D3.1.1 Report of trend survey of nutrients and other chemical parameters

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PROJECT AdSWiM

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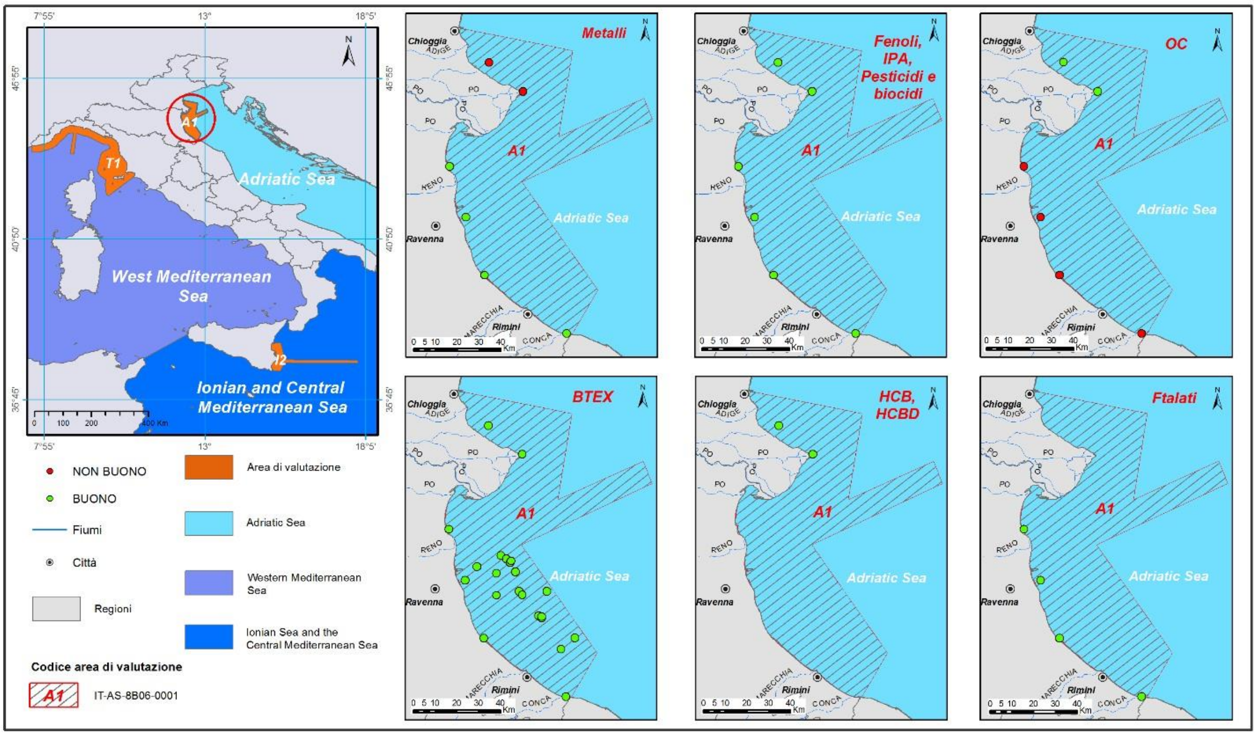
1. Introduction and literature data analysis

European Union legislation (Directive 2008/105/EC, Directive 2013/39/UE, DLgs 219/2010, DLgs 172/2015) provides for measures against chemical pollution of surface waters. There are two components – the selection and regulation of substances of European Union (EU)-wide concern (the priority substances) and the selection by Member States of substances of national or local concern (river basin specific pollutants) for control at the relevant level.
The first component constitutes the major part of the Union's strategy against the chemical pollution of surface waters. It is set out in Article 16 of the Water Framework Directive 2000/60/EC. This requires the establishment of a list of priority substances, these to be selected from amongst those presenting a significant risk to or via the aquatic environment at EU level. It also requires the designation of a subset of priority hazardous substances, and proposals for controls to reduce the emissions, discharges and losses of all the substances and to phase out the emissions, discharges and losses of the subset of priority hazardous substances.
Member States are required to take actions to meet the quality standards in the EQSD by 2015 as part of chemical status (Water Framework Directive Article 4 and Annex V point 1.4.3). For this purpose a programme of measures (according to Water Framework Directive Article 11) has to become operational by 2012.
In this context bathing water (BW) quality is of a major concern in EU policy. In fact, BW is not only essential for public health reasons. Clean unpolluted water is necessary to improve ecosystem resilience. Both can be achieved with more integrated and sustainable water resource management. This would require more robust implementation of the Water Framework Directive (EU, 2000), with River Basin Management Plans developed to improve the poorer quality bathing waters. This would serve to maintain the trend towards consistently high-quality EU bathing waters beyond 2020.
During the bathing season, samples from coastal and inland bathing waters are taken and analysed against two microbiological parameters that may indicate the presence of faecal pollution, namely intestinal enterococci and Escherichia coli (also known as E. coli). After the end of the bathing season, and based on 4 years of data, bathing waters are classified into one of the bathing water quality classes (excellent, good, sufficient or poor). Some bathing waters have not been classified because there were insufficient samples or because they are new or have undergone changes affecting water quality. Anyway a check of heavy metals pollution could represent an additional but very important indicator for the BW quality and for our seas in general as requested by Marine Strategy Directive. Anyway scarce information about metals pollution in Adriatic Sea are founded

