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 *Ε. SOUVERMEZOGLOU, Ε. KRASAKOPOULOU, A. PAVLIDOU* 

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## **Temporal and spatial variability of nutrients and oxygen in the North Aegean Sea during the last thirty years**

## **E. SOUVERMEZOGLOU1 , E. KRASAKOPOULOU2 and A. PAVLIDOU1**

1 Institute of Oceanography, Hellenic Centre for Marine Research, P.O. Box 712, 19013, Anavyssos, Greece 2 University of the Aegean, Department of Marine Sciences, 81100, Lesvos, Greece

Corresponding author: katerinasouv@hcmr.gr

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#### **Abstract**

Inorganic nutrient and dissolved oxygen data collected in the North Aegean Sea during 1986 - 2008 were analyzed in order to evaluate the role of the inflowing Black Sea originated surface water (BSW) in the nutrient regime of the area. In periods of high buoyancy inflow from the Dardanelles strait, a reduction of inorganic nutrients in the surface layer is observed along the north-west route of the BSW; in parallel, the underlying layer of Levantine intermediate water revealed an increase of inorganic nutrients, receiving the degradation material from the surface layer. The above spatial patterns suggest a contribution of the BSW to the observed enhanced production of the North Aegean Sea. Anomalously low buoyancy inflow of BSW combined with severe winter meteorological conditions promote deep-water formation events. The physical and chemical characteristics of the deep waters found in the different basins of the North Aegean Sea in 1997 (following the deep-water formation in the winter of 1992-1993) differed from those observed after the formation in winter 1987. These differences were probably related to the drastic changes that occurred in the deep waters of the Eastern Mediterranean in early 1990, caused by the Eastern Mediterranean Transient. Considering that deep-water formation processes occasionally provide inorganic nutrients to the euphotic layer, it appears that BSW, through its uninterrupted supply of small quantities of nutrients, plays an additional role in production in the North Aegean Sea.

**Keywords:** North Aegean, Nutrients, Dissolved Oxygen, Nutrient ratios.

#### **Introduction**

The Aegean Sea is one of the Eastern Mediterranean basins displaying a complicated hydrographic and biogeochemical structure due to its geographic position between the Black Sea and the Ionian and Levantine Seas (Zervakis *et al*., 2000; Siokou-Frangou *et al*., 2002). The Aegean Sea is separated by the Cycladic plateau into two sub-basins, the North Aegean and the South Aegean, with significantly different hydrographic characteristics mainly controlled by the influence of Black Sea waters and Levantine Sea waters, respectively. Due to the progressive considerable depletion of nutrients from the western to the eastern part of the Mediterranean basin, the intermediate and deep waters of the Aegean Sea have the lowest concentrations of nutrients. The South Aegean Sea, with nutrient concentrations eight times lower than in the Alboran Sea, has been characterised as one of the most oligotrophic areas of the Mediterranean Sea (Mc Gill, 1965; Souvermezoglou, 1999). However, higher phytoplankton and zooplankton biomass and production were observed in the North Aegean Sea compared to the South Aegean Sea, (Stergiou *et al*., 1997; Ignatiades *et al*., 2002; Siokou-Frangou *et al*., 2002).

The particularity of the North Aegean Sea (NAS) lies

in its connection with the Black Sea through a straits system comprising the Dardanelles strait, the Marmara Sea and the Bosphorus strait. As a result, highly saline water of Levantine and south-central Aegean origin, is diluted by the brackish Waters of Black Sea origin (hereafter BSW) outflowing through the Dardanelles strait and by the river runoff from the Greek and Turkish mainland. This water mass meets the warm and very saline water of Levantine origin, thus forming a pronounced thermohaline front that can be highly mobile in time scales of the order of 10 days (Zervakis & Georgopoulos, 2002). The Dardanelles current, in the form of a thin (about 20-30 m) surface layer, bifurcates east of Lemnos, and one branch follows a westward flow south of Lemnos, while the other follows a north-westward flow forming the Samothraki anticyclone, which is responsible for increasing the residence time of modified BSW in the North Aegean (Zervakis & Georgopoulos, 2002). The dominant water mass in the intermediate layer of the NAS below BSW is warm and saline, and called Modified Levantine Intermediate Water (MLIW); it consists of a mixture of LIW and intermediate water masses produced locally in both the North and South Aegean Sea during winter (Georgopoulos *et al*., 1989; Gertman *et al*., 2006; Velaoras &

Lascaratos, 2010). The cyclonic circulation brings highly saline LIW towards the North Aegean along the western coast of Asia Minor (Theocharis & Georgopoulos, 1993; Zodiatis, 1994). The salt content of the intermediate layer decreases by mixing with the low-salinity surface layer, and thus the waters turning south, along the eastern coast of continental Greece, exhibit lower salinity (Zervakis & Georgopoulos, 2002).

The bottom topography of the NAS is characterized by a series of three SW-NE oriented depressions (down to a depth of 1500 m), separated by shallow sills and shelves (Fig. 1). The Northern Sporades and Athos basins, reaching depths of 1468 and 1149 m, respectively, are separated by a 500 m deep sill, from the 1550 m deep Lemnos basin. All three of them form the North Aegean Trough and are separated by a 350 m sill from the northern Skyros and the Chios basins, lying to their south (Fig. 1). Severe meteorological conditions in winter promote dense water formation over the shelves (Samothraki in the north, Lemnos in the south) of the NAS. This newly formed dense water, slides towards the deeper layers following the isobaths and finally fills the deep basins. Ventilation of the deep basins takes place occasionally during massive water formation events producing one of the densest waters of the world oceans, with densities exceeding  $\sigma_{\theta} = 29.50$  (Zervakis *et al*., 2000). The great bathymetric variability imposes limitations on the deep circulation and communication between the various basins.

NAS typically acts like a dilution basin and rarely as a concentration basin. Zervakis *et al*. (2000) suggested that due to the high buoyancy inflow from the Dardanelles strait, the surface layer of NAS is an effective isolator be-

tween the deeper layers of the NAS and the atmosphere, hindering dense water formation (estuarine functioning). The deep water formation incidents coincided with periods of reduced water surplus of the Black Sea and, thus, a weaker surface layer of BSW in the NAS. During the long periods of estuarine functioning, the deep layers of NAS remain almost stagnant and the decomposition of dissolved and settling particulate organic matter results in gradual depletion of dissolved oxygen and accumulation of inorganic nutrients (Souvermezoglou & Krasakopoulou, 2002). Thus, during estuarine periods, the deep basins progressively become nutrient reservoirs for the Aegean Sea.

