Supplementary Materials:

(1) Scientific contributions achieved in Koiliaris CZO

A brief overview of the significant scientific contributions achieved in Koiliaris follows:

- Development and testing of modeling tools for the assessment of water quantity and quality of karstic Mediterranean watershed: The karst-SWAT model [1,2] was conceptualized and developed using geomorphological data and knowledge of the hydrologic processes occurring at the Koiliaris CZO. One key characteristic of the Karstic model is that it can account for the water that originates outside the hydrologic basin of Koiliaris CZO, i.e., the extended karst, as well as for the water quality and sediment transport within the karst by assuming two well mixed reservoirs that account for the varying hydraulic conductivities of the upper and lower karst. After the Karst-SWAT model was verified at the CZO, it was scaled-up to simulate the Region of Crete and assess the regional hydrologic budget [3] as well as the impacts of climate change to the region [4].

- Development of a dynamic, integrated soil critical zone model: The second advancement in the research conducted at Koiliaris CZO was the development of the Integrated Critical Zone (1D-ICZ) model [5,6]. The 1D-ICZ is a tractable mathematical model that links soil aggregate formation and soil structure development to nutrient dynamics, plant nutrition, and water flow and mass transport. The model simulates and quantifies four of the main soil ecosystem functions (biomass production, carbon/nutrient sequestration in relation to soil structure, water filtration and bacteria-fungi dynamics) by accounting for interactions between water flow, solute transport, soil structure dynamics, carbon and nutrient dynamics and plant biomass production. The core of the model is the CAST module [7] that simulates the dynamics of soil formation (aggregation and disaggregation), soil structure and nutrients. Soil structure (e.g., macro-aggregate content) depends strongly on SOC content which in turn influences soil hydraulic properties. The CAST model has been applied widely all over the world simulating the evolution of carbon sequestration and soil structure dynamics from the fore field of the Damma Glacier in the Swiss Alps, to China's Black soils, to Cretan Soils, US Mid-West soils, to Burkina Faso soil restoration experiments [8,9].

- Soil formation and degradation studies: The study of soil formation and degradation processes from the plot to watershed scale has been a major focus of the SOILTREC project at Koiliaris CZO [10]. The underlying principles of the soil critical zone have been reviewed extensively [11,12]. Detailed soil characterization of its structure, biology, and geochemistry as well as the rates of formation of Koilairis CZO have been also provided [7,13–16]. Finally, the environmental drivers affecting the spatial distribution of soil microbial community and the nitrogen functional genes as well as the cycling of nitrogen at the watershed scale was studied by Tsiknia et al. [17,18] and Paranychianakis et al. [19].

