm <sup>3</sup>	1				

**Table 1.** Environmental impact coefficient for VOCs related to their normative classification and limit values for emissions

Briefly, the equation for the AQIvoc indices evaluation is the following:

$$AQi_{voc} = 100 \cdot \frac{1 / \sum_{i=1}^{i=18} \alpha_i \cdot v_i}{\left(1 / \sum_{i=1}^{i=18} \alpha_i \cdot v_i\right)_{max}}$$
(2)

Where:

AQI<sub>voc</sub> = Air quality index related to VOCs concentrations  $\alpha_i$  = environmental impact coefficient for the i-th VOC

 $v_i$  =atmospheric concentration of the i-th VOC detected in the analysed intended use area

$$\left(1/\sum_{i=1}^{i=18} \alpha_i \cdot v_i\right)_{\max}$$
 = highest value of  $1/\sum_{i=1}^{i=18} \alpha_i \cdot v_i$  (related to the intended use portal area

with lower concentrations of VOCs pollution in the atmosphere)

Consequentially, these values, standardized in a range from zero to hundred, have a comparative nature, with the value 100 assigned to the lowest VOCs concentration detected (in a certain port, in a certain detected area and in a certain season).

#### 3. Case studies: The harbours of Anzio, Formia, Terracina and Ventotene

In order to validate the above mentioned methodology four ports of the Lazio region have been selected as case studies (Fig. 1)

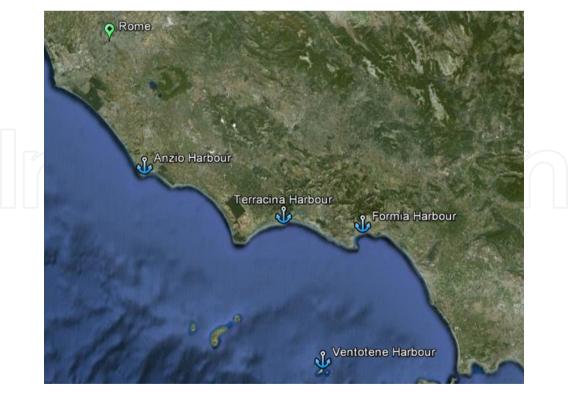


Figure 1. Geographic location of the harbours of Anzio, Formia, Terracina and Ventotene

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In each port, divided into subareas according with its different intended use zones, was carried out an annual field data gathering, detecting VOC concentration in each season.

Lastly, an air quality matrix with VOC concentrations and AQIvoc values (for each intended use area in each season) has been elaborated for each analysed port.

### 4. Data gathering methods

In each of these four ports were monitored the concentrations in atmosphere of the following 18 VOCs: Dichloromethane; 2-Methylpentane; Hexane; Methylcyclopentane; Chloroform; 2-Methylhexane; Cyclohexane; Benzene; Heptane; Trichloroethylene; Methylcyclohexane; Toluene; Tetrachloroethylene; Ethylbenzene; m- p- xylene; o- xylene; 1,2,4-Trimethylbenzene; 1,2-Dichlorobenzene.

The concentrations of these substances were sampled seasonally in each intended use area of the four ports, leaving many radial diffusive samplers called "Radiello ®" (Bruno et al., 2008) for a period ranging between 7 and 10 days per season (Fig. 2)



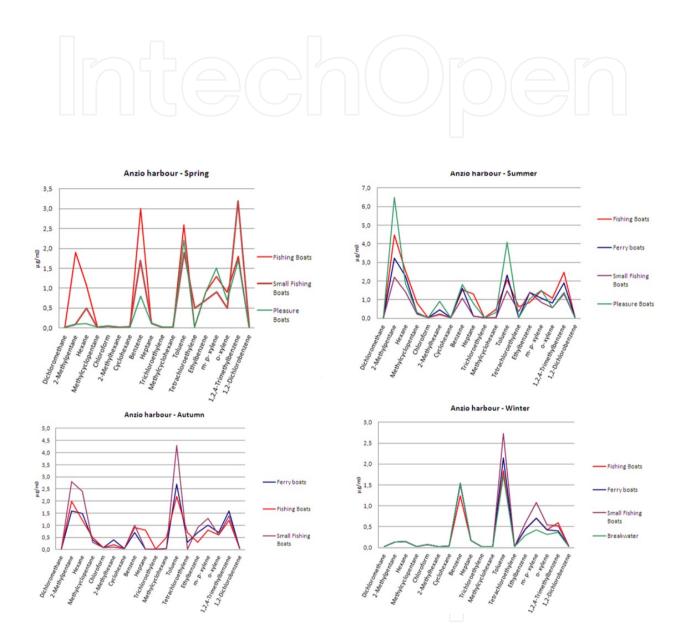
Figure 2. Two examples of VOCs monitoring in portal areas using radial diffusive samplers