The nutrient supply through the BSW, apart of its dependence on the buoyancy and the related water fluxes through the Dardanelles strait, is equally dependent on the nutrient content of the inflowing water mass. The inorganic nutrient fluxes through upper layer of the Dardanelles strait vary markedly with season, due to changes in both the concentrations and volume fluxes (Tugrul *et al.*, 2002) and are high in winter and very low in summer. The outflowing BSW through the Dardanelles strait is enriched in organic nutrients rather than inorganic (Polat & Tugrul, 1996). Recent measurements (Zeri *et al*., 2014) showed that surface waters in the Marmara Sea and the Dardanelles strait are enriched in DON (8.17  $\pm$  0.81 μmol L<sup>-1</sup> and 6.55  $\pm$  2.32 μmol L<sup>-1</sup>, respectively) and DIN (0.341  $\pm$ 0.351 µmol L<sup>-1</sup> and 0.308  $\pm$  0.206 μmol L-1, respectively) relative to the N. Aegean waters (DON: 4.11  $\pm 0.96$  µmol L<sup>-1</sup>; DIN:  $0.086 \pm 0.071$  µmol L-1). Regarding dissolved organic phosphorus (DOP), a mean value of 0.30 μmol L<sup>-1</sup> was reported by Sorokin (1983) in the Bosphorus surface outflow and 0.14 μmol



*Fig. 1:* Bathymetric chart of the North Aegean Sea with the location of deep basins discussed in the manuscript.

 $L<sup>-1</sup>$  in the Dardanelles surface outflow (Polat & Tugrul, 1996). Inorganic nutrient values in the surface layer of eastern NAS are slightly higher than in the western NAS and the south Aegean Sea (Siokou-Frangou *et al*., 2002); similar differences were observed in the nitrate values between the BSW in front of the Dardanelles strait and the neighbouring area covered by MLIW (Zervoudaki *et al*., 2007). However, plankton biomass and production was found to be significantly higher in the eastern NAS than in the western NAS and South Aegean Sea (Ignatiades *et al*., 2002; Siokou-Frangou *et al*., 2002), while the carbon flow within the pelagic food web seems to be quite efficient, affecting higher trophic levels (Stergiou *et al*., 1997; Siokou-Frangou *et al*., 2002). Thus, there is a potential link between the BSW and the enhanced productivity of the NAS; however, the influence of BSW in the trophic regime of NAS is an open question.

Abnormally low buoyancy inflow from the Dardanelles strait, combined with severe winter meteorological conditions, promote episodic dense water formation events (Zervakis *et al*., 2004; 2007; 2009). The dense water formation over the Samothraki and Lemnos shelves ventilates the deep basins of the NAS affecting its biochemistry in two different ways. On the one hand, it constitutes a mechanism for direct downward transport of inorganic and newly formed organic matter, from the surface layer. The organic matter that reaches the bottom layer, just after the deep water formation event, is rich in labile and easily oxidizable material, and its decomposition leads to significant oxygen uptake. On the other hand, it contributes to the enrichment of the euphotic and intermediate layers by large quantities of inorganic nutrients injected upwards, due to the displacement of the stagnant deep waters (rich in inorganic nutrients) caused by the deep water formation process. The upwelling of the inorganic nutrients stored in the deep basins throughout the estuarine periods, potentially provide the basis for extensive new production in the NAS; thus, a transition from a microbial loop-based to a new production-based ecosystem could be taking place (Zervakis *et al*., 2007).

The purpose of this article is to investigate the variability of oxygen and the nutrient regime in different areas of the NAS over a 30-year period, aiming to reveal the influence of BSW on the trophic status of the region. The objective of this work is to contribute to the efforts made to understand the mechanisms that control the biogeochemical processes in the NAS.

## **Materials and Methods**

During the period 1986 - 2008, dissolved oxygen (DO) and nutrient data were collected by the Hellenic Centre for Marine Research (HCMR) during several oceanographic campaigns conducted within the framework of national, international and EU-funded programs (Table 1). In this paper, we assembled these nutrient data (226 stations) in order to reveal the detailed pattern of nutrient distribution in NAS, the seasonality as well as temporal and spatial variability. The location of the stations (Table 1) visited during the oceanographic campaigns are shown in Figure 2. Most of the nutrient data in the area were mainly obtained during two seasons: spring and autumn. Therefore, they were grouped accordingly for their analysis.

CTD data were collected using Seabird Electronics profilers: an SBE-9 profiler was used till 1997 and an SBE-911+ after 1997 to 2008. Details on CTD data acquisition and raw data processing can be found in Theocharis & Georgopoulos (1993) and Zervakis *et al*. (2003). The CTD profiler was mounted on a General Oceanics rosette sampler equipped with 10 or 12 L Niskin bottles.

Water samples for the DO determination were drawn first from the Niskin bottles taking the precautions recommended to prevent any biological activity and gas exchanges with the atmosphere (Strickland & Parsons, 1977). The samples were analysed immediately after collection using the Winkler method, as modified by Carpenter (1965).

For the determination of nutrients, water samples were collected in 100 mL polyethylene bottles p rewashed with HCl and kept deep-frozen until their analysis at the laboratory. Nutrient samples obtained from 1987 to 1995 were measured with a TECHNIKON CSM-6 Autoanalyzer, from 1996 to 1999 with an ALPKEM autoanalyzer and after 1999 to 2008 with a BRAN + LUEBBE III autoanalyzer according to standard methods (Mullin & Riley 1955, for silicate; Strickland & Parsons 1977, for nitrate and nitrite). Phosphate measurements were performed

**Table 1:** Inventory of archived nutrient data analyzed in the present paper.

Project	<b>Sampling Period</b>	<b>Number of Stations</b>		
<b>POEM</b>	November 1986	9		
	March 1987	11		
	September 1987	10		
	March 1988	10		
	September 1988	10		
	March 1989	9		
	September 1989	10		
<b>MATER</b>	March 1997	5		
	September 1997	6		
	March 1998	4		
<b>INTERREG</b>	May 1997	27		
	February 1998	10		
	June 1998	23		
	September 1998	26		
	February 1999	14		
<b>KEYCOP</b>	September 1999	10		
	April 2000	7		
<b>EUR-OCEANS</b>	September 2005	3		
	April 2006	3		
<b>SESAME</b>	March-April 2008	8		
	September 2008	11		
	<b>TOTAL</b>	226		

using different UV/VIS spectrophotometers during the above mentioned periods, namely: Hitachi Model 100- 60, Perkin Elmer 20 Lambda and Perkin Elmer Lambda 25 Lambda (Murphy & Riley, 1962).