- Sustainable water and land management: Sustainable water management has been a major focus at Koiliaris CZO in terms of quantifying the available water at the CZO and by extension to the whole region. A crucial question that needed to be addressed was how climate change is going to affect water availability and management [4,20] and the uncertainties of the predictions. Developing adaptation strategies and setting priorities with the involvement of stakeholder has been the focus of the work of Demetropoulou et al. [21] and Lilli et al. [22]. Soil sustainability requires long-term social change. The scientific advancement made through the development of the 1D-ICZ model is the rigorous simulation and quantification of important soil functions that enables the assessment, understanding and quantification of complex interactions between the different processes in the soil-plant-water system as well as providing a tool to design sustainable agricultural management practices by taking into consideration the synergies and trade-offs of the different soil functions [23–25].
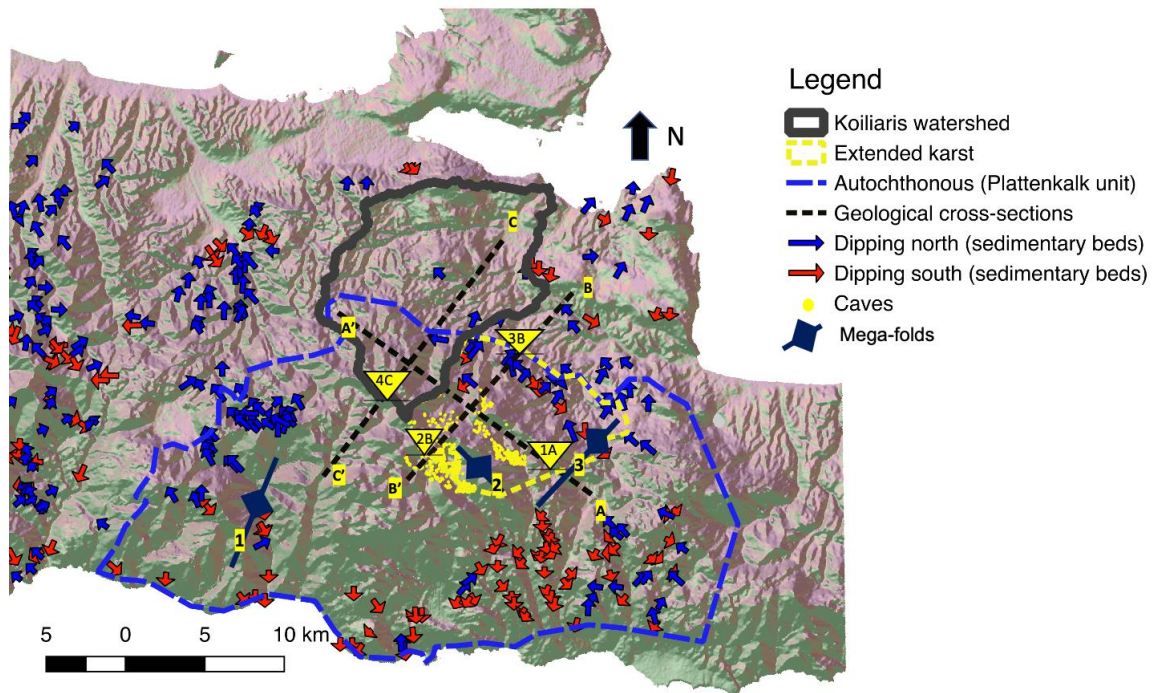
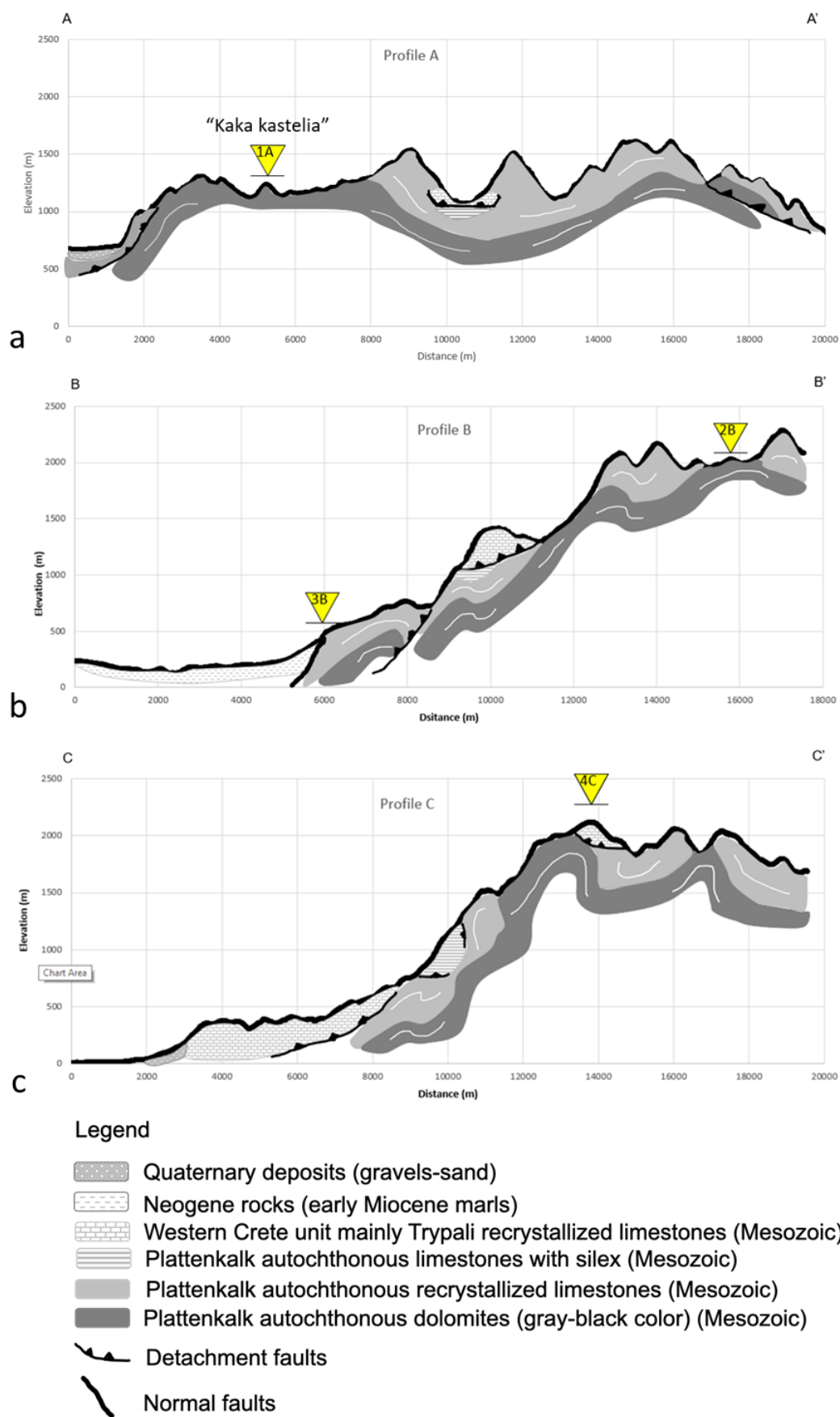## (2) Geomorphology analysis Supplementary Material

