Supplementary Material

1 PHYSICAL SURFACE CONDITIONS AND CHANGES UNDER RCP4.5

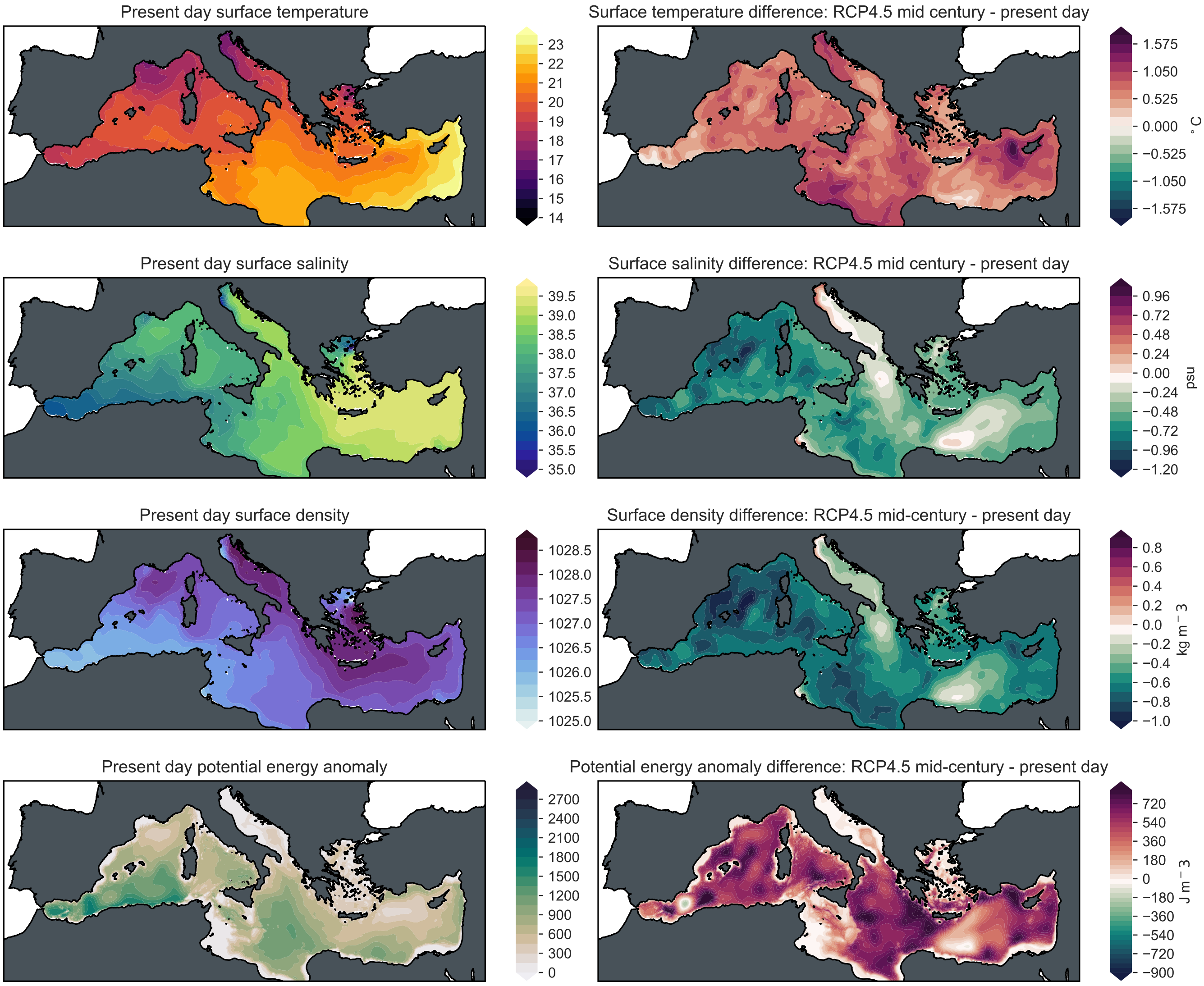

Figure S1. Present day conditions (2016-2020, left) and changes until mid-century (2046-2050, right) of surface temperature (top), salinity (upper centre), density (lower centre) and potential energy anomaly (bottom) under RCP4.5.