in literature and in EU, Local and Regional reports, even if the Water Framework Directive 2000/60/EC established provision for a list of Priority Substances (Annex X of the Directive). Decision 2455/2001/EC established the First list, and Directive 2008/105/EC (the Environmental Quality Standards Directive – EQSD) set the quality standards as required by Article 16(8) of the Water Framework Directive. Annex II to the EQSD replaced Annex X of the Water Framework Directive.

Among these cadmium, lead and mercury are listed as Priority Substance to monitor in water column. The figure below provided by ISRPA report on Marine Strategy (https://annuario.isprambiente.it/ada/downreport/pdf/6436) shows metal survey in Adriatic Sea, available just for 0.04% of valuation area (VA).



Area di valutazione A1= 16340 celle totali									
	Metalli	Fenoli	IPA	Pesticidi e biocidi	OC	BTEX	HCB	HCBD	Ftalati
% di celle buono	57	100	100	100	43	100	100	100	100
% di copertura dell'area di valutazione	0,04	0,04	0,04	0,04	0,04	0,14	0,02	0,02	0,02

A table with data collected by literature data in this first period of AdSWiM project is provided below. Specific requests are forwarded by PP4 to Local and Regional authorities to collect data not published on pollutants in Adriatic Sea.

Table 1. Data collection on heavy metals (Cd, Pb, Cu) of scientific paper concerning Adriatic Sea.

Site	Dissolved and (total) concentrations (nmol L^{-1})			Reference
	Cd	Pb	Cu	
Po plume 2002	0.12 ± 0.04 (0.14 ± 0.05)	0.33 ± 0.21 (0.52 ± 0.35)	5.3 ± 2.5 (7.1 ± 4.6)	(Illuminati et al., 2019)
Northern Adriatic Sea, 1994	0.083		7.14	(Tankere and Statham, 1996)
Northern Adriatic Sea, 1996			5.4 ± 2.5	(Zago et al., 2002)
Northern Adriatic Sea, 1997			6.4 ± 2.8	(Zago et al., 2002)
Central Adriatic Sea, 2000–2004	0.14 ± 0.06	0.24 ± 0.14	7.1 ± 3.6	(Annibaldi et al., 2009)
Southern Adriatic Sea, 1994	0.076		2.95	(Tankere and Statham, 1996)

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Being a semi-enclosed sea with limited water circulation, the Adriatic is extremely vulnerable to pollution events. Particularly, coastal pollution from excessive nutrient inflow, typically from agricultural and municipal runoff has been one of the main factors affecting the Adriatic waters and coastal areas, leading in many cases to fish kills, algal blooms and low-oxygen conditions, particularly in the northern region of the sea. For these reasons many studies are carried out in Adriatic Sea to check the nutrients levels and inputs, even if no studies consider the depuration plants effect.
A table with data collected by literature data in this first period of AdSWiM project is provided below.

Table 2. Data collection on nutrients from scientific paper concerning Adriatic Sea.