Figure S1. Hillshade and aspect map of the White Mountains greater area

Figure S2. Geological cross sections (**a**) Profile A, (**b**) Profile B, (**c**) Profile C. The yellow triangles depict the hinges of the different anticlines

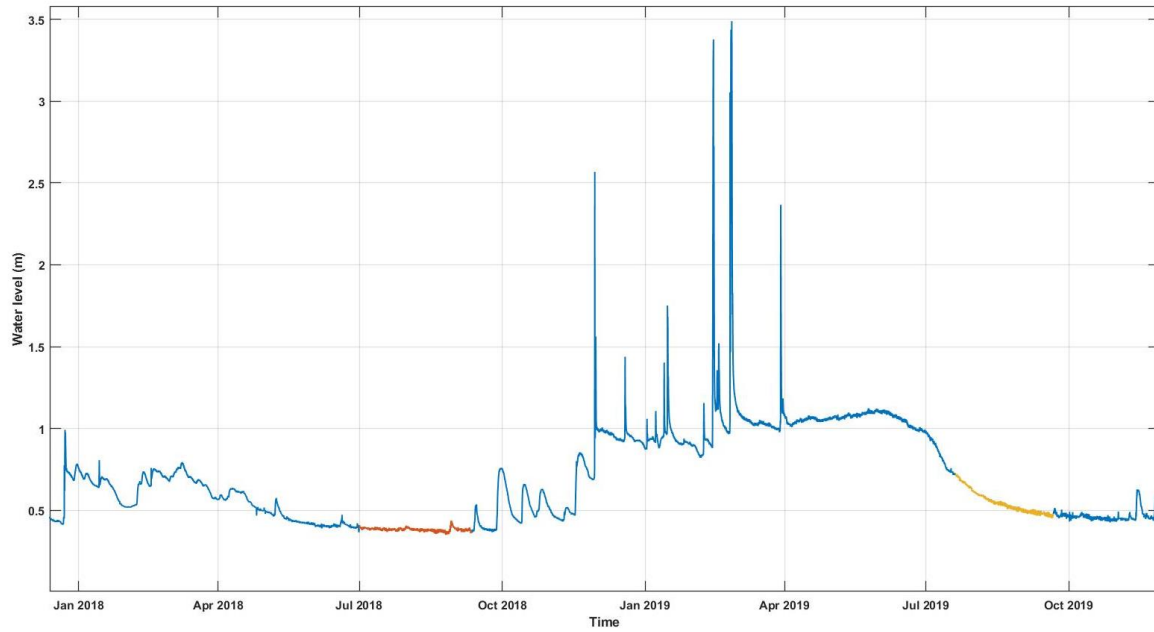**(3) Flow Frequency Analysis Supplementary Material**

Figure S3. Agios Giorgios station tidal analysis studied periods 2018 & 2019

Table S1. Tidal signals comparison for period 2019 ER, LR. Tidal constituents' amplitude and phase with 95% CI estimates; phases are at central time

Tidal component	Amplitude	Amplitude error	Phase (º)	Phase error(º)	Signal to noise ratio	Period (days)	Period
2SK5	**0.0003**	**0**	**307.9**	**28.33**	**4.2**	**0.200**	**ALL**
2SK5	0.0004	0	298.65	18.03	11	0.200	ER
2SK5	0.0003	0	326.04	37.53	2.4	0.200	LR
K1	**0.0087**	**0.001**	**242.33**	**8.48**	**47**	**0.997**	**ALL**
K1	0.0051	0.001	230.14	11.58	25	0.997	ER
K1	0.013	0.001	249.95	2.36	610.00	0.997	LR
M2	**0.0005**	**0**	**322.87**	**43.67**	**1.7**	**0.518**	**ALL**
M2	0.001	0	30.38	28.63	3.9	0.518	ER
M2	0.0007	0.001	282.12	38.44	2.2	0.518	LR
MO3	**0.0005**	**0**	**118.11**	**39.16**	**2.2**	**0.349**	**ALL**
MO3	0.0006	0	94.28	33.09	3.1	0.349	ER
MO3	0.0005	0	104.84	38.38	2.3	0.349	LR
P1	**0.0029**	**0.001**	**249.4**	**25.14**	**5.2**	**1.003**	**ALL**
P1	0.0017	0.001	237.21	34.27	2.8	1.003	ER
P1	0.0043	0.001	257.02	7.02	66	1.003	LR
S2	**0.0017**	**0**	**149.33**	**13.57**	**18**	**0.500**	**ALL**
S2	0.001	0	121.15	27.3	4.4	0.500	ER
S2	0.0023	0.001	165.76	12.64	21	0.500	LR
SK3	0.0007	0	80.29	31.32	3.5	0.333	ALL
SK3	0.0005	0	29.41	35.96	2.6	0.333	ER
SK3	0.0008	0	99.76	23.14	6.3	0.333	LR