#### 5. Results

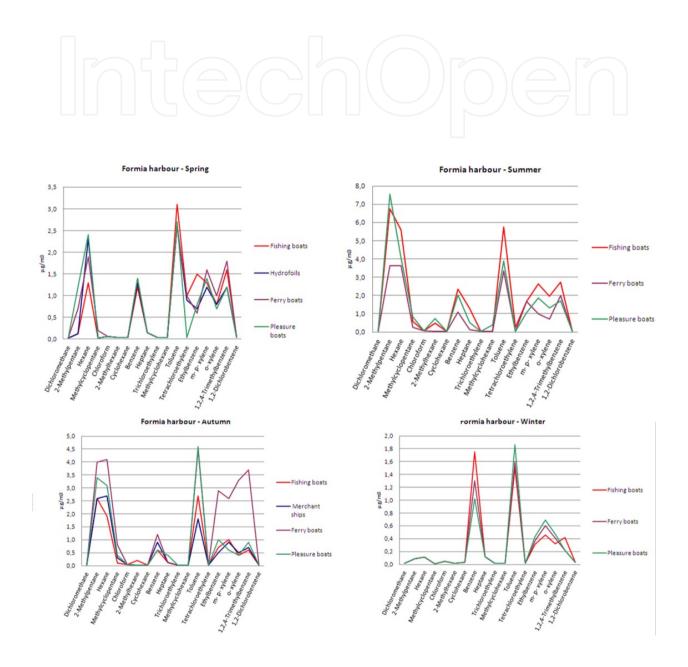
All the obtained VOCs concentrations have been compared spatially and seasonally in order to pinpoint portal areas and seasons where VOC pollution was higher.

#### 5.1. VOCs concentrations results in the four case study harbours

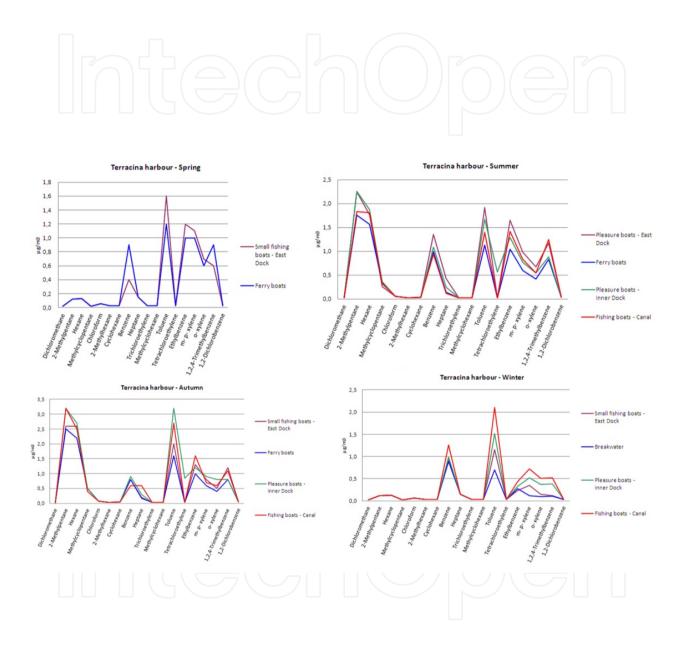
The following graphics summarize the results obtained in each port, considering the seasons and the intended uses zones.



