Observations on Continuous Nutrient Monitoring in Venice Lagoon

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***Abstract*- The deployment of WARMER (WAter Risk Management in EuRope) continuous monitoring platform at the Venice Lagoon was the second field test (duration of the field test: ca. 3 months) of the project and this study was conducted with the co-operation of Magistrato alle Acque di Venezia which maintains a continuous monitoring network (SAMANET) with ten stations. SAMANET stations are geared to measure number of parameters (pressure, temp., conductivity, salinity, DO, DO%, pH, Redox, Chlorophyll-a, Turbidity) continuously. In addition to above mentioned parameters WARMER pontoon is equipped with a nutrient analyser to measure dissolved nutrients continuously (SRP, nitrite, nitrate and ammonia). During the field test WARMER project intended to test the newly developed sensors for nutrients and metals. The pollution control division of the Magistrato alle Acque (SAMA) performed parallel field and laboratory controls, both through the continuous monitoring stations and nutrient laboratory analyses on samples collected in the Venice lagoon.**

Venice Lagoon is a large, eutrophic, shallow, turbid water body (ca.500 km²) with successive algal booms during the year with large nutrient fluctuations during the summer months. During the field test, WARMER monitoring pontoon was moored at the following SAMANET stations for a period of 3 - 4 weeks at each station, starting from mid May till end of August 2009 and samples were taken from 1m depth for continuous analysis:

- **Ve-4 Fondamenta Nuove: near the city, by the side of Murano Island; affected by pollution from boat traffic and Murano glass industry;**
- **Ve-7 Palude di Cona: at the outlet of the Dese river; brings point and diffused pollution from watershed;**
- **Ve-5 Porto Marghera: at the outlet of Porto Marghera industrial area, one of the heavily polluted sites.**

The lagoon with this well established continuous monitoring network, infrastructure with co-operating laboratories makes it an ideal location for field testing of nutrient probes. The results of this three months field experiment are presented in this paper with main focus on continuous nutrient measurements.

Keywords: Continuous water quality monitoring, in-situ nutrient analyzer, diffused and point-source pollution, recycling, fluxes, eutrophication.

I. INTRODUCTION

General description

The Venice Lagoon is the largest in Italy and the Mediterranean [1] with a total area of approx. 550 km^2 (50 km long and 8-14 km wide) and its morphology consists of shallows, tidal mud flats (140 km^2), salt marshes, islands and a net work of channels [2]. It is connected to the Adriatic Sea by means of three openings which function as inlets, allow port activities as well as tidal water exchanges. There is a dense network of natural and artificial canals to facilitate rapid transport within the estuary and three major channels originating from the inlets, divide the lagoon into four sub-basins. The mean depth is one meter at the flats, while it reaches up to 10 m in the channels connecting the 3 inlets. The Venice Lagoon is characterized by a high concentration of human activities in and around the lagoon [3]. Two main cities (Venice, Chioggia) and number of towns and villages are distributed around its perimeter and on some islands which account for 400,000 residents while tourists visiting per year are around 14 million.

The city of Venice is situated on an island in the middle of the lagoon and a large industrial complex (petrochemical, metallurgy, energy) located at the western edge (Porto Marghera) and both contribute heavily to the pollution of the estuary. In 1999, 117 pollution sources in Porto Marghera area were identified and classified by Magistrato delle Acque, most of them are treated by Fusina industrial waste water treatment plant. The main sources of point and non-point source pollution are industrial and agricultural activities around the lagoon which contribute contaminants to the lagoon via effluent discharge and run-off. In addition to this, Venice urban sewage with its associated toxicants without treatment is discharged directly into canals of Venice which enter the lagoon and subsequently coastal waters.

Due to these reasons, the water quality in the lagoon has been subjected to several studies during the recent past and a continuous monitoring network with 10 stations (SAMANET) has been established in the lagoon. Recent study shows that primary production in the lagoon amounts to 5.5t N/day, supported mainly by nitrate. More than 75% of this flux is recycled to ammonia, directly or through mineralization; 14% is exported to the Adriatic Sea, 6% transferred to higher level. Recycling processes generate a daily flux of 4t N/day which is added to 11t N/d coming from external sources. Sediments contributed to this flux more than half, and detritus ca. 25% [4,13,14]. All this information confirms the importance of continuous data records which could be used to develop better models useful for management of the lagoon [4,6].