Considering the major physical characteristics, four areas were distinguished in NAS, which are mainly influenced by three water types: low salinity waters with a high percentage of BSW occupying the surface water layer of  $\sim$ 20-30 meters with  $\sigma_{\theta}$  < 27.9; highly saline and warm waters of Levantine origin (MLIW) occupying intermediate water depths with  $\sigma_{\theta}$  between 28.9 and 29.2 and the very dense North Aegean Deep Waters (NAgDW) occupying the deep layers of the NAS with  $\sigma_{\theta} > 29.3$ . The selected areas discussed in this paper are the following (Fig. 2):

1. The "frontal area", east of Lemnos island in the vicinity of the Dardanelles Strait where the North Aegean Front (Siokou *et al*., 2010) is formed;

2. The "north of Lemnos area", influenced by the BSW;

3. The "Samothraki anticyclone area";

4. The "LW area", where waters of Levantine and South-Central Aegean origin occupy the layer from the surface to ~400m depth and BSW is only occasionally detected.



*Fig. 2:* Location of the stations sampled during the cruises from 1986 to 2008 with the four selected areas.



*Fig. 3:* θ-S diagram in the North Aegean Sea (all data were used) during spring and autumn for the 1987-2008 period.

## **Results and Discussion**

#### *Inorganic Nutrients in the different water masses of NAS*

The diagram of potential temperature versus salinity (θ-S) for spring (Fig. 3) shows the stratification of surface (BSW), intermediate (MLIW) and deep-water (NAgDW) masses in NAS. The BSW signal can be clearly identified, characterized by low salinity (and density) values; during autumn, top BSW layers turn warmer as they are being heated after the winter period, while the Levantine Surface Water (LSW) is also clearly detected, characterized by extremely high salinity values (>39.1), which make it denser than BSW. Below the surface water masses, MLIW was traced at intermediate depths down to about 400m and is identified as a temperature maximum. During both periods,  $\theta$ –S curves display very high densities (σ<sub> $\theta$ </sub>>29.50 kg/m3 ), which represent the dense deep-water (NAgDW) masses filling the deep basins (>400m) of NAS. It should be noted that the ending tips of the θ–S curves appeared to have quite different characteristics, reflecting the different characteristics of the deep waters in each North and Central Aegean Sea deep basin (Zervakis *et al*., 2000; Velaoras & Lascaratos, 2005).

The chemical characteristics corresponding to the different water masses can be identified in the plots of inorganic nutrients and DO versus sigma-theta (Fig. 4). The BSW exhibits relatively high DO concentrations (average concentration:  $5.96 \pm 0.41$  mL L<sup>-1</sup> during spring and  $5.13 \pm 0.23$  mL L<sup>-1</sup> during autumn) but relatively low inorganic nutrient concentrations, which varied significantly during the different sampling cruises ( $PO<sub>4</sub>$ : 0.024  $\pm$  0.019  $\mu$ mol/L and 0.040 ± 0.030  $\mu$ mol/L; NO<sub>3</sub>+NO<sub>2</sub>: 0.53±0.65  $μ$ mol L<sup>-1</sup> and 0.60±0.56  $μ$ mol L<sup>-1</sup>; SiO<sub>4</sub>: 2.37±1.62  $μ$ mol L<sup>-1</sup> and 1.75 $\pm$ 1.21 µmol L<sup>-1</sup> in spring and autumn periods, respectively). The NAgDW with  $\sigma_{\theta}$  > 29.30 was characterized by higher nutrient concentrations than the less dense MLIW that overlie it and exhibited less significant variation of the concentrations during the sampling cruises  $(PO<sub>4</sub>: 0.124 \pm 0.041 \mu mol L<sup>-1</sup>$  and  $0.128 \pm 0.039 \mu mol L<sup>-1</sup>;$  $NO_3 + NO_2$ : 2.56 $\pm 0.89$  µmol L<sup>-1</sup> and 2.94 $\pm 0.83$  µmol L<sup>-1</sup>; SiO<sub>4</sub>:  $4.41 \pm 0.89$  µmol L<sup>-1</sup> and  $4.65 \pm 1.52$  µmol L<sup>-1</sup> in spring and autumn periods, respectively).

Additionally, the data available for the four selected areas, namely "frontal area", "north of Lemnos area", "Samothraki anticyclone area" and "LW area" were vertically classified according to the presence of the three main water masses: low salinity waters with a high contribution of BSW occupying the surface water layer of ~20-30 meters, highly saline and warm MLIW occupying water depths between 100 and 400 m ( $28.9 < \sigma_0 < 29.2$ ); and NAgDW, which corresponds to dense waters ( $\sigma_{\theta}$  >29.3) filling the deep basins (>400m) of NAS. The data points that did not fall within the above mentioned definition of the water masses were not used in the calculation of the mean value, e.g. all the data in the transition layer between BSW and MLIW as well as between MLIW and NAgDW. The range and average dissolved oxygen and nutrients concentrations along with the hydrographic properties, for the period 1987-2008 and for all three water masses present in the four selected areas of the North Aegean are shown in Table 2 (spring) and Table 3 (autumn).

During the spring period (Table 2), the lowest salinity value of the BSW mass was found in the frontal area (average value 34.43) while the BSW in the north Lemnos and the Samotraki anticyclone areas had higher salinity (average 35.30 and 35.63, respectively). The LW area occasionally receives BSW and salinity in the surface layer is even higher (average value 36.93). The average phosphate and inorganic nitrogen  $(NO_3 + NO_2)$  content in the BSW in the frontal area (average  $0.038$  and  $0.75 \mu$ mol L<sup>-1</sup>, respectively) was higher than that in the north of Lemnos area (average 0.016 and 0.54 μmol L-1, respectively). Silicate concentrations were almost identical in the two aforementioned areas (2.22 and 2.24 μmol L-1, respectively). The Samothraki anticyclone area revealed similar phosphate and silicate content (average 0.019 and 2.59 μmol/L, respectively) with the north Lemnos area, but relatively lower inorganic nitrogen  $(0.44 \mu mol L^{-1})$ . The surface layer of the LW area had lower phosphate but similar inorganic nitrogen content with the frontal area  $(0.015$  and  $0.763$  µmol  $L<sup>-1</sup>$ , respectively; Table 2).