2 ADDITIONAL CARBONATE SYSTEM VARIABLES - CONDITIONS AND CHANGES UNDER RCP4.5

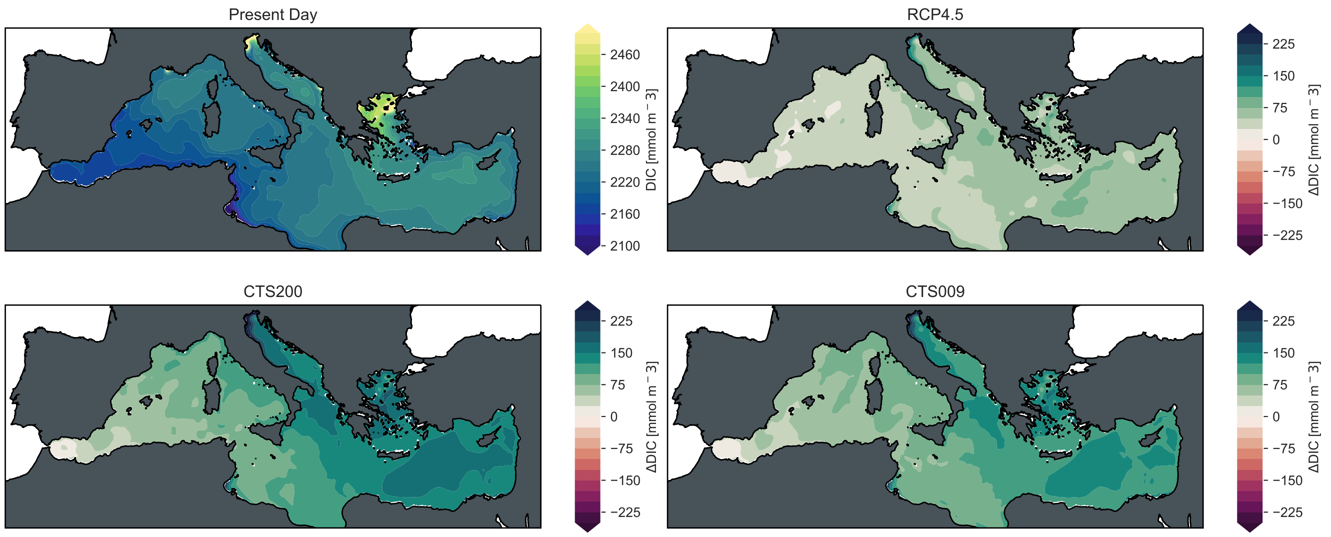

Figure S2. Present day conditions (2016-2020, top-left) and changes until mid-century (2046-2050) of surface dissolved inorganic carbon under RCP4.5 (top-right), CTS200 (bottom-left) and CTS009 (bottom-right).