Objectives

The WARMER project (duration: Sept. 2007- Aug. 2009), was aimed at developing a real-time water quality monitoring system to be used as a Risk Assessment tool, to support the management of hazardous pollution events in coastal areas, large rivers and lakes.

A set of modular multiparametric in-situ probes for chemical analysis using different analytical technologies and miniaturized sensors were studied and designed [5]; two of them were developed and integrated in a field deployable monitoring platform to detect nutrients and heavy metals. Field measurement data were linked to remote sensing Earth observations (EO) using a Web based management system.

The deployment of WARMER continuous monitoring platform at Venice Lagoon was the second field test after the first experiment conducted in England at Henningfield reservoir & Blackwater estuary. In Venice Lagoon there is a well established continuous monitoring network, infrastructure with co-operating laboratories, research institutes and universities, all these makes it an ideal location for the test.

Venice Lagoon is a large, eutrophic, turbid water body with successive algal booms during the year [3,9,12]. These developments are helpful for some of the remote sensing, tasks under taken by NERSC (Nansen Environmental & Remote Sensing Centre, Norway; a WARMER project partner) in attempting to use it as a tool to drive and calibrate models using chlorophyll-a, total suspended solids data and color spectra. This specific activity is also conducted annualy by the ICT department of Magistrato alle Acque using a self-developed heuristic model.

II. MATERIALS AND METHODS

Study sites

In Venice lagoon , Magistrato alle Acque di Venezia (Venice Water Authority) maintain the ten SAMNET monitoring stations located at strategic points for continuous monitoring of the following parameters: temperature, pressure, electrical conductivity, salinity, dissolved oxygen and oxygen saturation, pH, redox potential, chlorophyll-a and turbidity. From these stations three stations were selected (Fig. 2) for the WARMER field experiment based on following considerations:

- Ve-4 Fondamenta Nuove: it is located close to the Venice city and Murano Island; the main pollution sources are from boat traffic and Murano glass industry.
- Ve-7 Palude di Cona: this brackish water protected area is located in the vicinity of the Venice airport, and close to the outlet of the Dese river, which brings point source and diffused pollution from the watershed.
- Ve-5 Porto Marghera: it is located close to an outlet of the main channel serving the industrial area of Porto Marghera, which is a main shipping route.

Monitoring platform

The water quality monitoring platform developed for WARMER was designed as a catamaran system (430 cm length, 220 cm width) comprised of two floating aluminum cylinders connected by a horizontal aluminum structure on which a platform is mounted. Two water proof boxes mounted on the platform contain the data acquisition and remote data transmission unit, two sets of 100 Ah 12 Vcc batteries, two power voltage regulators and some accessories like DI water reservoir and waste container for the chemical probes. The platform is self-powered by 4 x60 W photovoltaic panels and a 4A power, supplementary wind generator. At each site, the platform was moored on the existing vertical anchorage poles nearby each SAMANET water quality monitoring station (Fig. 1).

Nutrient probe and supplementary instrumentation

At the study site, the Deep-sea Probe Analyzer (DPA, SYSTEA, Italy) was directly moored at 1 m depth in water through a basement position of the monitoring platform. The ambient water column was sampled continuously at 2 h intervals. The sample filtered through a filtration device (10 µm screen) before entering the analyzer and the and during cleaning cycles the filtering unit is flushed several times with compressed air to prevent any back clogging of the filter. The DPA was programmed for sequential measurement of four nutrient parameters, orthophosphate, ammonia, nitrate, nitrite and the procedures used are described in [7]. The following supplementary instruments were mounted on the platform to provide additional information from the ambient environment during the experiment: temperature, conductivity, salinity, pH, turbidity, dissolved oxygen, chlorophyll and blue green algae, (YSI 6600 V2-4); a fluorometric probe for the detection of polycyclic aromatic hydrocarbons (PAH) detection (Trios EnviroFlu, Germany), a water current and velocity single point over 3 axis sensor (Sontek Argonaut MD 3D, USA), a compact meteorological station including air temperature and pressure, wind direction and speed, solar radiation and a rain gauge.