The MLIW layer in the north of Lemnos area, during spring periods (Table 2), was richer in inorganic nutrients and poorer in oxygen (PO<sub>4</sub>: 0.046  $\mu$ mol L<sup>-1</sup>; NO<sub>3</sub>+NO<sub>2</sub>:  $1.06$  μmol L<sup>-1</sup>; SiO<sub>4</sub>: 1.7 μmol L<sup>-1</sup>, DO: 5.43 mL L<sup>-1</sup>) than the same layer in the LW area (PO<sub>4</sub>:  $0.024 \mu$ mol L<sup>-1</sup>,  $NO_3 + NO_2$ : 0.76 μmol L<sup>-1</sup>; SiO<sub>4</sub>:1.5 μmol L<sup>-1</sup>; DO: 5.48 mL L-1). The increased nutrient content of MLIW in the north Lemnos area was probably due to degradation of organic matter carried by the BSW mass in this area. The MLIW in the Samothaki anticyclone area had a similar content of phosphate with the north Lemnos area but higher inorganic nitrogen and silicate content and lower oxygen  $(PO<sub>4</sub>: 0.045)$  $\mu$ mol L<sup>-1</sup>; NO<sub>3</sub>+NO<sub>2</sub>: 1.5  $\mu$ mol L<sup>-1</sup>; SiO<sub>4</sub>: 2.33  $\mu$ mol L<sup>-1</sup>; DO: 5.29 mL L<sup>-1</sup>). The increased residence time of modified BSW and the influence of the anticyclonic circulation may further enrich the MLIW layer in inorganic nutrients consuming oxygen.

During autumn (Table 3), the lowest average salinity in the BSW mass was found in the Samothraki anticyclone area (34.670). In the BSW layer of this area, high average concentrations of phosphate, inorganic nitrogen and silicate  $(0.046, 0.831, 1.837 \mu mol/L,$  respectively; Table 3) were found. During autumn, the frontal and the Samothraki anticyclone areas displayed entirely the same average concentration of phosphate  $(0.046 \mu \text{mol L}^{-1})$  while the mean inorganic nitrogen concentration  $(0.512 \mu \text{mol L}^{-1})$  was lower and the mean silicate  $(2.124 \mu \text{mol L}^{-1})$  was higher in the frontal area (Table 3). Similarly to the observations during the spring period, the observed small decrease of nutrients in the BSW layer moving from the frontal area towards the north of Lemnos area could be due to their uptake for phy-



*Fig. 4:* Plots of oxygen and inorganic nutrients versus sigma-theta in the North Aegean Sea during spring and autumn for the 1987-2008 period.

toplankton and bacterial production (Table 3). The opposite occurs in the underlying MLIW, at least for the inorganic nitrogen content, where an increase was observed from the frontal to the north of Lemnos area, probably attributed to the degradation of organic matter derived from the BSW layer (Table 3). The increase of nutrients in the MLIW layer in the Samotraki anticyclone area is combined with dissolved oxygen decrease (Table 3).

Deep water (>400m) was found only in three of the

selected areas, since the depths of the stations located in the frontal area are not greater than 160 meters. The maximum depth of our sampling was 1550 m, 900 m and 1050 m in the north Lemnos area, the Samothraki anticyclone and the LW area, respectively. Additionally, the highest density  $(\sigma_{\theta}$ . 29.629) was found during spring in the LW area (Tables 2 & 3) and corresponds at 785 m depth of the MNB-3 station in the Skyros basin in March 1997 (Fig. 2). The highest oxygen concentration (DO: 5.61 mL L-1) was found in the

Spring (March-April-May)										
		<b>Salinity</b>	Pot.Temp.	$\sigma_{\theta}$	<b>D.O.</b>	PO <sub>4</sub>	SiO <sub>4</sub>	$NO3+NO2$		
Layer			$^\mathrm{o}\mathrm{C}$		$\text{mL/L}$	$\mu$ mol/L	$\mu$ mol/L	$\mu$ mol/L		
<b>Frontal area</b>										
	aver	34.432	13.006	25.941	6.08	0.038	2.222	0.749		
	min	30.914	10.459	23.180	5.51	0.005	0.550	0.035		
<b>BSW</b>	max	36.718	15.453	27.879	6.63	0.069	7.195	1.336		
	stdev	1.683	1.582	1.338	0.26	0.018	1.630	0.429		
	$\,$	23	23	23	23	22	22	21		
<b>MLIW</b>	aver	38.743	14.198	29.039	5.52	0.041	1.979	0.710		
	min	38.966	14.959	28.910	4.90	0.017	1.020	0.050		
	max	38.978	15.167	29.183	6.03	0.075	3.032	1.614		
	stdev	0.184	0.537	0.076	0.19	0.017	0.558	0.437		
	$\boldsymbol{n}$	$3\mathcal{9}$	39	39	39	$36\,$	$38\,$	$38\,$		
				North of Lemnos area						
	aver	35.304	12.796	26.660	6.02	0.016	2.243	0.542		
<b>BSW</b>	min	31.689	9.792	24.046	5.22	0.000	0.771	0.013		
	max	37.064	16.555	27.830	6.69	0.052	5.182	3.072		
	stdev	1.159	1.672	0.947	0.27	0.013	1.050	0.606		
	$\,$	$48\,$	$48\,$	$48\,$	$48\,$	$48\,$	$48\,$	47		
	aver	38.728	13.990	29.073	5.43	0.046	1.703	1.055		
	min	38.306	12.520	28.907	4.99	0.003	0.319	0.075		
<b>MLIW</b>	max	38.985	14.962	29.198	5.82	0.241	3.237	2.560		
	stdev	0.160	0.508	0.084	0.17	0.032	0.567	0.496		
	$\boldsymbol{n}$	$77\,$	77	77	75	$77\,$	$77\,$	$76\,$		
	aver	38.962	13.173	29.427	5.08	0.119	4.240	2.509		
	$min$	38.756	12.777	29.272	4.20	0.043	1.145	0.809		
<b>NagDW</b>	max	39.138	14.118	29.551	5.56	0.251	11.431	4.969		
	stdev	0.110	0.292	0.078	0.24	0.037	1.761	0.772		
	$\boldsymbol{n}$	$102\,$	102	102	101	$102\,$	102	101		
				Samothraki area						
	aver	35.633	12.687	26.931	6.03	0.019	2.586	0.444		
	min	34.326	10.401	25.337	5.68	0.003	1.102	0.024		
<b>BSW</b>	max	36.915	16.016	27.866	6.34	0.059	5.763	3.128		
	stdev	0.697	1.942	0.743	0.21	0.015	1.332	0.599		
	$\boldsymbol{n}$	$29\,$	$29\,$	$29\,$	$29\,$	$29\,$	$29\,$	$29\,$		
	aver	38.798	14.452	29.026	5.29	0.045	2.329	1.503		
	min	38.537	13.909	28.907	5.01	0.009	1.005	0.636		
<b>MLIW</b>	max	38.980	15.113	29.183	5.46	0.085	3.616	2.925		
	stdev	0.132	0.440	0.094	0.11	0.019	0.716	0.697		
	$\boldsymbol{n}$	$16$	16	16	16	$16$	$16$	16		
	aver	39.028	13.232	29.469	4.91	0.136	5.383	2.886		
	min	39.004	13.071	29.299	4.67	0.096	2.627	1.777		
<b>NagDW</b>	max	39.059	13.943	29.527	5.12	0.184	7.769	4.129		
	stdev	0.015	0.214	0.055	0.13	0.024	1.364	0.634		
	$\,$	$17\,$	17	17 <b>LW</b>	17	17	17	17		
					area					
	aver	36.913	16.216	27.158	5.71	0.015	2.351	0.763		
<b>BSW</b>	min	34.372	12.388	25.324	5.54	0.005	1.354	0.068		
	max	37.968	18.278	27.884	5.95	0.035	5.884	1.337		
	stdev	0.971	1.761	0.728	0.15	0.010	1.415	0.339		
	$\boldsymbol{n}$	$12\,$	$12\,$	12	12	12	$12\,$	12 (continued)		