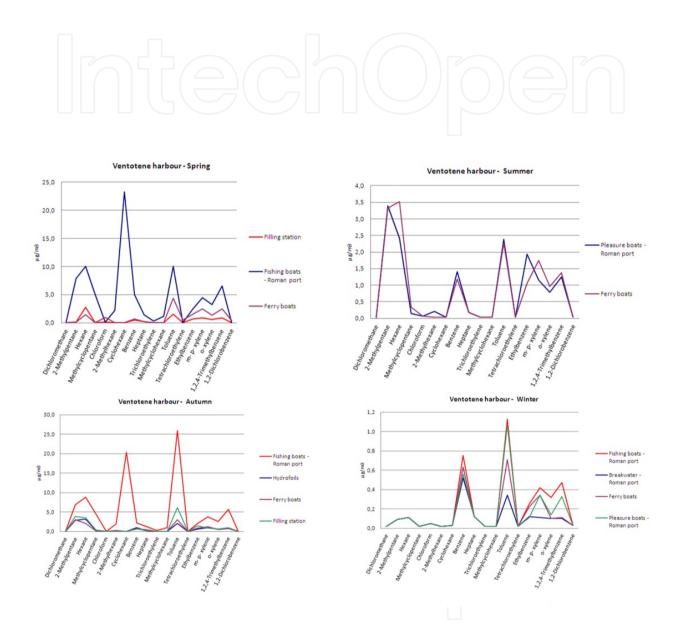
**Figure 3.** VOCs concentrations in atmosphere in the different seasons and intended use areas of the harbour of Anzio in 2010



**Figure 4.** VOCs concentrations in atmosphere in the different seasons and intended use areas of the harbour of Formia in 2010



**Figure 5.** VOCs concentrations in atmosphere in the different seasons and intended use areas of the harbour of Terracina in 2010



**Figure 6.** VOCs concentrations in atmosphere in the different seasons and intended use areas of the harbour of Ventotene in 2010

The sums of all the 18 VOCs concentrations recorded during each data gathering were compared, in order to rank in each port the intended use areas and the seasons according with their VOCs pollution (Tables 2 and 3). In order to have a reference value to define the "minimum" VOCs pollution of each port, a Radiello was placed in the most area distant from every sources of pollutant emissions (end of the breakwater) during the season with lower portal activity (winter). Unfortunately, it was no possible to obtain this value in the harbour of Formia because the Radiello in the breakwater has not been found at the end of the ten sampling days.

Anzio Harbour		Fo
Season and intended use area	Total VOCs concentratio ns μ g/m3	Se
Summer - Pleasure Boats	21,18	Su
Summer - Fishing Boats	20	Au
Summer - Ferry boats	15,6	Su
Autumn - Small Fishing Boats	15,41	Su
Spring - Fishing Boats	13,85	Au
Autumn - Fishing Boats	12,12	Sp
Autumn - Ferry boats	11,88	Sp
Summer - Small Fishing Boats	11,34	Sp
Spring - Small Fishing Boats	10,32	Sp
Spring - Pleasure Boats	8,37	A
Winter - Small Fishing Boats	7,74	Au
Winter - Ferry boats	6,44	Wi
Winter - Fishing Boats	6,04	Wi
Winter - Breakwater	5,41	Wi

Formia Harbour	
Season and intended use area	Total VOCs concentratio ns μ g/m3
Summer - Fishing boats	32,21
Autumn - Ferry boats	27,45
Summer - Pleasure boats	26,12
Summer - Ferry boats	17,67
Autumn - Pleasure boats	15,62
Spring - Ferry boats	13,18
Spring - Fishing boats	12,32
Spring - Pleasure boats	12,23
Spring - Hydrofoils	11,52
Autumn - Merchant ships	11,25
Autumn - Fishing boats	11,13
Winter - Fishing boats	5,3
Winter - Pleasure boats	5,23
Winter - Ferry boats	5,04

**Table 2.** Total VOCs concentrations in atmosphere in the different seasons and intended use areas of the harbours of Anzio and Formia