Fig. 1 WARMER water quality monitoring platform moored nearby VE-5 station

Fig. 2 Field test experiment sites (VE-4 F. Nuove, VE-7 P. di Cona, VE-5 P. Marghera)

III. RESULTS AND DISCUSSION

The first field experiment was conducted at the Ve-4 Fondamenta Nuove from 13th June 2009 till the end of the month but there were interruptions due to damages to the pontoon from strong wave action arising from rapid boat traffic, as the station is situated close to a main shipping route. The pontoon was repaired before the second experiment which started on 7th June at Ve-7, Palude di Cona and terminated on 3rd August. The duration of the third experiment at Ve-5 Porto Marghera was from 5th – 31st August (the data only up to 25th Aug. are presented here). The nutrient data continuous measurements (for PO_4-P, NO_3-N, NH_4-N, NO_2-N analyzed at 2 h intervals) along with relevant supplementary data (tide, electrical conductivity, dissolved oxygen and chlorophyll-a; measured continuously at 15 min. interval) from the deployments at the stations Ve-7 and Ve-5 are presented in Fig. 3 and 4 respectively.

During the period of investigation, more or less similar number of samples were analyzed for nutrients at both stations (Ve-7, Palude di Cona, n = 240; for Ve-5 Porto Marghera, n = 218). Dissolved nitrogen and phosphorous concentrations show quite large differences, indicating contrasting influences of the loading patterns characteristic for the two stations. Dissolve phosphate values are fairly high at Ve-7 (range 6- 275 µg/L, median 25 µg/L), compared to Ve- 5 (range 4-104 µg/L, median 23 µg/L), reaching a relatively high level, 11 times higher than the median concentration. In contrast, Porto Marghera (Ve-5) receiving industrial effluents as well as domestic sewage show a lower concentration but it is interesting to note that both stations show similar median values(23 and 25 µg/L resp.), indicating that Ve-7 probably confronted with intermittent nutrient pulses from Dese, a major river emptying close to the station.

Dissolved nitrogen measured as ammonia, nitrate and nitrite (N-NOx) show more or less a similar pattern, Ve-7 recording higher concentrations compared to that of Porto Marghera. Both stations record similar ammonia values which are relatively high: Ve-7, (range 6-207 µg/L, median 58 µg/L) and at Ve-5 (range 4-205 µg/L median 81 µg/L), but with higher median concentrations at Marghera. Both Ve-7 and Ve-5 seems to receive similar N-NOx inputs; (Ve-7, nitrates: range 4- 320, median 44 µg/L; Ve-5, range 20-280 µg/L, median 60 µg/L). Nitrite concentrations at both stations show close similarity with maximum values 23 and 27 µg/L and median concentration of 8 and 9 µg/L (Ve-7, Ve-5 resp.).

During this investigation, routine grab samples were taken from both stations for chemical analyses by Magistrato alle Acque di Venezia (Venice Water Authority) at their laboratory and the complete results are available for Ve-7 stn. The samples were taken on four consequent days at the inception of the experiment followed by weekly sampling. Although the sampling times doesn't coincide exactly with the DPA sample intake for continuous analysis (the lag time is ca. 55 min), the lab results are quite in agreement with the continuous monitoring data. We compared continuous monitoring data, pooled during an hour from the time of grab-sample collection and with laboratory analyses and the results show significant correlations for: N-NOx (R^2= 0.95), NO2-N (R^2= 0.98), NH_4-N (R^2= 1.00); correlation coefficient for PO4-P is lower but they are positively correlated (R^2= 0.62) and within the 95% confidence limits.