**Table 2.** Range and average values of nutrients and oxygen along with the hydrographic characteristics of the different layers and areas of the North Aegean, in spring.

**Table 2** *(continued)* 



**Table 3.** Range and average values of nutrients and oxygen along with the hydrographic characteristics of the different layers and areas of the North Aegean, in autumn.



*(continued)* 





north of Lemnos area at 1450 m depth in late August 1987, after the deep water formation event of the preceding winter. The north of Lemnos area exhibited the lowest average nutrient concentrations during both spring and autumn (Tables 2 & 3). High average oxygen concentrations in the deep basins corresponded to low average nutrient concentrations and vice versa. The N/P ratio in the deep waters varied between 20 and 23 while the Si/P between 35 and 39.

## *Surface layer*

Previous numerical and observational studies (Gerin *et al*., 2014 and references therein) have shown that the Dardanelles plume entering the North Aegean east of the island of Lemnos has a pronounced westward extension with initial pathways branching around Lemnos Island. Two major pathways were identified: an initial transport to the west and then to the northwest between the islands of Lemnos and Gokçeada and a more direct westerly transport south of Lemnos. Zodiatis *et al*. (1996) attribute the bifurcation pathways to wind forcing caused by the summer Etesian winds (northerly direction) enhancing the branch south of Lemnos. The BSW forms a thin, 20-40 m thick surface layer that expands all over the NAS following a cyclonic flow towards the west and the southwest.

The surface (2m) distribution of oxygen and nutrients in February and September 1998 (Fig. 5) allows us to discriminate the different distribution patterns of nutrients and DO between winter and summer according to the dominant circulation. In both periods, **e**levated DO and nutrient concentrations were observed in the vicinity of the Dardanelles. In February 1998, high concentrations of dissolved oxygen and phosphate were depicted northeast of Lemnos island, giving evidence of the northwest direction of the BSW during wintertime. In contrast, in September**,** high concentrations of DO and phosphate were found south of Lemnos, as well as north of Lemnos, confirming the bifurcation of the BSW jet.

Figure 6 represents the average phosphate, inorganic nitrogen and silicate concentrations, as well as the N/P ratio in the BSW mass in the four areas during the period 1987-2008. We selected the samples with salinity values lower than 35.5, in order to investigate the evolution in the core of BSW from the frontal area to the north Lemnos area. During spring, the concentrations of phosphate, inorganic nitrogen and silicate in the frontal area were



*Fig. 5*: Distribution of dissolved oxygen and phosphate at the surface layer of the North Aegean Sea during February 1998 (upper panel) and September 1998 (lower panel).



*Fig. 6:* Average phosphate, nitrate concentrations and N/P ratio, over the period 1987-2008, in the BSW mass, at the selected areas.

higher than in autumn. An important decrease of inorganic nitrogen from 0.83 in spring to 0.49  $\mu$ mol L<sup>-1</sup> in autumn was observed while the decrease, from spring to autumn, of phosphate concentrations from 0.04 to 0.03 µmol  $L^{-1}$  and of silicate from 2.40 to 2.05 µmol  $L^{-1}$  was less important. Our results are consistent with those presented by Tugrul *et al*. (2002) at the exit of the Dardanelles strait for nitrate and phosphate, which exhibit peak values in early winter months and the lowest values in late spring and summer; namely nitrate and phosphate from 0.36 and 0.09  $\mu$ mol L<sup>-1</sup> in winter, are reduced to a third in summer being  $0.12$  and  $0.03$  µmol  $L<sup>-1</sup>$ , respec-

tively. In the north of Lemnos area, phosphate concentration was higher in autumn, while the nitrate concentration was similar for the two investigated periods (Fig. 6).

A clear decrease of both phosphate and inorganic nitrogen concentrations in the BSW mass was detected from the frontal area to the north of Lemnos area for both periods (Fig. 6). The potential explanation for the decreasing nutrient content of the BSW, as it circulates from the frontal area to the north of Lemnos area, is utilization for the production of organic material. The differences in primary, bacterial and copepod production between these areas that have been observed by Siokou *et al*. (2002) confirm the hypothesis that organic matter production leads to progressive nutrient reduction. The increase of the N/P ratio from the frontal area towards the north Lemnos area in spring can be attributed to the greater uptake of inorganic phosphorus compared to that of inorganic nitrogen (Fig. 6).