Terracina Harbour		Ventotene Harbour	
Season and intended use area	Total VOCs concentratio ns μ g/m <sup>3</sup>	Season and intended use area	Total VOCs Concentrati on μ g/m <sup>3</sup>
Autumn – Pleasure boats – Inner Dock	15,6	Autumn – Fishing boats – Roman port	86,93
Autumn – Fishing boats – Canal	14,29	Spring – Fishing boats – Roman port	83,06
Autumn – Small fishing boats – East Dock	12,76	Autumn – Filling station	19,02
Summer – Pleasure boats – East Dock	12,64	Spring – Ferry boats	16,65
Summer – Pleasure boats – Inner Dock	11,72	Summer – Ferry boats	16,24
Autumn – Ferry boats	10,89	Summer – Pleasure boats – Roman port	15,49
Summer – Fishing boats – Canal	10,65	Autumn – Hydrofoils	12,65
Summer – Ferry boats	9,02	Autumn – Ferry boats	12,63
Spring – Small fishing boats – East Dock	6,28	Spring – Filling station	8,52
Spring – Ferry boats	6,28	Winter – Fishing boats – Roman port	3,89
Winter – Fishing boats – Canal	6,23	Winter – Pleasure boats – Roman port	3,1
Winter – Pleasure boats – Inner Dock	4,78	Winter – Ferry boats	2,66
Winter – Small fishing boats – East Dock	3,63	Winter – Breakwater – Roman port	1,84
Winter – Breakwater	2,88		

**Table 3.** Total VOCs concentrations in atmosphere in the different seasons and intended use areas of the harbours of Terracina and Ventotene

#### 5.2. AQIvoc indices in the four case study harbours

The AQIvoc index equation has been used for the elaboration of four air quality matrices that provide an overview of the air quality level within each one of the four portal areas. This approach allows to highlight those portal activities that have a major impact on air quality, and will be preparatory for the choose of which BAT or best practices is better to use for the mitigation of air pollution in each particular harbour.

In order to facilitate the reading of the comparison of the results, the AQIvoc values have been subdivided into three categories: low VOCs pollution, values under the twenty-fifth percentile (green boxes); average VOCs pollution, values between the twenty-fifth and the

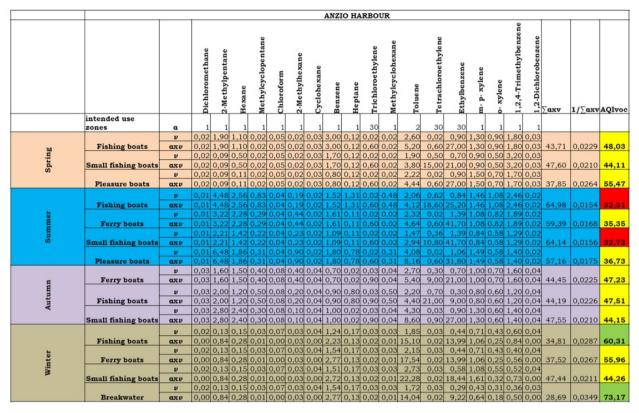


Figure 7. Air quality matrix for the evaluation of the AQIvoc values in Anzio harbour

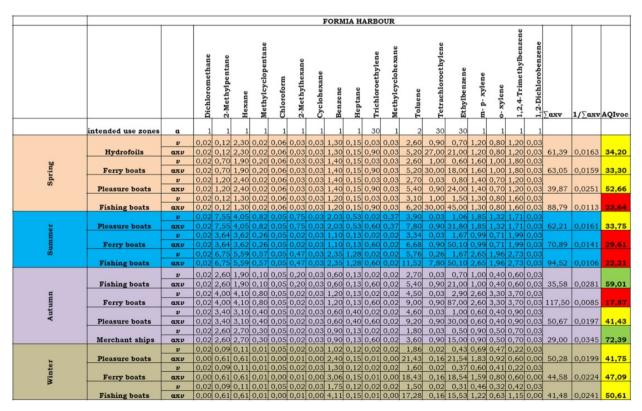


Figure 8. Air quality matrix for the evaluation of the AQIvoc values in Formia harbour

