39. Data time-series formation and studies of long-term trends for marine water quality indicators in the coastal zone regions of the north-western Black Sea

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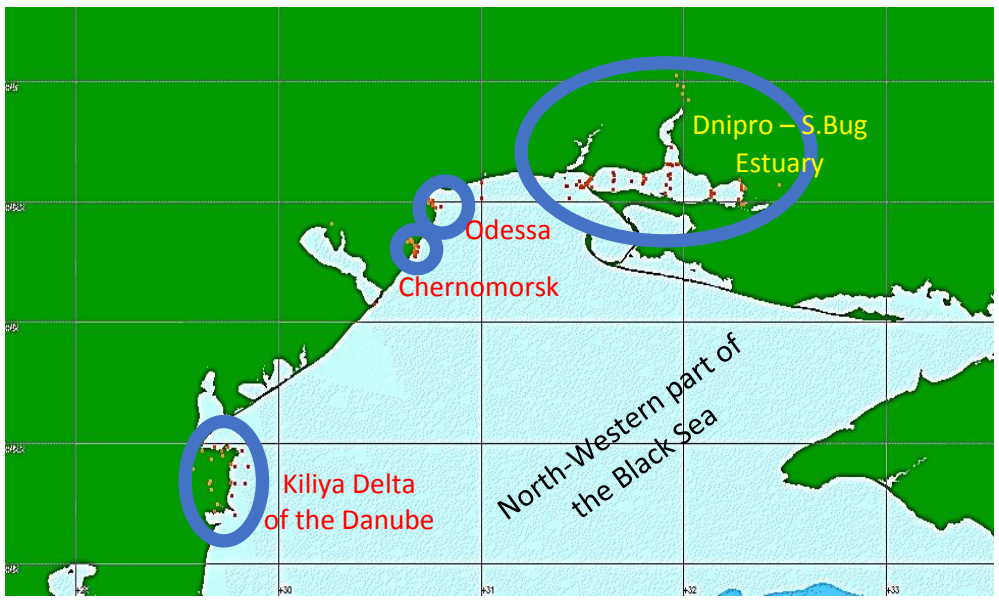
1) Introduction. Variability of hydrological and chemical indicators in the marine coastal and estuarine waters is the product of both natural and anthropogenic influences. Multi-annual (decadal) trends may be connected with climate change effects (global warming, fresh water inflow, sea level rise, acidification, etc.) as well as systematic reducing/increasing of pollutant emissions or improvement/worsening of waste water treatment. The aim of this work was to identify linear trends in water quality indicators by means of non-parametric statistical testing with account of serial correlation of time series. Results are demonstrated for the important sites of the Black Sea coastal zone: harbor of city Odessa; harbor and seashore of city Chernomorsk (former Ilyichevsk); Kiliya delta of the Danube river.



4) Further analysis considers three groups of the sea water quality indicators that are regularly researched during 1992 – 2016, i.e. for them a homogeneous time series can be constructed:

- ✓ general water quality (temperature, °C, salinity, PSU, dissolved oxygen concentration, mmol/kg, and saturation, %, pH and alkalinity, mmol/m^3);
- ✓ content of dissolved nutrients (silicates, phosphates, total phosphorus, nitrites, nitrates, ammonium and total nitrogen, mmol/m^3);
- ✓ content in water of technogenic pollutants (total petroleum hydrocarbons (TPHs), anionic detergents and total phenols, mg/m^3).

6) Results obtained by means the described technologies are illustrated on the Table below.

	Temper.	Salinity	Ox. cont	Ox. satu	pH	Alkalinit	Silicate	Phosph.	Tot.phos	Nitrite	Nitrate	Ammon.	Tot.nitr	TPHs	Deterg.	Phenols
Danube, Kiliya delta*							+	–	–			–	+	–	–	–
Chernomorsk harbor and seashore	+	–	–	–			–			–	–	–	–	–	–	–
Odessa harbor		–	+		+		–	–	–	–	–	–	–	–	–	–

Table: Trend analysis results for the NW Black Sea coastal zone regions.
+/- means the increasing/decreasing long-term trend significant on the 95 % level, detected by MK test with coefficients determined by PW regression.
* Average values for year without winter months (XII, I, II).

8) Conclusion. Only Chernomorsk's harbor and open sea has the clear climate change manifestation: water temperature increasing and decreasing of salinity and dissolved oxygen's content and saturation. No one coastal site does not characterized by acidification – there are not pH decreasing and the rise of alkalinity. For nutrient contents, significant long-term negative trends were revealed in Odessa and Chernomorsk regions (except phosphorus in Chernomorsk). In the Danube delta the long-term rise of silicate and total nitrogen contents were discovered while phosphorus species and ammonium concentrations decreased. Technogenic pollutants were steady decreased everywhere probably because of better waste water treatment and other marine environment protection measures implemented on both national and regional levels.