Due to lack of a sufficient number of samples with salinities lower than 35.5 for the Samothraki anticyclone area and the LW area, we included DO and nutrients data corresponding to salinities up to 36.7 in our calculations. These data correspond to depths of less than 30 meters for the Samothraki **a**nticyclone area and to depths of less than 20 meters for the LW area. The average phosphate, inorganic nitrogen and silicate concentration for the period 1987-2008 in the LW area was higher than in the north Lemnos area during spring (March) but similar during autumn (September). The phosphate concentrations showed important enrichment in the Samothraki area during autumn, slightly exceeding those of the frontal

area in the same period (Fig. 6). However, this is not the case for inorganic nitrogen. Particularly low concentrations of inorganic nitrogen were recorded in the Samothraki anticyclone area in both periods of our observations. The high phosphate concentrations can be justified by the important stratification during summer and the extended period of residence of the BSW. According to Zervakis & Georgopoulos (2002), the Samothraki anticyclone is responsible for increasing the residence time of modified BSW in this area. The possibility of faster and more efficient mineralization of phosphorus relatively to nitrogen from the organic matter (Loh & Bauer, 2000) produced within or carried by the BSW, could also be considered. Generally, a lower N/P ratio was found during autumn in the four areas. The lowest N/P ratio for the two periods was found in the Samothraki anticyclone area (Fig. 6).

#### *Intermediate layer*

The intermediate layer of NAS is dominated by the MLIW lying below the BSW. The distribution of oxygen and nutrients along a transect from the LW area towards the north of Lemnos area passing through the frontal area in May 1997 (Fig. 7) shows considerable differences in nutrient and oxygen values in the intermediate layer. The intermediate layer of the stations located in the north of Lemnos area (I-30, MNB-5, I-36) appear richer in nutrients and poorer in oxygen than the intermediate layer of the stations located in the frontal area (MNB-4, I-64, I-72)

A remarkable increase of both phosphate and inorganic nitrogen content of the MLIW layer is apparent



*Fig. 7:* Dissolved Oxygen and nutrient transects from the LW area towards the north Lemnos area during May 1997.





*Fig. 9:* Temporal variation of the mean depth integrated phosphate, inorganic nitrogen concentrations and N/P ratio in the MLIW (Modified Levantine Water) mass of north of Lemnos area and LW area. Mr=March, Sp=September, My=May, Fb=February, Jn=June, Ap=April, Mr87=March 1987.

My Sp Fb Mr Jn Sp Fb Ap Ap Sp Ap Sp<br>97 97 98 98 98 98 99 00 05 05 08 08<br>LWAREA

My Sp Fb Mr<br>97 97 98 98<br>**LW AREA** 

**MLIW** 

 $\frac{Jn}{98}$  $\frac{\mathsf{Sp}}{98}$  $\frac{Fb}{99}$ 

Mr<br>89

 $\blacksquare$ N/F

-D-Salini

 $\frac{Sp}{89}$ 

Mr<br>97

38.2

38.0

39.4

39.2

39.0

 $38.8 \geq$ 

 $38.6 \frac{1}{6}$ 

38.4

38.2

 $38.0$ 

Ap Ap Sp Ap Sp<br>00 05 05 08 08

from the frontal area towards the north of Lemnos area during both investigated periods (Fig. 8). Similarly, the MLIW layer of the Samothraki anticyclone area appeared more nutrient-enriched in relation to the frontal area. The degradation of sinking organic matter carried by the BSW and/or produced in the surface layer (Frangoulis et al., 2010) seems to enrich the underlying MLIW with inorganic nutrients, as the bifurcated BSW jet follows its route. Recently, a short-term Lagrangian experiment using free-drifting sediment traps following the anticyclonic track of the BSW around Samothraki Island showed that the POC exported from the BSW layer increased progressively along the drifter track **(**Frangoulis *et al*., 2010).

It is interesting to compare the interannual distribution of phosphate, nitrate and the N/P ratio of the MLIW layer between the north of Lemnos area and the LW area (Fig. 9). The MLIW in the north of Lemnos area was much more affected by the overlying BSW and presented higher concentrations of phosphate and nitrate than in the LW area while the N/P ratio was lower (Figs. 8 & 9). The phosphate concentrations measured in the north of Lemnos area were higher than  $0.04 \mu$  mol L<sup>-1</sup> for most of the study period, while the N/P ratio did not exceed 40. According to Tugrul *et al*. (2002), the Marmara Sea acts as a sink for nitrate in the upper layer while it is an additional source of phosphate transported from the Black Sea to the NAS surface layer through the straits system. In general, a decrease in the N/P ratio in the water masses affected by the presence of BSW is observed, which is probably attributed to the higher phosphorus content of BSW in both inorganic and organic forms.

Combining the above findings, a scenario describing the indirect effect of BSW on the nutrient levels of the intermediate layer in the north Lemnos area can be proposed. The BSW jet exiting the Dardanelles strait contains slightly more phosphate than the surrounding oligotrophic waters of NAS (Fig. 5), and the BSW layer of the frontal area exhibits higher phosphate content in relation to the north of Lemnos area (Fig. 6). The organic matter produced in the BSW layer as it propagates to the north of Lemnos area might be rich in phosphorus. The degradation of the sinking organic matter that is enriched in phosphorus leads to increased concentrations of inorganic phosphorus in the MLIW layer of the north of Lemnos area compared to the frontal area. Therefore it appears that the inorganic nutrients together with those derived from the degradation of organic matter have the potential to trigger, support and enhance biological activity in the region. The BSW plume entering the NAS, although rather poor in inorganic nutrients, constantly and uninterruptedly provides small amounts of nutrients, which are transformed and redistributed in the water column and play a key role in the production capacity of the Aegean.

The Samothraki anticyclone area revealed the highest nutrient concentrations among the study areas (Fig. 8). It is interesting to point out that MLIW has the lowest concen-

*Deep layer* Historical hydrographic data suggest that during the last decades there was extensive production of dense wa-

ter in the North Aegean Sea on two occasions: the winters of 1987 and 1992-1993 (Theocharis & Georgopoulos, 1993; Zervakis *et al*., 2000). Intermediate-intensity formation took place in 2008 and minor events in the winters of 2001 and 2005 (Zervakis *et al*., 2009). The high resolution of nutrients and DO data obtained during the periods after the above major dense water formation events, i.e. periods of stagnation, permitted to follow the formation and the step by step evolution of oxygen consumption and nutrient regeneration in the deep layers of the different basins of the NAS.

trations of inorganic phosphorus in the LW area, while the inorganic nitrogen content of this area is higher, compared to the frontal area, mainly in autumn (Fig. 8). This is related to the presence of the overlying BSW in the frontal area and its absence (for the most of the time) from the LW area.