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	TERRACINA HARBOUR																						
			Dichlorom et hane	2-Methylpentane	Hexane	Methylcyclopentane	Chloroform	2-Methylhexane	Cyclohexane	Benzene	Heptane	Trichloroethylene	Methylcyclohexane	Toluene	Tetrach loro eth ylene	Ethylbenzene	m- p- xylene		1,2,4-Trimethylbenzene	1,2-Dichlorobenzene	∑axv	1/∑axv	AQIvoc
	intended use zones	a	1	1	1	1	1	1	1	1	1	30	1	2	30	30	1	1	1	1			
20	Small fishing boats -	v	0,02		0,13		0,06						0,03		0,03				0,60		11.10	0.0005	47.06
Spring	East Dock	axv v	0,02		0,13		0,06					0,90		3,20	0,90				0,60		44,42	0,0225	47,26
so.	Ferry boats	axv	0,02				0,06					0,03				30.00					38,22	0,0262	54,93
	Pleasure boats -	v	0,02	2,26	1,87	0,36	0,05	0,02	0,03	1,09	0,24	0,02	0,02	1,67	0,56	1,29	0,77	0,54	0,88	0,03			
	Inner Dock	ax <i>v</i>	0,02		1,87		0,05		0,03			0,60		3,34	16,80				0,88		67,62	0,0148	31,05
Summer	Ferry boats	<i>v</i> ax <i>v</i>	0,02				0,05					0,60	<i>.</i>	1,13	0,60		0,60		0,83	0,03	41,47	0,0241	50,62
Sum	Fishing boats -	v	0,02				0,05			-		0,02		1,39	0,02		0,83		1,25	0,03	54.00		
	Canal	axv v	0,02		1,81		0,05	-	0,03			0,60		2,78	0,60		0,85		1,25		54,09	0,0185	38,81
	Pleasure boats - East Dock	axv	0,02		1,77		0,05		0,03			0,60		3,82	0,60					0,03	63,56	0,0157	33,03
	Pleasure boats -	v	0,02				0,07			0,90		0,03		3,20	0,84				0,80				
	Inner Dock	axv v	0,02	_			0,07	_				0,90		1,60	0.03	36,00			0,80		78,83	0,0127	26,63
l ii	Ferry boats	axv	0,02	_			0,07					0,90		3,20		30,00					43,23	0,0231	48,56
Autumn	Small fishing boats -	v	0,02				0,07			_		0,03		2,00	0,03			_	1,20	_			
	East Dock	axv	0,02				0,07					0,90		4,00	0,90						54,20	0,0185	38,73
	Fishing boats - Canal	v axv	0,02	3,20			0,07					0,03	0,03	2,70	0,03	1,60		0,60			65,13	0,0154	32.23
	Canar	v	0,02	0,1	0.13	0,40	1 march	0,00	0,04		0.2		0,00	0.7	0.03	Surger and	1.000	1.1.1.1		0,04	55,15	0,0104	
	Breakwater	axv	0,00				0,00	0,00				0,02	0,00	1,58	0,03		0,07	-		0,00	11,89	0,0841	100,00
	Small Gabing boots	v	0	0,1	0,13	0	0,1	0	0,03	1	0,2	0	0	1,15	0,03	0,23	0,4	0,2	0,1	0			
Winter	Small fishing boats - East Dock	axv	0,00	0,21	0,20	0,01	0,00	0,00	0,00	0,94	0,02	0,02	0,00	2,60	0,02	7,18	0,21	0,06	0,10	0,00	11,57	0,0864	100,00
IM	Pleasure boats -	v	0	0,1	0,13	0	0,1	0	0,03	1	0,2	0	0	1,52	0,03	0,33	0,5	0,4	0,4	0			
	Inner Dock	ax v	0,00		0,20	0,01	0,00	0,00	0,00	0,97		0,02	0,00	3,44	0,02			0,16		0,00	15,97	0,0626	100,00
	Fishing boats -	v	0		0,13	0	- / -	0	0,03		0,2	-	<u> </u>	2,11	0,03					0			
	Canal	axv	0,00	0,21	0,20	0,01	0,00	0,00	0,00	1,25	0,02	0,02	0,00	4,77	0,02	13,42	0,43	0,21	0,43	0,00	20,99	0,0476	100,00

Figure 9. Air quality matrix for the evaluation of the AQIvoc values in Terracina harbour