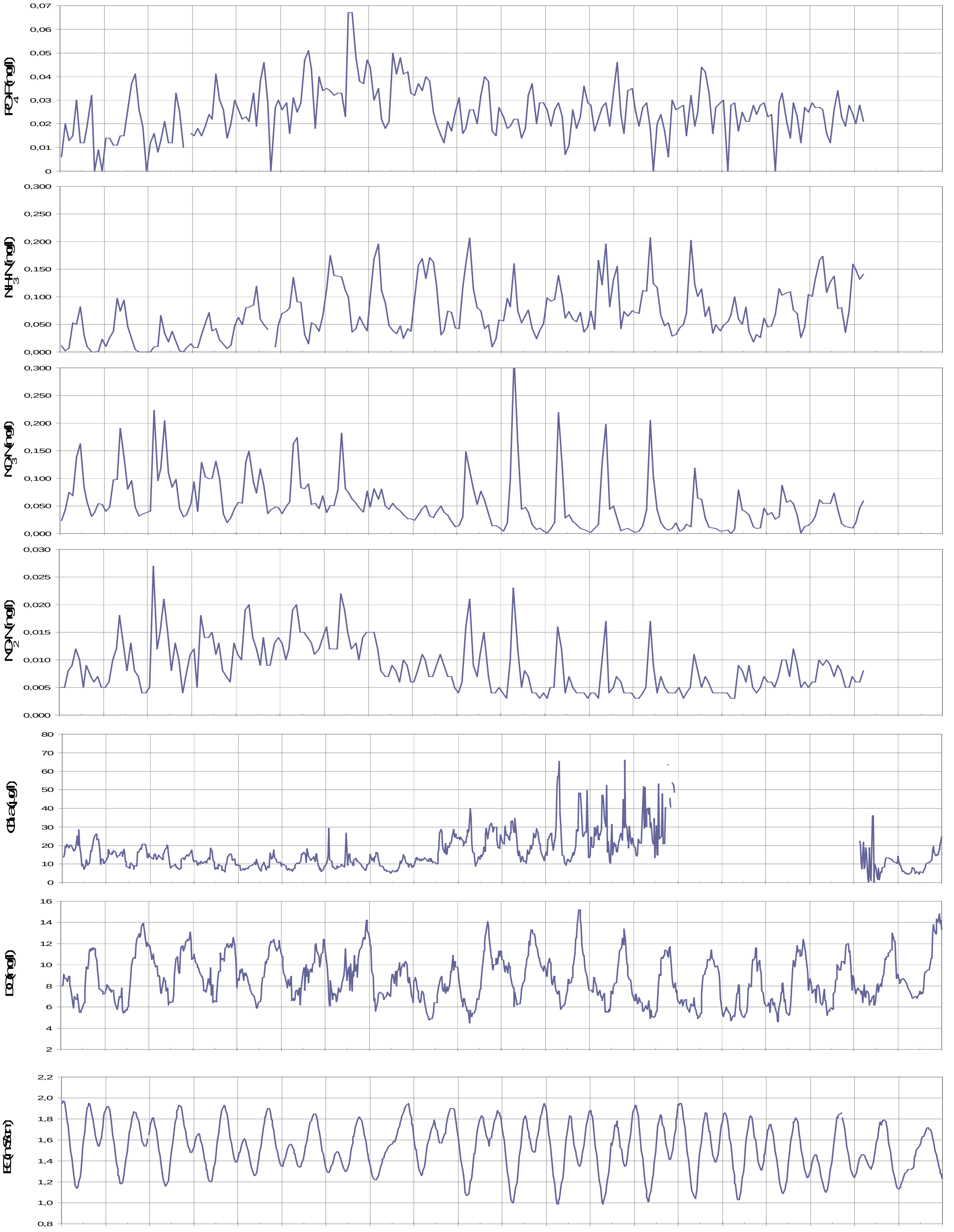

Fig. 3. The nutrient dynamics at the station VE-7 – Palude di Cona, form 10 – 30 Aug. 2009 showing diurnal variations in dissolved nitrogen (NO3-N, NO2-N, NH4-N; mg/L) and phosphate (PO4-P, mg/L). The ancillary data collected show the accompanying variations in algal biomass (as chlorophyll-a, in µg/L), dissolved oxygen (mg/L) and changes in electrical conductivity (mS/cm).