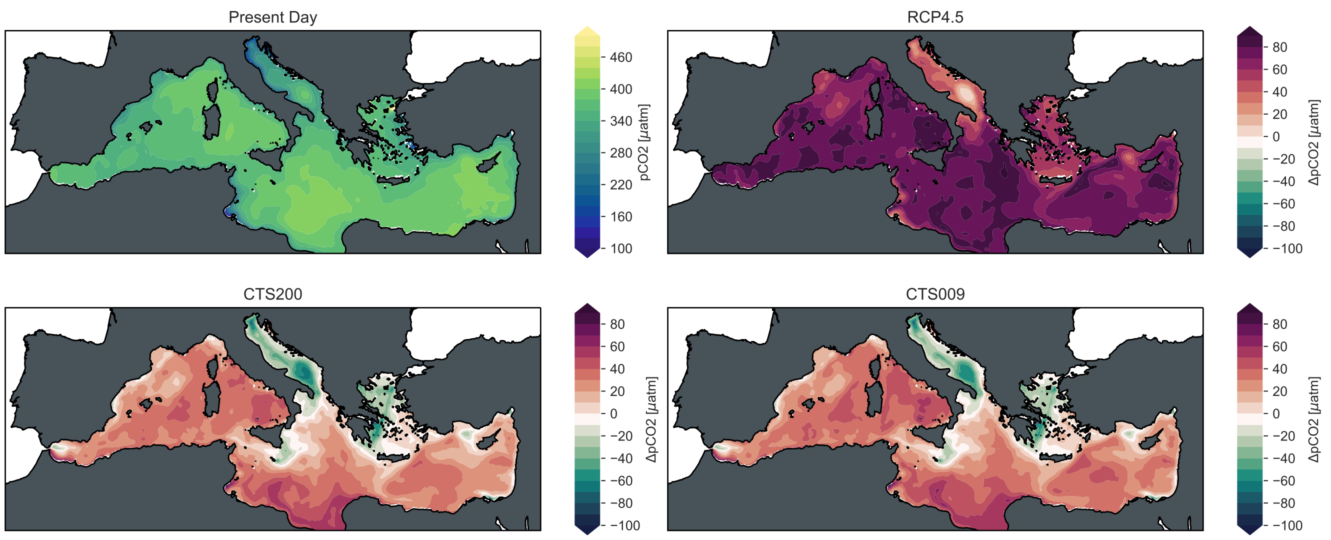

Figure S3. Present day conditions (2016-2020, top-left) and changes until mid-century (2046-2050) of surface partial pressure of CO_2 in seawater under RCP4.5 (top-right), CTS200 (bottom-left) and CTS009 (bottom-right).

3 REFERENCE CONDITIONS OF PHYSICAL STATE AND CARBONATE SYSTEM OF THE MEDITERRANEAN

Figure S4 shows surface mean fields of temperature, salinity, dissovled inorganic carbon and alkalinity at present day for comparison with the fields from the model simulations of this study depicted in figure 6 in the main article and figures S1 and S2 in these supplments. It is not our intention here to provide an in-depth model skill assessment, which is not the scope of this work, but rather to illustrate that the large scale patterns in the model simulations give a feasible representation of the actual dynamics at present in the Mediterranean Sea.

The reference conditions of surface temperature and salinity fields in this figure are obtained from the last release of the reanalysis product for the Mediterranean Sea within the Copernicus Marine Environment Monitoring service (Escudier et al., 2020), that combines an extensive set of temperature, salinity and altimetry observation with a numerical ocean model into a coherent representation of the Meditterranen Sea dynamics. Comparisons show that the modelling system in this study reproduces the large scale structures of the Meditterranena Sea dynamics well without any substantial biases reflecting the eastward increase of temperature and salinity, the comparatively colder margins around the Gulf of Lions and the Northern Adriatic Sea and the main freash water inputs through the Strait of Gibraltar and the Dardanelles.

For the carbonate system variables the availability of synoptic fields of the Mediterranean Sea based on observations is very limited, mainly due to the scarcity of conprehensive measurement data. We have chosen here to extract the fields covering the Mediterranean Sea from the OceanSODA-ETHZ dataset of global ocean surface carbonate system (Gregor and Gruber, 2020), a promising approach to reconstruct constistent surface maps from the spatially disjoint and temporally discontinuous observational data available using a cluster ensemble regression method, unfortunately still at a relatively coarse spatial resolution of 1 degree. Given these limitations the comparison of the surface fields of dissolved inorganic carbon and alkalinity show coherent patterns across the Western and Eastern basin of the Mediterranean Sea with lower levels in both variables in the Western part, particularly in the Alboran Sea, and higher values in the Levantine, with possibly a slight positive bias in the model simulations for both variables. The spatial resolution in the OceanSODA-ETHZ dataset doesn't allow for any meaningful comparsion in the highly dynamic enviroments of the Adriatic and the Aegean Sea, where the comparatively high values of the model simulations are a direct consequence of the riverine forcing data described in the section 5 of these supplements.