		VENTOTENE HARBOUR																					
			Dichloromethane	2-Methylpentane	Hexane	Methylcyclopentane	Chloroform	2-Methylhexane	Cyclohexane	Benzene	Heptane	Trichloroethylene	Methylcyclohexane	Toluene	Tetrachloroethylene	Ethylbenzene	n- p- xylene	- xylene	1,2,4-Trimethylbenzene	,2-Dichlorobenzene	∑axv	1/\\[ axv	4.01-10-
	intended use zones	α	1	1	1	1	1	1	1	1	1	30	1	2	30	30	1	1	1	1	2		
	Ferry boats	v axv	0,02									0,03				1,50					79,92	0.0125	26.27
Spring	Filling station	v axv	0,02	0,13	2,80	0,03	0,07	0,03	0,04	0,50	0,17	0,03	0,03	1,50	0,03	0,70	0,90	0,60	0,90	0,04	32,06	0,0312	
ŝ	Fishing boats - Roman port	v axv			10,00	5,00	0,07	2,20	23,30 23,30	5,00	1,40	0,30	1,10	10,00	0,03	2,50	4,50	3,20	6,50	0,04		0,0057	
mer	Pleasure boats - Roman port	v axv	0,02	3,39 3,39		0,14			0,04	1,41	0,17		0,03	2,39 4,78	0,03	1,93 57,90					75,59	0,0132	27,77
Sum	Ferry boats	υ αχυ		3,33 3,33										2,28 4,56	0,03						50,71	0,0197	41,40
	Ferry boats	<i>v</i> ax <i>v</i>	0,02		2,10	0,10	0,05	0,20	0,03	0,70	0,13	0,02 0,60	0,02	6,00	0,90		1,20	0,50	0,70	0,03		0,0248	52,12
Autumn	Hydrofoils	v axv	0,02	2,90 2,90	3,10	0,30	0,05	0,02	0,03	1,00	0,13		0,02	4,00			1,00	0,60	0,80	0,03	33,50	0,0299	62,67
Aut	Filling station	υ αχυ	0,02		3,50	0,40	0,05	0,02	0,03	0,60	0,50	0,60	0,02	12,20	0,90		0,90	0,60	1,00	0,03	67,17	0,0149	31,26
	Fishing boats - Roman port	v axv		6,90 6,90					20,35 20,35					25,95 51,90							179,00	0,0056	11,73
	Fishing boats - Roman port	υ αχυ	0,00	0,1	0,11	0,00	0,1	0,00		0,8		0,02	0,00	1,13	0,02	0,25 14,48				0,00	22,89	0,0437	91,70
Winter	Breakwater - Roman port	<i>v</i> ax <i>v</i>	0,00	0,1 0,31	0,11	0	0,1	0	0,03	0,5	0,1	0,02	0	0,34	0,02	0,12	0,1	0,1	0,1	0		0,0973	
	Ferry boats	U QXV	0	0,1	0,11	0,00		0,00	0,03	0,6		0,02	0,00	0,71	0,02	0,22				0,00	18,27	0,0547	100,00
	Pleasure boats - Roman port	v axv	0.00	0,1	0,11	0	0,1	0	0,03	0,6	0,1	0	0	1,07	0,02	0,11	0,3		0,3	0		0,0723	100.00

Figure 10. Air quality matrix for the evaluation of the AQIvoc values in Ventotene harbour

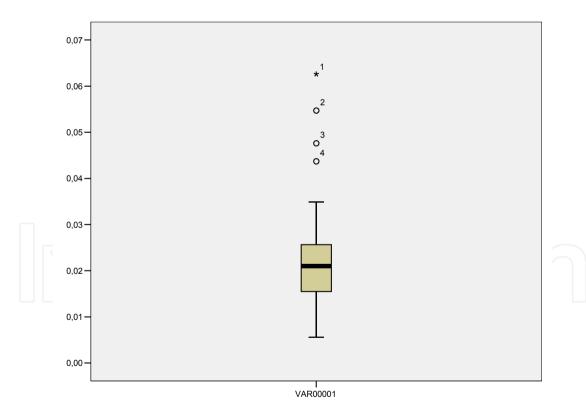
seventy-fifthpercentile (yellow boxes) and high VOCs pollution, values over the seventy-fifth percentile (red boxes).

Before that, the statistical distribution of the data has been considered, highlighting unusual observations (outliers and extreme values) by means of boxplot analysis.