Table S2. Tidal signals comparison for period 2018 ER, LR. Tidal constituents' amplitude and phase with 95% CI estimates; phases are at central time

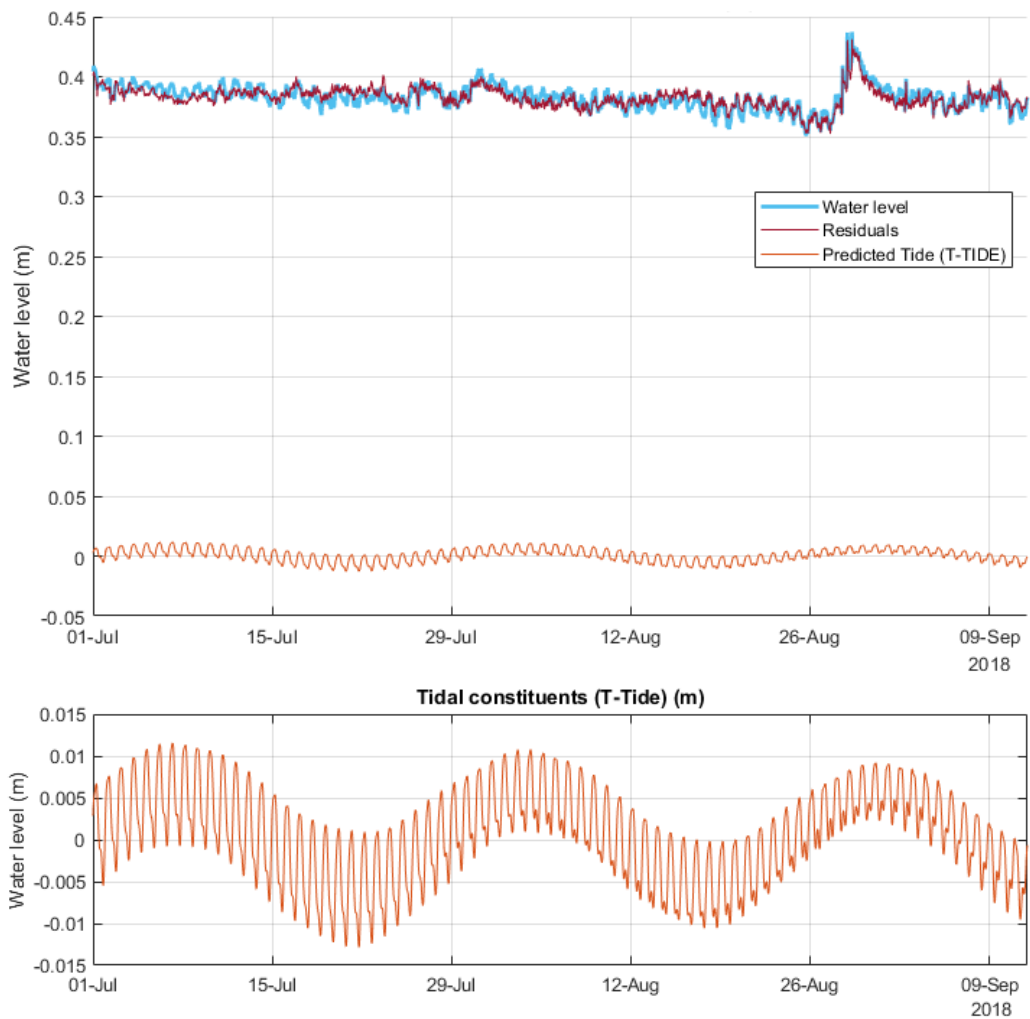| Tidal component	Amplitude	Amplitude error	Phase (°)	Phase error(°)	Signal to noise ratio	Period (days)	Period
SK3	0.001	0	163.91	11.53	28	0.3	ALL
SK3	0.0009	0	154.91	16.62	13	0.3	ER
SK3	0.0013	0.001	169.44	40.48	2.2	0.5	LR
S2	0.0012	0	79.5	17.88	10	0.5	ALL
S2	0.002	0	97.96	7.78	54	14.8	ER
S2	0.0008	0	0.45	33.43	2.9	1.0	LR
P1	0.0016	0.001	258.81	23.7	5.8	1.0	ALL
P1	0.0014	0.001	243.44	21.22	7.2	1.0	ER
P1	0.0023	0.001	276.78	37.27	2.3	1.0	LR
K1	0.005	0.001	251.74	8.38	53	1.0	ALL
K1	0.0041	0.001	236.37	7.52	66	1.0	ER
K1	0.0069	0.001	269.71	13.14	21	14.8	LR

Figure S4. Tidal analysis of water stage for the period of 1 July 2018 till 11 September 2018, showing the predicted tidal component and the residual between the predicted tide and the field data