The surveys carried out in the NAS during spring (March) and autumn (August-October) 1987 testified a major formation event during late winter 1987. The dense water formation process over the Samothraki and Lemnos plateaus at the beginning of March 1987 has been presented in detail in Theocharis & Georgopoulos (1993). The dramatic increase in the oxygen content below 200 m that was recorded between March and August 1987 in the Lemnos basin (Fig. 10a) and between March and August 1987 in the north Sporades basin (Fig. 11a) constitutes additional proof of the harshness of this formation event. Furthermore, the observed increase of oxygen was followed by a corresponding decrease of the nutrients content (Figs. 10 and 11). In August 1987, in the Lemnos basin, the very dense deep water ( $\sigma_{\theta} = 29.43$ ) had the following chemical characteristics: DO= 5.6 mL  $L^{-1}$ , PO<sub>4</sub> = 0.07  $\mu$ mol L<sup>-1</sup>, NO<sub>3</sub> = 1.6  $\mu$ mol L<sup>-1</sup>, SiO<sub>4</sub> = 2.7  $\mu$ mol L<sup>-1</sup> (Fig. 10 left panel). Slightly lower densities and dissolved oxygen concentrations, during the 1987 formation were observed in the Athos basin ( $\sigma_{\theta}$ =29.36, DO=5.3 mL L<sup>-1</sup>; Fig. 12 left panel) and in the north Sporades basin ( $\sigma_{\theta}$ =29.35, DO=5.5 mL  $L^{-1}$ ; Fig. 11 left panel), indicating that a more severe formation took place in the Lemnos basin. However, the variation in oxygen and nutrient concentrations between March and August 1987 was more important for the deep layers of the north Sporades basin (Fig. 11, left panel). The increase of oxygen in the deep layers of the north Sporades and Lemnos basins reached  $0.63$  and  $0.45$  mL  $L^{-1}$  of DO, respectively, while the accompanying decrease of nitrate was 1.39 and 0.95  $\mu$ mol L<sup>-1</sup>; of silicate 4.06 and 2.25  $\mu$ mol  $L$ <sup>-1</sup> and of phosphate 0.045 and 0.040 µmol  $L$ <sup>-1</sup>. The observed differences, in the oxygenation degree of the deep basins is due to the fact that the north Sporades basin was occupied by 'older' waters (lower oxygen - higher nutrient content) prior to the formation event. Our observations



*Fig. 10:* Evolution of dissolved oxygen, inorganic nutrients (mean depth integrated values) and N/P ratio in the deep layer of the north Lemnos basin from November 1986 to September 1989 (left panel) and from March 1997 to September 2008 (right panel). Nv=November, Mr=March, Ag=August, Oc=October, Sp=September, My=May, Jn=June, Ap=April, Nv86=November 1986.

carried out over this period, showed that the degree of oxygenation and the nutrient content in the deep basins of the NAS differ considerably, indicating limited communication between the basins, the possible existence of several source water masses of different composition, and probably the different intensity and timing of deep water formation (Souvermezoglou & Krasakopoulou, 2002; 2003).

The N/P ratio (calculated from the integrated nitrogen and phosphorus concentrations) of the sinking water in the north Lemnos basin, detected in August 1987, (Fig. 10d) is about 24. It is interesting to remark that the deep waters formed during the same period had a similar N/P ratio in the other basins of the NAS. This ratio was about 23 in the Athos basin (Fig. 12d) and about 19 in the north Sporades basin (Fig. 11d).

The lack of oxygen and nutrients data between 1989 and 1997 did not permit us to define the exact timing of the next deep water formation event but, according to Zervakis *et al*. (2000), the extremely strong winters of 1992-1993 caused massive deep water production. The characteristics of the deep water in the north Lemnos basin found in March 1997 (about four years after the formation), were  $\sigma_{\theta}$  ~ 29.54; DO ~ 5.0 mL L<sup>-1</sup>; PO<sub>4</sub>: 0.12 μmol L<sup>-1</sup>; NO<sub>3</sub>: 3.4  $\mu$ mol L<sup>-1</sup>; SiO<sub>4</sub>: 5.1  $\mu$ mol L<sup>-1</sup> (Fig. 10 right panel). These values suggest the presence of a water mass equally old as the water mass found in the same basin in March 1987 just



*Fig. 11:* Evolution of dissolved oxygen, inorganic nutrients(mean depth integrated values) and N/P ratio in the deep layer of the north Sporades basin from November 1986 to September 1989 (left panel) and of the Skyros basin from March 1997 to September 2008 (right panel). Nv=November, Mr=March, Sp=September, Jn=June, Ap=April, Nv86=November 1986.

before the previous formation event (Fig. 10, left panel). The increased density of 1997 compared to 1987 provides further evidence of the very intense formation event during the winters of 1992 and 1993, related to the intensification of the Eastern Mediterranean Transient (EMT) (Zervakis *et al*., 2000; Velaoras & Lascaratos, 2010). The gradual decrease of oxygen concentrations and the concomitant increase of nutrients during the period from March 1997 to February 1999 indicate that the deep waters are in a stagnation phase (Fig. 10, right panel).

Based on the average oxygen consumption and nutrient regeneration rates for the periods 1987-1990 and 1997- 1999, we estimated that the newly formed water in winter

1993 should have an oxygen concentration of about 5.75 mL L<sup>-1</sup>, phosphate  $\sim 0.02$  µmol L<sup>-1</sup>, nitrate  $\sim 0.55$  µmol L<sup>-1</sup> and silicate  $\sim$ 1.5 µmol L<sup>-1</sup>. The period from March 1997 to September 2008, was characterized by significantly elevated concentrations of phosphate, nitrate, silicate and considerably lower concentrations of oxygen (right panel of the Figs 10, 11  $&$  12) compared to the period of August 1987 to September 1989 (left panel of the Figs 10, 11 & 12). The unexpected high densities ( $\sigma_{\theta}$ ~29.54) found in March 1997, four years after the last deep-water formation episode of 1993 (Figs 10e, 11e & 12e), suggest that extraordinarily dense NAgDW was produced under the forcing of the extremely strong winters of 1992 & 1993.