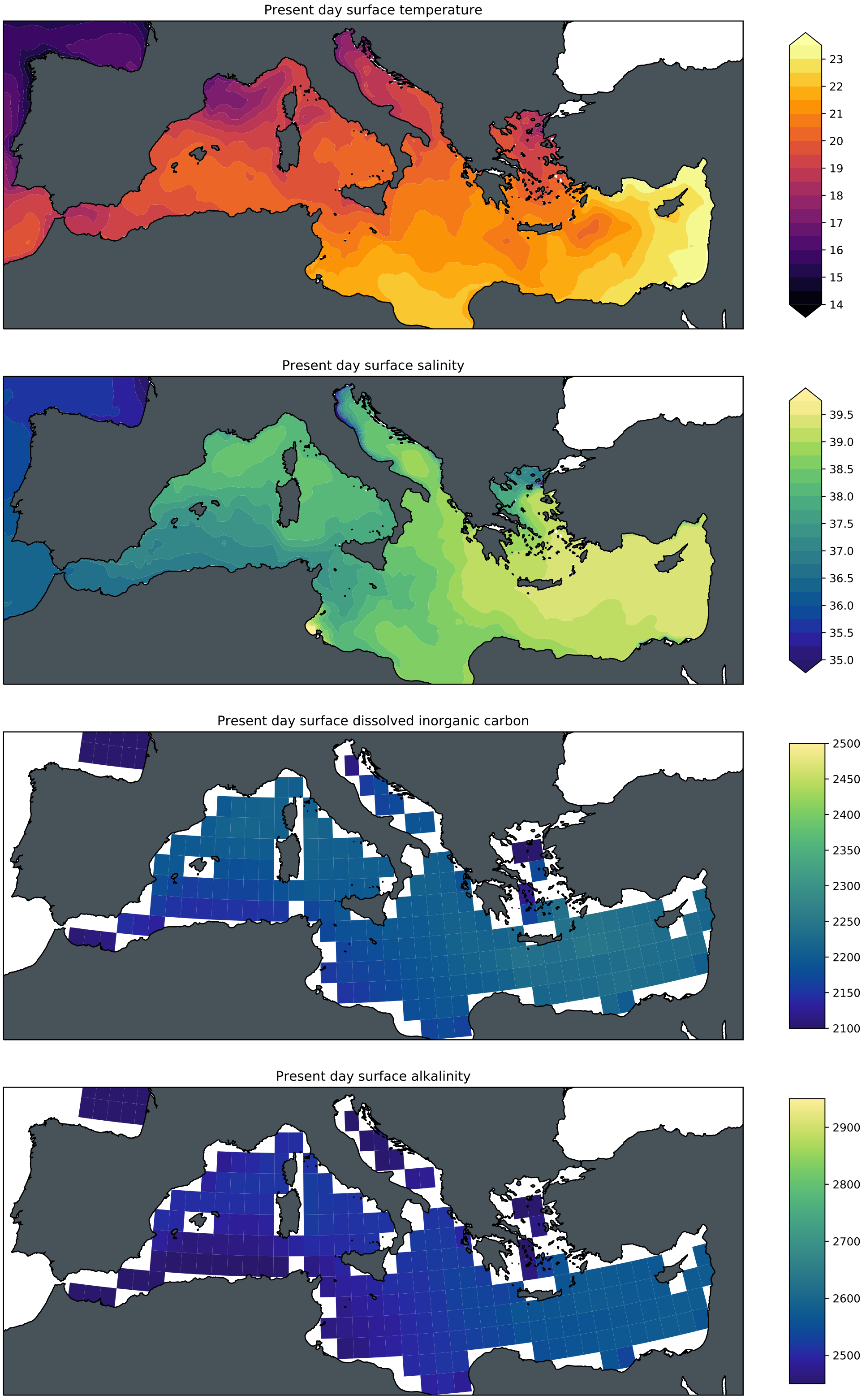

Figure S4. Present day mean surface conditions of temperature (top), salinity (upper centre), dissolved inorganic carbon (lower centre) and alkalinity (bottom). Temperature and salinity fields (2016-2018) are obtained from the latest reanalysis of the Mediterranean Sea within the Copernicus Marine Environment Monitoring Service (Escudier et al., 2020), dissolved inorganic carbon and alkalinity (2016-2019) are extracted from the OceanSODA-ETHZ dataset (Gregor and Gruber, 2020).

4 PERTURBATION EXPERIMENTS OF PH RESPONSE TO ALKALINISATION

A series of alkalinisation experiments was performed using a 1D water column model using the same NEMO-BFM modelling system applied in the full scale experiments. The idealised model set-up was run under perpetual climatological forcing, calibrated and spun-up to conditions representative of a stable location in the Eastern Mediterranea in order to approximately reflect conditions present in the full scale experiments. The system was then perturbed with surface alkalinisation fluxes ranging from 0 to 20 mmol m-2 d-1 (corresponding to 0 to 650 Mt $Ca(OH)_2$ y-1 if upscaled to the entire Mediterranea basin) in steps of 0.2 mmol m-2 for simulations of 1 year to determine the resulting surface pH changes. Figure S5 illustrates the response of the system to these perturbations suggesting a linear relationship between the alkalinity perturbations and the surface pH response in this idealised set-up.