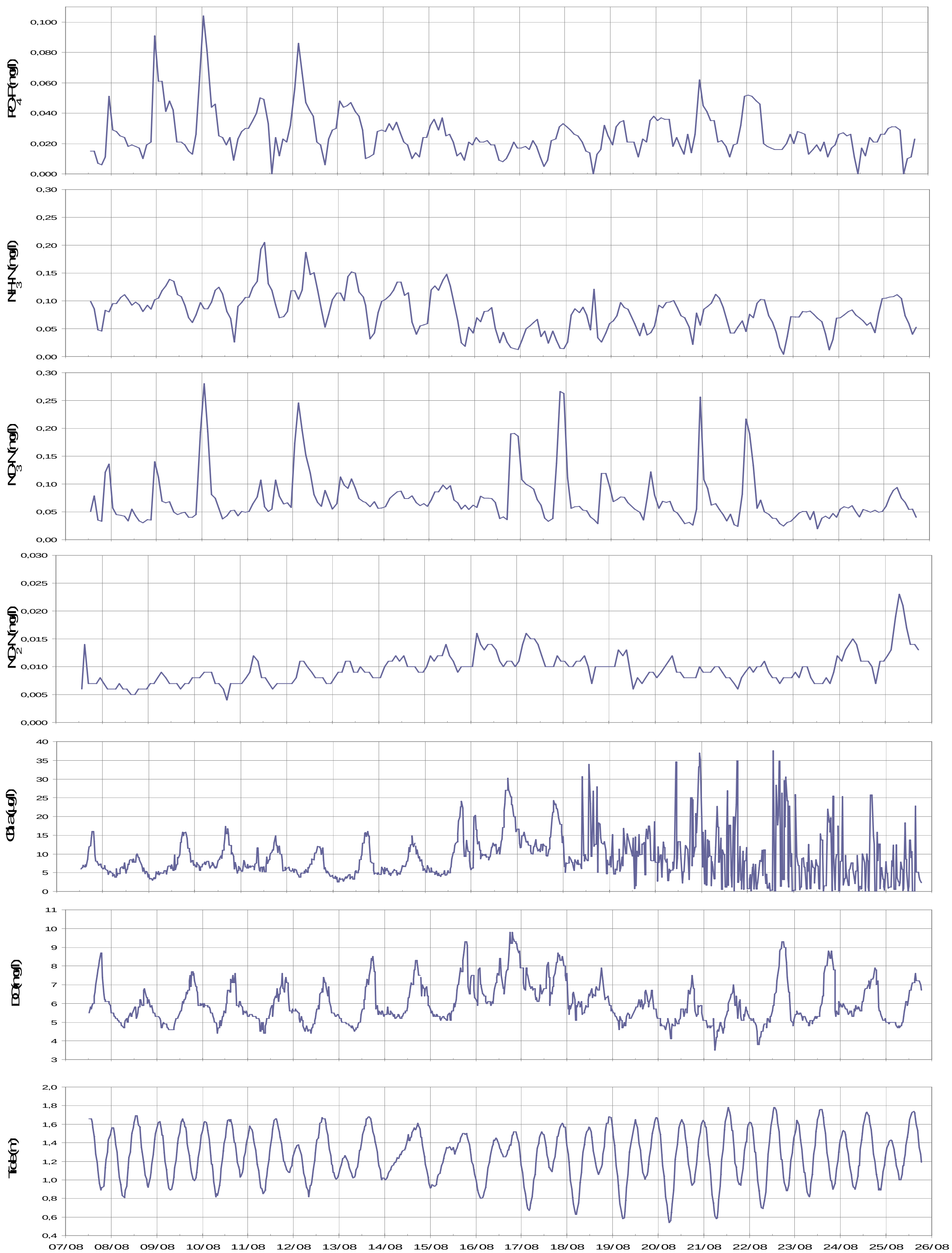

Fig. 4. The nutrient dynamics at the station VE-5 – Porto Marghera, from 07 – 25 Aug. 2009 showing diurnal variations in dissolved nitrogen (NO_3-N, NO_2-N, NH_4-N; mg/L) and phosphate (PO_4-P, mg/L). The ancillary data collected show the accompanying variations in algal biomass (as chlorophyll-a, in µg/L), dissolved oxygen (mg/L) and tide (m) showing the influence of hydro dynamics.

The continuous measurements of nutrients with other ancillary parameters (Fig. 3, 4) show the contrasting influences exerted on the lagoon by the watershed, sea and the metabolic activities going on in the lagoon. These produce gradients of physical and chemical variables through water movement (tidal effects), salinity, and nutrient dynamics are coupled to on-going biological activity and sediment nutrient fluxes. The characteristic diurnal variations shown in Fig.3 and Fig. 4, reflect the daily pattern of on-going nutrient transformations in the water column with different intensity and are governed by several environmental parameters.