Site (year)	Phosphorous		Nitrogen					Silicon/ Carbon	Reference
Coastline of Pesaro (2000)	Tot-P 0 – 30 (μg/l)			N-NO_3 0 – 600 (μg/l)	N-NH_3 0 – 50 (μg/l)				Penna et al., 2004
Sutern Adriatic Surface water (2007-2008)									
2007	TDP 0.08 ± 0.02 (μM)	SRP 0.03 ± 0.02 (μM)	TDN 4.7 ± 0.8 (μM)	DIN 0.17 ± 0.3 (μM)	DON 4.6 ± 0.9 (μM)			DOC 70 ± 7 (μM)	Santinelli et al., 2012
2008	TDP 0.12 ± 0.04 (μM)	SRP 0.08 ± 0.04 (μM)	TDN 6.2 ± 1.5 (μM)	DIN 2.0 ± 1.2 (μM)	DON 4.1 ± 1.0 (μM)			DOC 53 ± 3 (μM)	Santinelli et al., 2012
Gulf of Trieste (2006-2007)	P-PO_4 0.01 – 0.12 (μM)							Si-$Si(OH)_4$ 0.29 – 5.93 (μM)	Cibic et al., 2018 (1)
Gulf of Trieste (2006-2007)	P-PO_4 0 – 0.12 (μM)		N-NO_2 0 – 0.93 (μM)	N-NO_3 0 – 8.75 (μM)	N-NH_4 <0.53 – 3.41 (μM)			Si-$Si(OH)_4$ 0 – 6.80 (μM)	Cibic et al., 2018 (2)
North Adriatic (1972-1975)									
Western side	TP 0.27W (m mol/m3)	PO_4 0.06 (m mol/m3)	NO_2 0.20 (m mol/m3)	NO_3 1.08 (m mol/m3)	NH_4 0.75 (m mol/m3)	TIN 2.08 (m mol/m3)	DON 3.33 (m mol/m3)	$Si(OH)_4$ 3.22 (m mol/m3)	Degobbis et al., 1990
Eastern side	TP 0.13 (m mol/m3)	PO_4 0.02 (m mol/m3)	NO_2 0.13 (m mol/m3)	NO_3 0.41 (m mol/m3)	NH_4 0.58 (m mol/m3)	TIN 1.08 (m mol/m3)	DON 2.86 (m mol/m3)	$Si(OH)_4$ 1.83 (m mol/m3)	Degobbis et al., 1990
Central Adriatic (1990-1992)	P-PO_4 0.02 – 0.10 (μM)		N-DIN 0.7 – 9.6 (μM)	N-NO_3 0.3 – 12.3 (μM)				Si-SiO_2 0.9 – 5.5 (μM)	Zoppini et al., 1995
North Adriatic (1991)	PO_4 0.10 ± 0.19 (μM)		NO_2 0.19 ± 0.21 (μM)	NO_3 1.56 ± 1.91 (μM)	NH_3 2.07 ± 1.35 (μM)	TIN 3.87 ± 2.83 (μM)			Kaltenböck et al., 1992
Jabuka Pit (1993-1994)									

1993	PO_4 0.090 – 0.147 (µmol/kg)		NO_3 2.44 – 3.92 (µmol/kg)			SiO_4 3.45 – 4.84 (µmol/kg)	Krasakopoulou et al., 2005
1994	PO_4 0.216 – 0.481 (µmol/kg)		NO_3 5.8 – 6.64 (µmol/kg)			SiO_4 7.09 – 9.89 (µmol/kg)	Krasakopoulou et al., 2005
Adriatic sea historical data							
Shallow Northern Adriatic	PO_4 0.05 – 0.12 (µM)		NO_3 0.58 – 3.18 (µM)			SiO_4 0.51 – 5.63 (µM)	Zavatarelli et al., 1998
Deep Northern Adriatic	PO_4 0.02 – 0.07 (µM)		NO_3 0.40 – 1.25 (µM)			SiO_4 1.34 – 2.52 (µM)	Zavatarelli et al., 1998
Middel Adriatic	PO_4 0.06 – 0.07 (µM)		NO_3 0.63 – 0.84 (µM)			SiO_4 4.03 – 4.76 (µM)	Zavatarelli et al., 1998
Southern Adiatic	PO_4 0.04 – 0.06 (µM)		NO_3 0.77 – 1.21 (µM)			SiO_4 2.06 – 3.52 (µM)	Zavatarelli et al., 1998
Gulf of Trieste (1992-1993)	PO_4 <0.1 - ~1 (µM)		NO_3 <5 - ~25 (µM)	NH_3 ~1 - ~5 (µM)		SiO_2 <5 - ~25 (µM)	Reisenhofer et al., 1996
Mljet Island, Croatia (1997-1999)							
1997	PO_4 0.01 – 0.15 (µmol/dm3)	NO_2 0.01 – 0.33 (µmol/dm3)	NO_3 0.1 – 3.42 (µmol/dm3)	NH_4 0.07 – 0.33 (µmol/dm3)	Ntot 2.19 – 7.82 (µmol/dm3)	SiO_4 0.61 – 37.99 (µmol/dm3)	Benovic et al., 2000
1998	PO_4 0 – 0.26 (µmol/dm3)	NO_2 0.01 – 0.62 (µmol/dm3)	NO_3 0.01 – 4.54 (µmol/dm3)	NH_4 0.21 – 1.2 (µmol/dm3)	Ntot 0.68 – 32.13 (µmol/dm3)	SiO_4 0.54 – 28.71 (µmol/dm3)	Benovic et al., 2000
Northern Adriatic (1993-1994)	PO_4 0.12 – 0.21 (µM)		NO_3 1.03 – 3.33 (µM)	NH_4 0.46 – 1.02 (µM)		SiO_2 0.72 – 4.23 (µM)	Granéli et al., 1999
Ancona, central Adriatic (2009-2010)							
2009	PO_4 <5 - ~20 (µM)	DIN <5 - ~20 (µM)					Accoroni et al., 2012
2010	PO_4 ~5 - >30 (µM)	DIN ~5 - >30 (µM)					Accoroni et al., 2012

Since the lack of information about heavy metals and about the depuration plant effect on nutrientslevel in Adriatic Sea the AdSWiM aims are of paramount importance for the environment and thescientific knowledge about these aspects

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