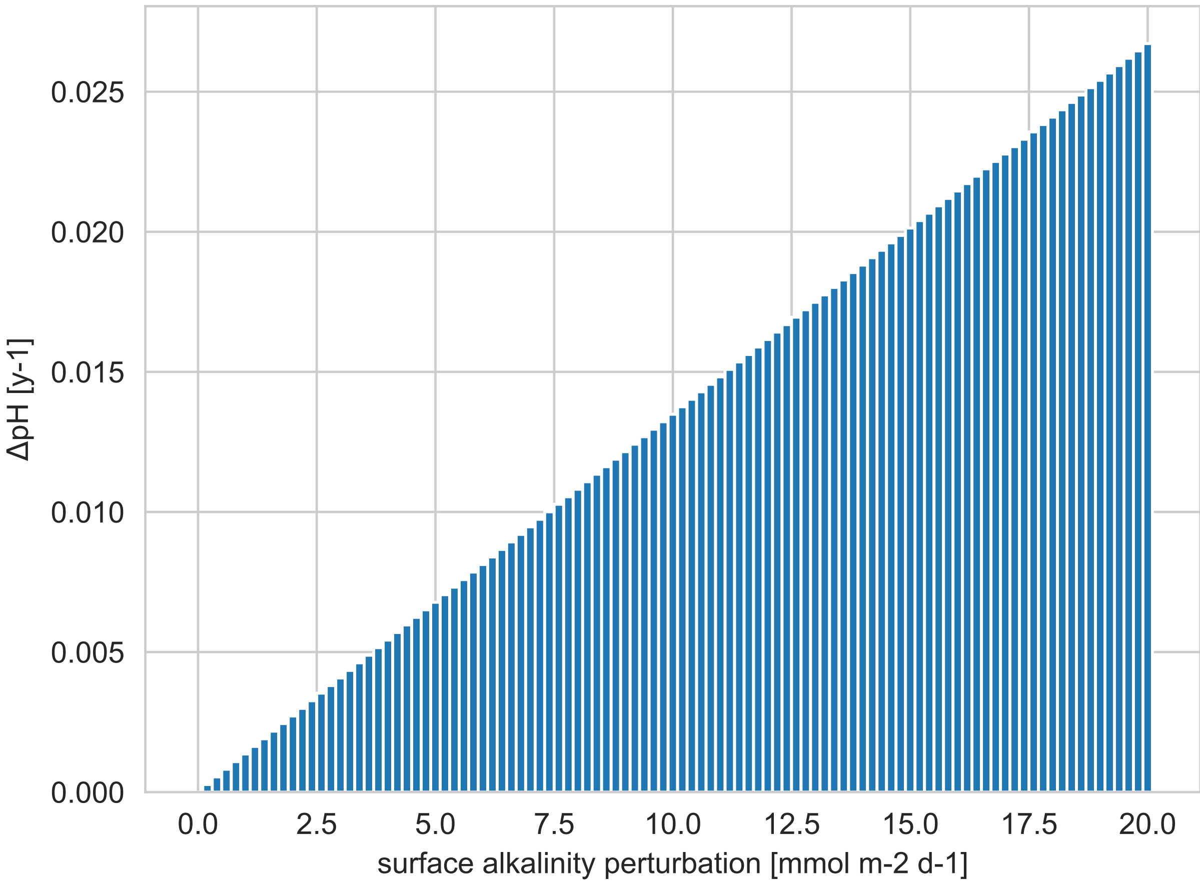

Figure S5. Change in surface pH in response to varying perturbations of surface alkalinity after one year of simulation in an idealised one-dimensional NEMO-BFM model system.

5 ALKALINITY AND DISSOLVED INORGANIC CARBON INPUTS FROM MEDITERRANEAN RIVERS

As the contribution of riverine Dissolved Inorganic Carbon and Alkalinity inputs to the Mediterranean basin is poorly constrained, a first dataset was compiled by collecting observed concentrations of these two variables for a wide set of rivers, which account for about 75% of the total freshwater inputs of this system. A rather heterogeneous set of sources was considered with the objective to include the longest available time-series, use data from monitoring points close to the river mouth, and obtain an adequate spatial coverage over the 10 different Mediterranean sub-basins defined by Ludwig et al. (2009). In table S1 are reported the annual concentrations values (computed from the different data sources) for Dissolved Inorganic Carbon and Total Alkalinity in 66 Mediterranean rivers. The river annual flow rates were obtained from Ludwig et al. (2009) as well as the code identifier composed by the pertaining sub-basin name and river number. River locations are also reported referring to the position of the sampling station of source data. Note that some river with rather small annual flow value were also included as data were found in the collection process. A gridded dataset of river inputs was computed as the product of punctual freshwater flows from Ludwig et al. (2009) averaged over the period 1990-2009 and river concentration values and when the latter was missing the corresponding sub-basin average was used instead.

Table S1. Dissolved Inorganic Carbon and Alkalinity concentrations (μM) in 66 Mediterranean rivers averaged over the entire period of data availability.