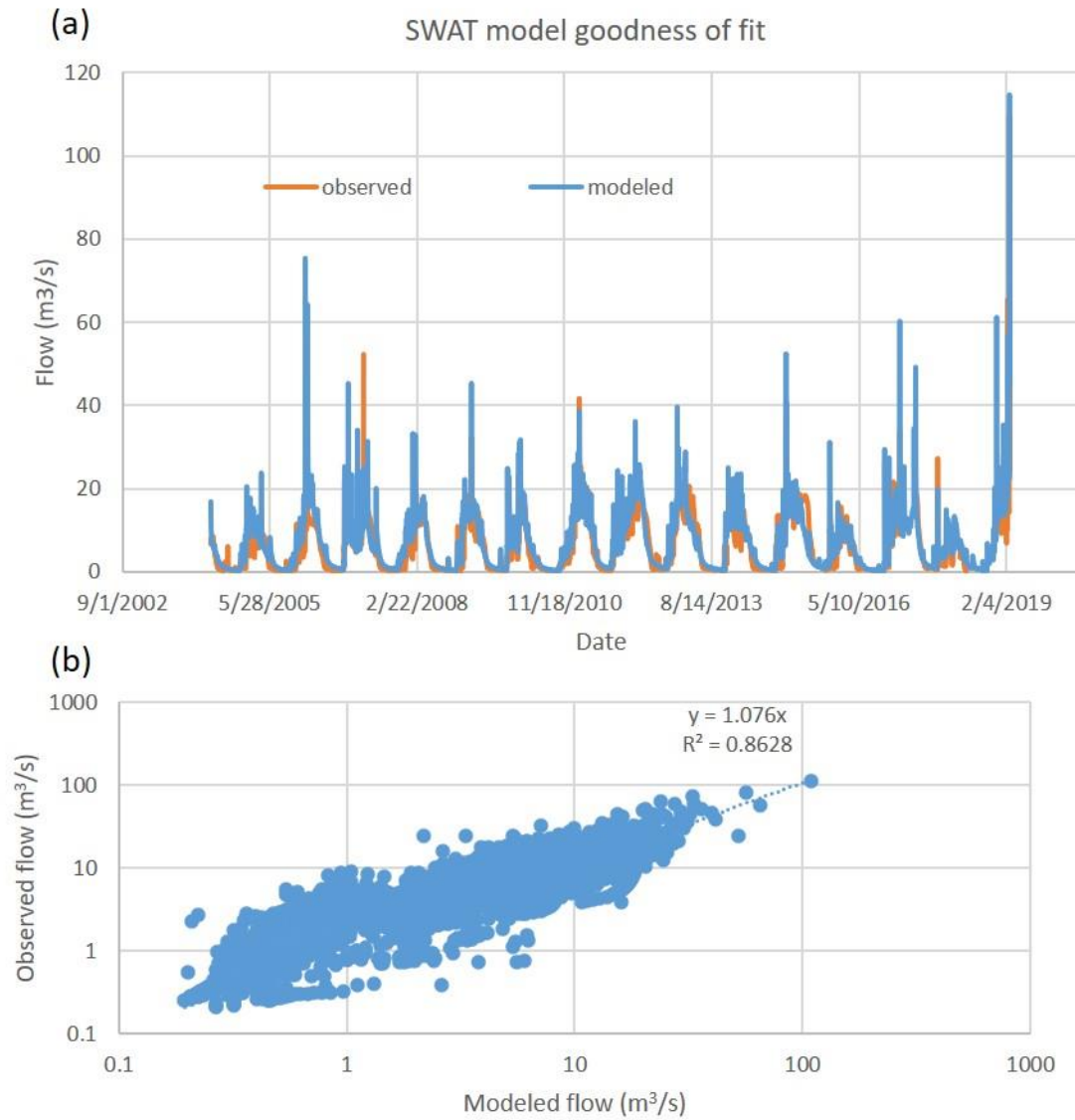**(4) Hydrologic analysis Supplementary Material**