In particular, the box-plot method analyzes the distribution of data considering the median, the interval between interquartiles, the outliers values and the extreme values of individual variables. The length of the box was considered as the range of values between interquartiles, or rather between the twenty-fifth and seventy-fifth percentile. Consequently, the outliers values are those that are at a distance between 1.5 and 3 boxes from the top or the bottom edge of the box, between the twenty-fifth and seventy-fifth percentile; at the same way, the extreme values are distant more than 3 boxes from the top or bottom edge of the box. The purpose of the method is therefore to identify these values in order to get a distribution composed by values statistically attributable to the same population.

The box-plot application proceeds step by step in order to be able to select all the extreme and outliers values up to a statistically homogeneous distribution of the population.

In this way, the 4 unusual values have been pinpointed and removed assigning to them the maximum IQAcov value of one hundred (Figure 11).



**Figure 11.** Boxplot statistical methods: 1 outliers (star) and 3 extreme values detection trough SPSS software

It was therefore possible to elaborate the 100 standardization of the IQAcov value, considering a statistically homogeneous distribution (Table 4).

	Va	ılid	Mis	sing	Total					
	Ν	Percent	Ν	Percent	Ν	Percent				
VAR00001	51	92,7%	4	7,3%	55	100,0%				

**Table 4.** Statistical data analysis of the 55 IQAvoc indices of the four case study ports

Moreover, the results have been registered in a GIS (Geographic Information System) database that contains a comparative spatial analysis of IQAvoc values in order to produce thematic maps able to pinpoint areas where the VOCs pollution was higher (some examples of these maps will be reported in the following maps).

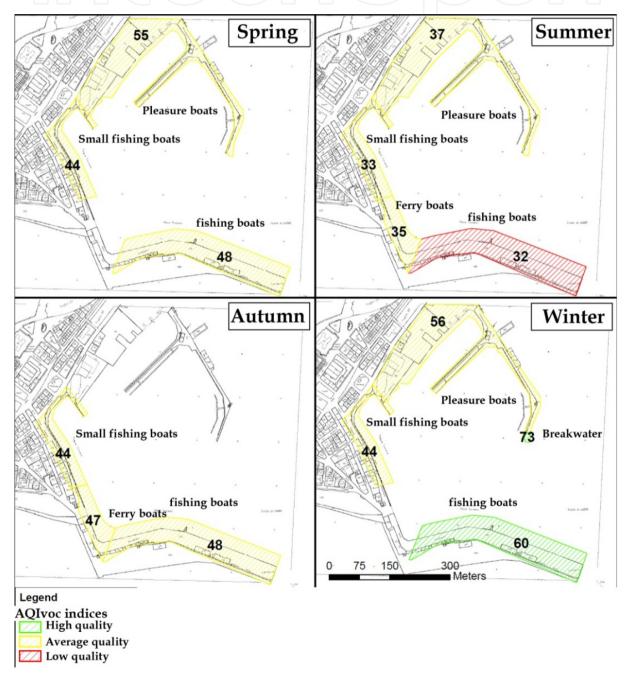
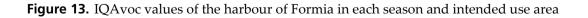
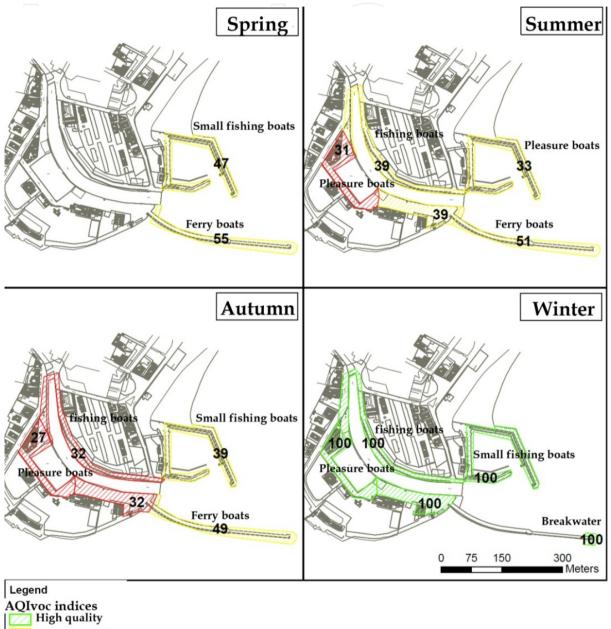


Figure 12. IQAvoc values of the harbour of Anzio in each season and intended use area