River	Longitude deg. E	Latitude deg. N	Code	Flow km^3/y	TA μM	DIC μM	Station	Period	Source
Adige	12.33	45.16	ADR51	7.39	2259.3		206	2010-2017	ARPA Veneto (2018)
Drin	19.57	41.75	ADR330	21.83	2460.0		Al_RV_30	2005-2007	Environmental Agency (2008, 2009)
Isonzo	13.56	45.72	ADR10	5.34	2371.6		GO02	2009-2010	Del Zotto and Zanolin (2011)
Neretva	17.44	43.02	ADR209	9.37	3560.0	3560.0	76	1998–2002	Štambuk-Giljanović (2005)
Po	11.65	44.88	ADR110	48.96	2728.4		227	2010-2017	ARPA Veneto (2018)
Savio	12.22	44.25	ADR112	0.02	4708.4		13000900	2010-2017	ARPA EMR (2018)
Seman	19.37	40.82	ADR345	3.21	3400.0		Al_RV_18	2005-2007	Environmental Agency (2008, 2009)
Shkumbin	19.44	41.04	ADR319	2.37	3640.0		Al_RV_14	2005-2007	Environmental Agency (2008, 2009)
Vjose	19.32	40.64	ADR349	5.83	3560.0		Al_RV_19	2005-2007	Environmental Agency (2008, 2009)
Aliakmonas	22.53	40.52	AEG225	2.03	3900.0	3700.0	Ilariona	1981-1997	Central Water Agency (2006)
Axios	22.97	40.63	AEG97	3.13	3300.0	3300.0	Chalastras	1977-1997	Central Water Agency (2006)
Buyuk Menderes	27.33	37.67	AEG602	3.87	5050.0	4490.0	706	1985-2002	Odemis and Evrendilek (2007)
Evros	26.17	40.88	AEG81	6.97	3300.0	3300.0	Peplo	1991-1998	Central Water Agency (2006)
Gediz	26.80	38.58	AEG494	1.66	6180.0	5400.0	523	1970-2002	Odemis and Evrendilek (2007)
Nestos	24.80	40.85	AEG16	2.09	2500.0	2500.0	Toxotes	1980-1997	Central Water Agency (2006)
Pinios	22.88	39.75	AEG308	2.60	4200.0	4100.0	W. Larisa	1980-1997	Central Water Agency (2006)
Simav	28.51	40.39	AEG307	4.27	4000.0	3630.0	316	1983-2002	Odemis and Evrendilek (2007)
Strymonas	23.87	40.80	AEG49	4.18	4000.0	3900.0	Myrkinou	1983-1997	Central Water Agency (2006)
Cheliff	0.12	36.02	ALB162	0.47	4700.0	4700.0	N/A	2004-2005	CIRCE project (2011)
Guadalhorce	-4.46	36.67	ALB56	0.24	6510.0	5994.6	MA1053B004	2008-2011	Rediam (2016)
Guadiaro	-5.28	36.28	ALB68	0.33	4098.2	3592.0	MA00000082	2008-2011	Rediam (2016)
Moulouya	-2.42	35.08	ALB163	0.45	4000.0	4000.0	Barrage Md V	2003	El Mandour (2011)
Tafna	3.80	36.87	ALB160	0.11	6344.3	6344.3	18 (Isser)	2000	Petrov (2011)
Salso	13.95	37.10	CEN23	0.20	3178.7	3178.7	St. 1	1991-1992	Favara et al. (2000)
Zeroud	10.22	35.83	CEN89	0.44	2100.0	2100.0	N/A	1980	Bahri (1993)
Acheloos	21.10	38.33	ION152	3.97	2800.0	2700.0	Neochori-Katochi	1989-1997	Central Water Agency (2006)
Alpheios	21.45	37.61	ION231	2.04	3600.0	3600.0	Karitaina	1988-1997	Central Water Agency (2006)
Arachthos	21.07	39.01	ION96	2.60	2900.0	2800.0	Megali-Gonitsa	1995-1997	Central Water Agency (2006)
Thyamis	20.14	39.59	ION71	1.72	3600.0	3600.0	Kalamas Dam	1988-1996	Central Water Agency (2006)
Asi	35.92	36.12	NLE270	1.25	4830.0	4370.0	1908	1997-2002	Odemis and Evrendilek (2007)
Ceyhan	35.82	37.03	NLE78	7.74	3440.0	3130.0	2004	1984-2002	Odemis and Evrendilek (2007)