Figure S5. (**a**) Observed and modeled daily flow vs. time at Ag. Georgios station (basin exit), and (**b**) XY scatter plot with logarithmic axes, and trend line of observed vs. modeled flows at Ag. Georgios station (basin exit)
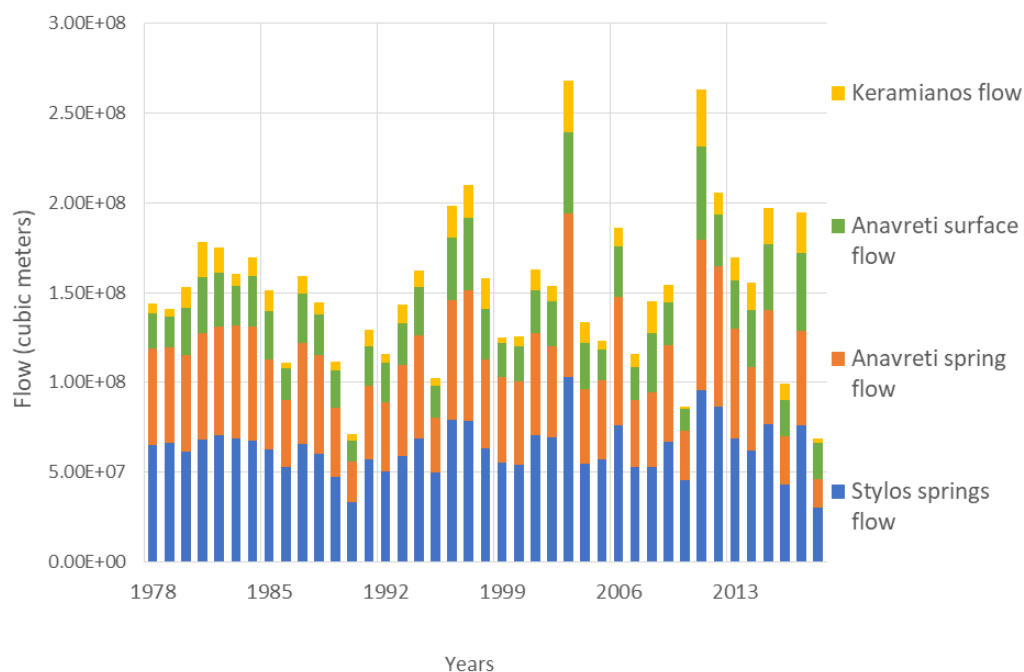
Figure S6. Components of the mean annual flow of the stream network of the Koiliaris CZO

Table S3. Mean contribution (%) of each stream and spring to the total flow (at the basin exit) and contribution during a wet and dry year

source	Keramianos	Anavreti surface	Anavreti spring	Stylos spring
% on total flow (mean year)	7.2	16.9	33.9	41.5
% on total flow (wet year)	10.6	16.7	33.8	38.3
% on total flow (dry year)	5.2	16.0	31.8	47.2

Table S4. Flow (m³/s) and contribution of each stream and spring to the total flow during an extreme flood event (25 February 2019)

source	Keramianos	Anavreti surface	Anavreti spring	Stylos spring	Total flow
flow (m³/s)	28.8	40.3	20.6	18.8	108.5
% on total flow	26.5	37.2	19.0	17.3	100.0

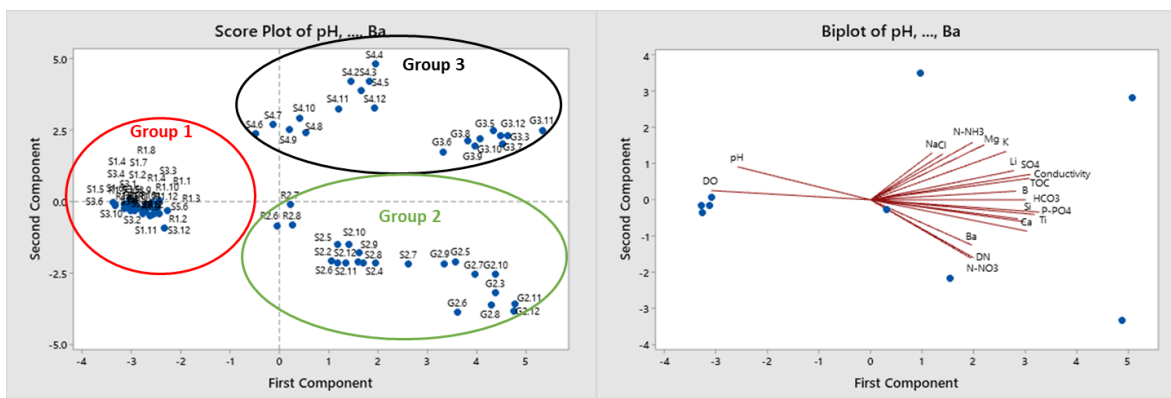**(5). Geochemical analysis Supplementary Material**

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Figure S7. Groups resulting from PCA in water bodies of Koiliaris CZO using the average values of chemical species
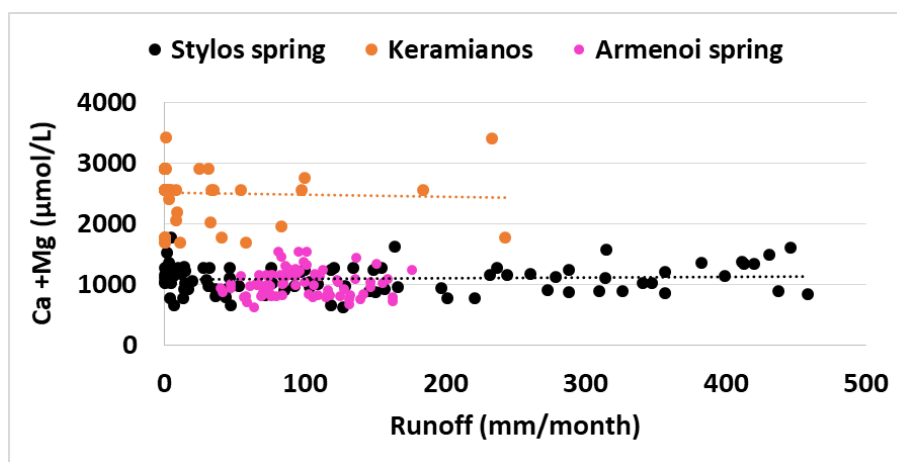