*Fig. 12:* Evolution of dissolved oxygen, inorganic nutrients (mean depth integrated values) and N/P ratio in the deep layer of the Athos basin from March 1987 to September 1989 (left panel) and from March 1997 to March 2008 (right panel). Nv=November, Mr=March, Sp=September, Jn=June, Ap=April, Nv86=November 1986.

Zervakis *et al*. (2000) suggest that the initiation of the EMT took place in the NAS in the winter of 1986/1987 and was intensified by formation episodes in 1992/1993. Important quantities of organic matter transported in the deep basins after the strong flushing, caused apparently high oxygen consumption and high regeneration of inorganic nutrients (Figs 10, 11 & 12). However, it should be noted that the oxygen consumption rates varied significantly between the different deep basins of the North Aegean. This can be attributed to the irregular contribution of BSW to the water masses formed on the different shelves of the NAS as well as to the different composition and quantity of the regenerated organic matter. During

stagnation periods, in parallel with local dissolved oxygen consumption by organic matter oxidation, its concentration in the deep layer of the basins also depends on the turbulent diffusive flux of dissolved oxygen. The higher eddy diffusivity was estimated for the Lemnos basin (Zervakis *et al*., 2003) and the different intensity of mixing among the basins affects the decay rate of DO in each basin. The most important consumption rate (about 13.5 mmol  $O_2L$ <sup>1</sup>yr<sup>1</sup>) was observed in the Lemnos basin during the period 1987-1989 (Souvermezoglou & Krasakopoulou, 2002).

During the winter of 2008, after a limited intensity formation event (Zervakis *et al*., 2009), newly formed water was found in the north Lemnos basin (Fig. 10e), while it was

not observed in the other sub basins of the North Aegean Trough (Figs 11e and 12e). This recent formation event in the north Lemnos basin was also apparent on the total inorganic carbon  $(C_T)$  distributions since the  $C_T$  concentrations in the deep layer of the north Lemnos basin were lower than the corresponding concentrations in the order basins (Souvermezoglou *et al*., 2010).

The water formed in the north Lemnos basin ( $\sigma_{\theta}$ =29.38, Fig. 10e) in winter 2008, had similar density with that formed in the same area during the winter of 1987 ( $\sigma_{\theta}$ =29.43, Fig. 10a). Despite their similar densities, the chemical composition and the N/P ratio of the water formed in the north Lemnos basin in 2008 (Figs 10f, 10g and 10h), differed from that formed in 1987. In the north Lemnos basin, the dissolved oxygen content of the sinking water was lower, while the nutrient concentrations were higher in 2008. The N/P ratio of the sinking water was around 6, a value much lower than that of 1987 (Figs. 10d & 10h).

The data gathered in March 2008 in the Skyros basin suggest the presence of partially ventilated water (Fig. 11e). However, bottom layers are still occupied by stagnant NAgDW of higher density ( $\sigma_{\theta}$ =29.48), lower oxygen (4.7 mL  $L^{-1}$ ), and higher nutrients (phosphate 0.21 µmol  $L^{-1}$ , nitrate 1.8  $\mu$ mol L<sup>-1</sup>, silicate 2.8  $\mu$ mol L<sup>-1</sup>) compared to those of the north Lemnos basin (Figs 11e, 11f, 11g,10e, 10f, 10g). It should be noted that usually the surface waters of North Skyros basin, are not strongly affected by the presence of the insulating BSW and consequently the bottom waters of this basin are denser and saltier than the deep waters of the north Lemnos basin (Zervakis *et al*., 2000). The N/P ratio of the deep waters of the Skyros basin in March 2008, approximately 8 (Fig. 11h), was as low as in the north Lemnos basin **(**Fig. 10h). If we examine more thoroughly the decrease of the N/P ratio, it becomes apparent that it has been more affected by the increased values of phosphate.

The injection of the inorganic nutrients stored in the deep basins, via the deep water formation processes may provide the basis for extensive new production in the NAS. Unfortunately, the ecosystem response to the dense-water formation events of 1987 and 1992 was precluded due to lack of relevant data for that period, including satellite chl-a images. However, Zervakis *et al*. (2007) have searched for evidence in the upper layers of the food chain by analyzing the small pelagic fish stocks (sardine and anchovy), which are known to be the most sensitive to changes in environmental conditions, as well as the anchovy predator, i.e. mackerel. Their analysis showed that the fishery landings increased significantly over the 1-3 year period that followed the major densewater formation events of 1987, 1992 and 1993.

## **Conclusions**

Despite the large amount of nutrients and dissolved oxygen data collected during several projects in NAS, their partial analysis (i.e. for each project) did not provide a satisfactory hypothesis for the nutrient regime supporting the observed increased production compared to the south Aegean Sea.

The attempted detailed analysis of available data from 1986-2008 showed clearly that the continuous supply of even small quantities of nutrients by the BSW is able to affect, in a direct and/or indirect way, the nutrient regime of the area. The observed reduction of inorganic nutrients in overlaying BSW towards its north-west route and the increase of nutrients in the underlying intermediate MLIW layer, as well as the POC exported from the BSW layer (Frangoulis *et al*., 2010) contribute to confirming the hypothesis about the role played by BSW as regards enhanced productivity in the NAS reaching the higher trophic levels. More detailed studies at temporal scale and including parallel nutrient measurements (inorganic and organic) and plankton production could elucidate the biochemical processes and further advance the "solution of the enigma". Previous studies hypothesized a direct effect of the outflowing BSW on the pelagic food web (Stergiou *et al*., 1987; Siokou-Frangou *et al*., 2002; Frangoulis *et al*., 2010). Interestingly, our analyses showed the role played by BSW (through its buoyancy) in the replenishment of the deep layers water with oxygen during the events of deep water formation (NagDW). Nutrient enrichment of the deep layers was also revealed during the stagnation periods, which could be injected in the euphotic layer during the formation processes. The impact of enhanced nutrient concentration on the pelagic ecosystem is far from being clearly proven and further investigations are necessary. This becomes more important in view of the probable effects of climate change on BSW density (buoyancy) and thus the hydrology of the NAS.

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