Dalaman	28.73	36.70	NLE18	2.30	3700.0	3350.0	812	1970-2002	Odemis and Evrendilek (2007)
Esen	29.26	36.29	NLE98	0.99	2890.0	2680.0	815	1995-2002	Odemis and Evrendilek (2007)
Goksu	34.03	36.32	NLE106	3.70	2660.0	2460.0	1714	1970-2002	Odemis and Evrendilek (2007)
Koprucay	31.17	36.83	NLE19	3.83	2930.0	2700.0	902	1983-2002	Odemis and Evrendilek (2007)
Manavgat	31.43	36.78	NLE43	4.09	4140.0	3760.0	302	1970-2002	Odemis and Evrendilek (2007)
Seyhan	34.88	36.72	NLE49	8.38	2700.0	2500.0	1818	1970-2002	Odemis and Evrendilek (2007)
Arno	10.28	43.68	NWE121	2.78	2944.4		MAS-102	2010	ARPA Toscana (2018)
Aude	3.24	43.21	NWE140	1.27	3412.4	3379.1	6180900	2002-2011	Naiades (2016)
Ebro	0.52	40.82	NWE247	9.40	4081.8	3678.2	0027-FQ	2002-2013	CHEBRO (2016)
Herault	3.44	43.28	NWE82	1.02	3725.4	3725.4	6184000	2006-2011	Naiades (2016)
Jucar	-0.65	39.12	NWE309	0.75	4399.2	3488.4	Azud Marquesa	1990-2012	SIA Jucar (2016)
Llobregat	2.15	41.32	NWE195	0.44	4175.6	3975.6	Edar d'Abrera	2007-2013	ACA (2016)
Orb	3.30	43.25	NWE80	0.89	2645.4	2645.4	6188500	2002-2011	Naiades (2016)
Rhone	4.85	43.33	NWE72	55.31	2786.9	2786.9	6131550	2002-2011	Naiades (2016)
Serchio	10.27	43.78	NWE47	2.46	2757.1		MAS-007	2010	ARPA Toscana (2018)
Turia	-0.32	39.45	NWE292	0.23	3910.6	3099.2	La Presa	1996-2012	SIA Jucar (2016)
Var	7.20	43.65	NWE50	1.54	2288.0	2288.0	6213000	2007-2011	Naiades (2016)
Alexander	34.87	32.40	SLE82	0.06	4441.1	4441.1	15120	2007-2010	Water Authority (2008, 2009, 2010)
Lakhish	34.64	31.82	SLE139	0.03	3493.2	3493.2	19185	2008-2010	Water Authority (2008, 2009, 2010)
Nile	31.80	31.43	SLE228	14.92	2610.1	2410.3	N/A	2007	Elewa and El Nahry (2009)
Qishon	35.03	32.82	SLE77	0.06	5292.6	5292.6	8146	2007-2010	Water Authority (2008, 2009, 2010)
Yarqon	34.78	32.10	SLE118	0.03	2445.9	2445.9	17135	2007-2009	Water Authority (2008, 2009, 2010)
El-Kebir Est	6.09	36.87	SWE205	0.27	4426.0		23	2005-2008	Chaïb and Samraoui (2011)
Mazafran	2.81	36.69	SWE214	0.11	3787.2	3787.2	N/A	2006	Hamaidi-Chergui et al. (2013)
Segura	-0.65	38.08	SWE103	0.02	5291.0	5291.0	SE0914B029	2000-2013	CHSEGURA (2016)
Seybouse	7.78	36.92	SWE222	0.36	4026.7	4026.7	SO4	1999	Debieche (2002)
Soummam	5.07	36.75	SWE223	0.37	4200.0	4200.0	E	2009	Saou et al. (2012)
Tirso	8.54	39.89	SWE23	0.31	2745.9	2745.9	4	2003	Cidu et al. (2007)
Flumendosa	9.63	39.43	TYR158	0.14	2786.9	2786.9	9,8	2003	Cidu et al. (2007)
Garigliano	13.75	41.22	TYR80	2.35	5700.6		G2	2018	ARPA Campania (2019)
Medjerda	10.17	37.18	TYR265	1.00	2980.0	2980.0	N/A	1964-1990	Bahri (1993)
Ombrone	11.01	42.66	TYR10	0.83	4426.2		MAS-036	2010	ARPA Toscana (2018)
Sele	14.93	40.48	TYR129	1.38	4434.1		Sl6	2018	ARPA Campania (2019)
Tevere	12.48	41.90	TYR50	5.79	3870.0		F4.05	2013-2016	ARPA Lazio (2019)
Volturno	13.92	41.02	TYR100	2.06	5540.1		V9	2018	ARPA Campania (2019)

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