Figure S8. Relationship between weathering intensity and instantaneous water discharge

References

1. Nikolaidis, N.P.; Bouraoui, F.; Bidoglio, G. Hydrologic and geochemical modeling of a karstic Mediterranean watershed. *J. Hydrol.* **2013**, *477*, 129–138.

2. Nerantzaki, S.D.; Giannakis, G.V.; Efstathiou, D.; Nikolaidis, N.P.; Sibetheros, I.A.; Karatzas, G.P.; Zacharias, I. Modeling Suspended Sediment Transport and Assessing the Impacts of Climate Change in a Karstic Mediterranean Watershed. *Sci. Total Environ.* **2015**, *538*, 288–297.

3. Malagò, A.; Efstathiou, D.; Bouraoui, F.; Nikolaidis, N.P.; Franchini, M.; Bidoglio, G.; Kritsotakis, M. Regional scale hydrologic modeling of a karst-dominant geomorphology: The case study of the island of Crete. *J. Hydrol.* **2016**, *540*, 64–81.

4. Nerantzaki, S.D.; Efstathiou, D.; Giannakis, G.; Kritsotakis, M.; Grillakis, M.; Koutroulis, A.; Tsanis, I.; Nikolaidis, N.P. Climate Change Impact on the Hydrologic Budget of a large Mediterranean island. *Hydrol. Sci. J.* **2019**, *64*, 1190–1203.

5. Giannakis, G.V.; Nikolaidis, N.P.; Valstar, J.; Rowe, E.C.; Moirogiorgou, K.; Kotronakis, E.; Paranychianakis, N.V.; Rousseva, S.; Stamati, F.E.; Banwart, S.A. Integrated Critical Zone Model (1D-ICZ): A Tool for Dynamic Simulation of Soil Functions and Soil Structure. *Adv. Agron.* **2017**, *142*, 277–314, doi:10.1016/bs.agron.2016.10.009.

6. Kotronakis, E.; Giannakis, G.V.; Nikolaidis, N.P.; Rowe, E.C.; Valstar, J.; Paranychianakis, N.V.; Banwart, S.A. Modeling the Impact of Carbon Amendments on Soil Ecosystem Functions Using the 1D-ICZ Model. *Adv. Agron.* **2017**, *142*, 315–352, doi:10.1016/bs.agron.2016.10.010.

7. Stamati, F.; Nikolaidis, N.P.; Banwart, S.A.; Blum, W.E. A Coupled Carbon, Aggregation, and Structure Turnover (CAST) Model for topsoils. *GeoDerma* **2013**, *211–212*, 51–64.

8. Giannakis, G.V.; Panakoulia, S.K.; Nikolaidis, N.P.; Paranychianakis, N.V. Simulating Soil Fertility Restoration using the CAST model. *Procedia Earth Planet. Sci.* **2014**, *10*, 325–329, doi:10.1016/j.proeps.2014.08.027.

9. Panakoulia, S.K.; Nikolaidis, N.P.; Paranychianakis, N.V.; Menon, M.; Schiefer, J.; Lair, G.J.; Kram, P.; Banwart, S.A. Factors Controlling Soil Structure Dynamics and Carbon Sequestration Across Different Climatic and Lithological Conditions. *Adv. Agron.* **2017**, *142*, 241–276, doi:10.1016/bs.agron.2016.10.008.

10. Banwart, S.A.; Bernasconi, S.; Blum, W.; de Souza, D.M.; Chabaux, F.; Duffy, C.; Kercheva, M.; Kram, P.; Lair, G.; Lundin, L.; et al. Soil Functions in Earth's Critical Zone—Key results and conclusions. *Adv. Agron.* **2017**, *142*, 1–27, doi:10.1016/bs.agron.2016.11.001.

11. Banwart, S.A.; Nikolaidis, N.P.; Zhu, Y.G.; Peacock, C.L.; Sparks, D.L. Soil Functions: Connecting Earth's Critical Zone. *Annu. Rev. Earth Planet. Sci.* **2009**, *47*, 333–359.

12. Nikolaidis, N.P.; Bidoglio, G. Soil Organic Matter Dynamics and Structure. *Sustain. Agric. Rev.* **2013**, *12*, 175–200.