During the day, from late morning until sunset dissolved oxygen concentrations show a characteristic pattern (Fig. 3, 4) and these coincide with the chlorophyll-a peaks. Oxygen is liberated during the photosynthesis and it approaches a maximum at the period of peak primary production (up to 14-15 mg/L). The high chlorophyll values observed in both stations show the fluctuations of the phytoplankton biomass (Ve-7: range 3- 66; median 13; Ve-5: range 6-38, median 7.5 µg/L) due to continuous mixing of the shallow water column (through tidal affects, wave action). Coupled to these are changes in the transformations in the dissolved nutrients. During the production peak (afternoon), dissolved nutrients taken are rapidly taken up by both macroalgae and phytoplankton. Thus dissolved nutrients peaks too coincide with chlorophyll-a peaks after a short lag but show a similar distribution pattern. During photosynthesis, the P requirements are met with by phosphate and N preferably ammonium (ammonium preference by algae, over nitrate). The latter can be quite evident from the dynamic changes observed in the ammonium and NO-x peaks through nitrification and denitrification processes (Fig. 3, 4). When peak production in the water column coincides with low tide the rapid changes taking place in nutrients become quite evident; the nitrate get transformed very fast to ammonium as shown in Fig. 3 (Ve-7) during 16-18 July and in Fig. 4 (Ve-5) from 13-15. Another factor could be the fluxes from sediments (both natural man-made). When anoxic bottom sediments are brought to suspension by strong wind and water movements, change in redox potential favor fast transformation of nitrate to ammonia. In general, in the lagoon, spatial distribution of water quality variables is mostly driven by the dispersive processes and is correlated to salinity [

Scavenging of nutrients is not limited to phytoplankton. The large macroalgal biomass and the active heterotrophic communities are other competitors for the common nutrient pool. The on going research show that there is a rapid increase of the nitrophilic Ulvales (*Ulva, Enteromorpha*), which invaded large portion of the lagoon since early eighties aggressive competitors to the common nutrient pool [3, 9, 10-12], in fact they inhibit phytoplankton production. The main cause of increase of *Ulva* boom in the lagoon probably due to the increase of nutrients, and particularly nitrogen compounds [3,6]. The major tributaries (total- 11) entering the lagoon (e.g. Dese, near Ve-7) bring annually ca. 35 $m^3 s^{-1}$ of fresh water into the lagoon and the total nitrogen and phosphorous loads entering the lagoon are ca. 4000 t N yr^{-1} and 230 t P yr^{-1} respectively [13, 14] and such large quantity of nutrients entering the lagoon naturally drive the system towards eutrophy. The trophic index (TRIX) values [15] range from 1 (oligotrophy) to 10 (hypertrophy) and, for water body in good trophic state, it should not exceed 5. For Venice lagoon, TRIX values falls within the range from about 3 to 7.5 [6].

IV. CONCLUSIONS

Temporal trends in nutrient dynamics in the lagoon could be accurately and better interpreted by the use of continuous monitoring data rather than with weekly or monthly series of grab sample information [16,17]. Continuous, high frequency data is a useful source of information for the understanding of seasonal chemical and biological changes in the in the lagoon. Integration of continuous nutrient monitoring to the existing real-time monitoring system operating in the lagoon offers an improved monitoring design in order to facilitate comprehensive analyses of changes in trends, patterns in space and time. They are useful to estimate nutrient dynamics, primary and secondary production as well as to assess C, N, P fluxes associated with biogeochemical cycling and toxicant transport.

More and better water quality data is needed for to calculate Maximum Permissible Loading in all EU countries (or Total Maximum Daily Loads). We need better data to assess trends, to determine current status of waters and their impairments, and to test water quality models. The European water framework directive (WFD) extends the requirement for close monitoring of the coastal waters because all land-based inputs of pollutants pass through the coastal zone to the open waters [4, 5,18,19]

Data and models show that eutrophication of the Venice Lagoon has improved in recent years [4,11]. Total P concentration has decreased from 40 to 15-20 µg/L which is well below the target goal [6]. Such success in the Venice Lagoon and similar locations elsewhere (e.g. Lake Erie, U.S) demonstrate the importance and utility of high quality data gathering and modeling efforts.

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