ZZZ Average quality ZZZ Low quality



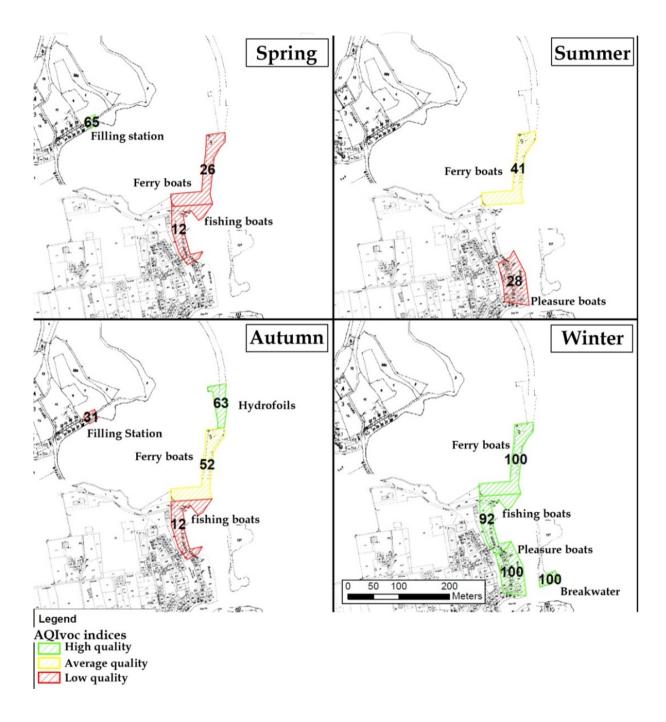


Figure 15. IQAvoc values of the harbour of Ventotene in each season and intended use area

## 6. Best practices for air quality improvement in portal areas

Aim of this paragraph is to illustrate some BAT (Best Available Technologies) and best practices for mitigating VOCs concentrations and improving local air quality in those portal areas characterized by high concentrations of pollutants.

The obtained results show that the main sources of pollutant emissions in the four analyzed harbours are the Internal Combustion Engines (ICE) of Ro/Pax ferries and hydrofoils, pleasure boats, fishing boats as well as cars and trucks circulating in the ports.

Excluding fishing boats, these sources of emission are all highly dependent on tourism activities which involve an increase of vehicular traffic in the port areas, an enhanced number of daily trips of ferries and hydrofoils and, last but not least, a heavy pleasure boats traffic.

Nowadays, the best practices and technologies for mitigating air pollution in portal areas are:

- SSE (Shore-Side Electricity) enables ships at port to use electricity from a local power grid through a substation at the port to power loading and unloading activities, electronic systems, fuel systems, discontinuing the use of their auxiliary engines. The emission reduction efficiency of this solution is about 94% for VOCs (De Jonge et al., 2005).
- DWI (Direct Water Injection) is a technology which consists in introducing into the cylinder a mixture of water and pressurized fuel which allows lower consumption and emissions (Wahlström at al., 2006).
- Use of low emission fuels: in particolar seaweeds hold a huge potential as a biofuel. Briefly, biofuels are used for fighting climate changes because the same amount of CO<sub>2</sub> that is released from combusting biofuels has previously been taken up from the atmosphere as the plant grows, thus not leading to any net increase in the concentration of CO<sub>2</sub> in the atmosphere (Opdal & Johannes, 2007).
- Optimization of combustion processes in ship engines by means of particolar devices able to optimize combustion disaggregating hydrocarbons (gas emission reduction up to 75-80%).

## 7. Conclusion

The use of the IQAcov index and the implementation of the best practices and technologies described in the last paragraph could be considered useful tools for monitoring and improving air quality in portal areas for stakeholders and decision makers such as port/maritime authorities, licensed port company operators and local and governmental authorities involved in port jurisdiction.

Indeed, as recommended by the European Sea Port Organisation (ESPO, 2003), among the main environmental objectives which the EU port sector should aim to achieve there is the increase of environmental awareness, the implementation of environmental monitoring and the use of best practices and technologies on environmental issues.

These targets, together with the promotion of environmental monitoring in ports, are fully included among the ESPO top ten environmental objectives that the European port sector should pursue.

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