13. Rousseva, S.; Kercheva, M.; Shishkov, T.; Lair, G.J.; Nikolaidis, N.P.; Moraetis, D.; Krám, P.; Bernasconi, S.; Blum, W.; Menon, M.; et al. Soil Water Characteristics of European SoilTrEC Critical Zone Observatories. *Adv. Agron.* **2017**, *142*, 29–72, doi:10.1016/bs.agron.2016.10.004.

14. Van Leeuwen, J.P.; Moraetis, D.; Lair, G.; Bloem, J.; Nikolaidis, N.P.; Hemerik, L.; de Ruiter, P.C. Ecological soil quality affected by land use and management on semi-arid Crete. *Soil Discuss.* **2015**, *2*, 187–215.

15. Regelink, I.C.; Stoof, C.R.; Rousseva, S.; Weng, L.; Lair, G.J.; Kram, P.; Nikolaidis, N.P.; Kercheva, M.; Banwart, S.; Comans, R.N.J. Mechanistic linkages between soil aggregates, soil porosity and soil chemical properties. *GeoDerma* **2015**, *247–248*, 24–37.

16. Moraetis, D.; Paranychianakis, N.; Nikolaidis, N.P.; Banwart, S.; Rousseva, S.; Kercheva, M.; Nenov, M.; Shishkov, T.; Ruiter, de P.; Bloem, J.; Blum, W.E.H.; et al. Sediment provenance, soil genesis, and carbon storage in fluvial and manmade terraces at Koiliaris River Critical Zone Observatory. *J. Soils Sediments* **2015**, *15*, 347–364.

17. Tsiknia, M.; Paranychianakis, N.V.; Varouchakis, E.A.; Nikolaidis, N.P. Environmental Factors Shaping the Distribution of Nitrogen Cycling Functional Genes at a Watershed Scale. *FEMS Microbiol. Ecol.* **2015**, *90*, 139–152.

18. Tsiknia, M.; Paranychianakis, N.; Varouchakis, E.; Moraetis, D.; Nikolaidis, N.P. Environmental drivers of soil microbial community distribution at the Koiliaris Critical Zone Observatory. *FEMS Microbiol. Ecol.* **2014**, *90*, 139–152.

19. Paranychianakis, N.V.; Tsiknia, M.; Giannakis, G.V.; Nikolaidis, N.P.; Kalogerakis, N. Nitrogen cycling and relationships between ammonia oxidizers and denitrifiers in a clayey soil. *Appl. Microbiol. Biotechnol.* **2013**, *97*, 5507–5515, doi:10.1007/s00253–013-4765-5.

20. Nerantzaki, S.D.; Hristopulos, D.T.; Nikolaidis, N.P. Estimation of the uncertainty of hydrologic predictions in a karstic Mediterranean watershed. *Sci. Total Environ.* **2020**, *717*, 137131, doi:10.1016/J.SCITOTENV.2020.137131.

21. Demetropoulou, L.; Lilli, M.A.; Petousi, I.; Nikolaou, T.; Fountoulakis, M.; Kritsotakis, M.; Panakoulia, S.; Giannakis, G.V.; Manios, T.; Nikolaidis, N.P. Innovative methodology for the prioritization of the Program of Measures for integrated water resources management of the Region of Crete, Greece. *Sci. Total Environ.* **2019**, *672*, 61–70.

22. Lilli, M.A.; Nerantzaki, S.D.; Riziotis, C.; Kotronakis, M.; Efstathiou, D.; Kontakos, D.; Lymberakis, P.; Avramakis, M.; Tsakirakis, A.; Protopapadakis, K.; et al. Vision-Based Decision-Making Methodology for Riparian Forest Restoration and Flood Protection Using Nature-Based Solutions. *Sustainability* **2020**, *12*, 3305.

23. Banwart, S.; Bernasconi, S.; Bloem, J.; Blum, W.; Brandao, M.; Brantley, S.; Chabaux, F.; Duffy, C.; Lundin, L.; Kram, P.; et al. Assessing Soil Processes and Function across an International Network of Critical Zone Observatories: Research hypotheses and experimental design. *Vadose Zone J.* **2011**, *10*, 978–987.

24. Banwart, S.A.; Bernasconi, S.; Bloem, J.; Blum, W.; de Souza, D.M.; Chabaux, F.; Duffy, C.; Lundin, L.; Kram, P.; Nikolaidis, N.P.; et al. Soil Processes and functions across an International Network of Critical Zone Observatories: Introduction to experimental methods and initial results. *Comptes Rendus Geosci.* **2012**, *344*, 758–772.

25. Banwart, S.A.; Black, H.; Cai, Z.; Gicheru, P.; Joosten, H.; Victoria, R.; Milne, E.; Noellemeyer, E.; Pascual, U.; Nziguheba, G.; et al. Benefits of soil carbon: Report on the outcomes of an international Scientific Committee on Problems of the Environment Rapid Assessment Workshop. *Carbon Manag.* **2014**, *5*, 185–192.