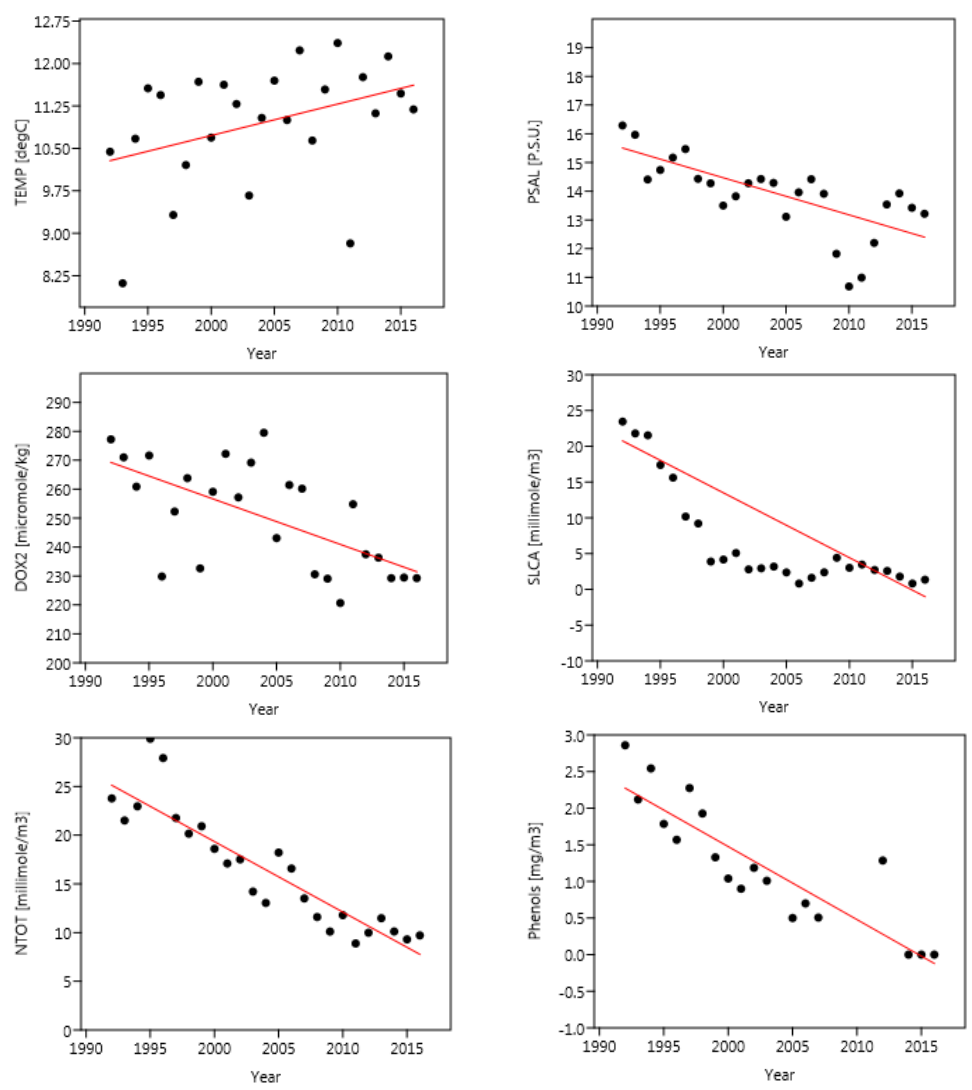
2) Data and methods. In the framework of the international project EMODnet Chemistry [1], the array of hydrological and chemical data obtained in 1992-2016 was created. Sampling and primary data processing were performed by marine units of the Ukrainian hydrometeorological network in the marine coastal regions. For each of the monitoring areas spreadsheets were created containing the meta-information and data on all physical and chemical parameters that were measured. Data quality control was performed and the metadata bases for the specified areas on the websites of SeaDataNet and EMODnet Chemistry projects were replenished. Data of these observations in the format of Ocean Data View [4] were uploaded on the server of Ukrainian Hydrometeorological Institute.

3) For the studies of long-term (decadal) variability, every observational site may be considered as the single point, while shallow coastal waters can be described by the averaging of measurements on surface, bottom and intermediate depths. So, the following algorithm of the time-series construction and analysis was adopted for each region.

- ✓ To identify all oceanographical stations where observations were executed during the entire 1992-2016 years period.
- ✓ To determine the mean annual values of all indicators for the water column together with other statistics (standard deviation, errors) by means the data averaging for all the selected stations and all sampling depths.
- ✓ To estimate the linear trends and their statistical significance for each water quality indicator time series.

5) Reliable estimates of the significant long-term tendencies of variability can only be obtained through statistical methods applied for time series, the main feature of which is usually serial correlation, i.e. each successive value of a series depends somewhat on previous values (this is especially true for the series of averaged values). This means that the residuals after extracting the difference between the initial and estimated values are not statistically independent and standard methods for trend assessing should not be applied without additional tests or correction procedures [5]. Moreover, indicators of chemical status and pollution only theoretically correspond to the normal (Gaussian) probability distribution, and in practice almost never. To avoid the serial correlation effect, Prais-Winsten (PW) regression method was applied to the trend parameters estimation while non-parametric Mann-Kendall (MK) test was used for the detection of significant trends [2]. Both procedures are implemented in a freely accessible statistical analysis software PAST [3].

7) Examples of significant trends (PW regression) for the region of Chernomorsk: left column, from up to bottom – temperature, oxygen content, total nitrogen; rigt column, from up to bottom – salinity, silicate, total phenols



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