LONG - TERM BIOLOGICAL CHANGES ALONG DANUBE AND DANUBE DELTA SYSTEMS AFTER INDUSTRIALIZATION PERIOD

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Abstract

Over the last 50 years humans have converted the export of fluvial materials which induced significant changes in biology, chemistry and morphology of the aquatic systems. The study presents the long-term changes induced on biotic communities alongside chemical parameters in Danube Delta systems after industrialization period in the context of compliance with Water Framework Directive requirements. The Danube basin has been subject to some important ecological changes, caused mainly by: hydrotechnical works, the built up of two large reservoirs (Iron Gates I and II) for hydrotechnical power plants, the conversion of floodplains into agricultural lands, opening the Danube-Black Sea canal which linked Cernavoda to Agigea, multiple uses of chemicals in agriculture which enrich the Danube waters fertilizers and pollutants, navigation development, uncontrolled tourism. The survey was done along Danube and Danube Delta (St. Gheorghe Branch) based on field experiments over 10-years (2003-2013), researches and national reports before and after industrialization period.

The main problems identified in the basin were: contamination with hazardous substances, contamination with substances that enhance the heterotrophic organism's growth, oxygen depletion, microbiological contamination, high nutrient loads and eutrophication. Those changes affected the biocenosis structure reflected by biodiversity reduction, the loss of the equilibrium between plankton species – benthos fauna, the algal blooms causing eutrophication, diatoms abundance, and loss of sensitive taxa, high number of endangered species and the decrease of biological productivity.

The results assessment will allow the present ecological status to be redefined.

Keywords: Danube, St. Gheorghe Branch, industrialization, biotic communities, ecological status.

INTRODUCTION

The development of human civilization is the most significant environmental event of the last 10.000 years (Zalasiewicz et al., 2010). Since the industrial revolution, by-products of industrial processes have been discharged increasingly into the environment. One area which suffered such exposure was the Danube River and Danube Delta (Keller and Cristofor, 1998). The Danube

River, draining ~ 30% of central and Eastern Europe, provides over 60% of the entire runoff reaching the Black Sea (Özsoy, 1997). Because fluvial nutrients feed the surface mixed layer that accounts for only 13 % of the entire basin volume, there is a strong coupling between Danube fluxes and the Black Sea biogeochemistry and ecology (Humborg et al., 1997; Kideys, 2002). After 1960`s, the Black Sea was transformed within a decade into the largest eutrophic water body in the world, by discharge of industrial, domestic and agricultural waste coming primarily from the Danube watershed (Kideys, 2002). Also, the construction of dams within the Danube watershed substantially reduced dissolved silicate loads to the Black Sea obstructing siliceous phytoplankton, like diatoms in favor of algal bloom. The breakdown of communist economies in Eastern Europe after 1990 led to a partial recovery of Black Sea ecosystems (Giosan et al., 2012).

The eutrophication period, characterized by drastic changes of the food web structure is explanatory of the sensitivity of the basin. Similary, it has been accepted that the Danube-Black Sea system was influenced by changes in pre-industrial land use that modulated material fluxes to the Black Sea (Degens et al, 1991). The industrialization, multiple uses of chemicals in agriculture and urbanization of the Danube River Basin determined an increase of water mineralization and alteration of the composition of the Danube water solvate salts. There is a significant increase in chlorides, phosphates and nitrates (Balaban, 2008). All those changes affected the biocenosis structure reflected by biodiversity reduction, the loss of the equilibrium between plankton species and benthos fauna.

Recently, broad-scale assessments at larger spatial scales have become more common and there has been a strong focus on assessing biotic endpoints to infer the ecological condition of rivers, based on the hypothesis that biological integrity will directly reflect physical and chemical integrity (Clapcott et. al, 2012).

The aim of this study was to investigate the long- term biological changes along Danube Delta systems after industrialization period.

MATERIALS AND METHODS

Study area

The Danube Delta is one of the most important wetland systems in Europe. During the last few decades, the driving forces has driven the evolution of the Danube Delta, especially St. Gheorghe Branch, to their present conditions. The St. Gheorghe Branch is the most southern branch carrying 23% of the Danube water discharge and 21% of the Danube sediment discharge (Jugaru et al, 2009). This highly sinuous branch was cut off in 1984-1988 by an artificial canal opened to shipping which caused significant changes of the river flow velocity in the natural channel (see the map of the Danube Delta in *Figure 1*). Samples were collected from 3 sampling sites situated along St. Gheorghe branch as follows: 2011-2009 (S1), 2013-2003 (S2, S3). Sampling stations were localized on Mahmudia meander taking into accont the point and non-point pollution sources. The sampling sites location was performed using GPS system map 60CSx - Garmin.

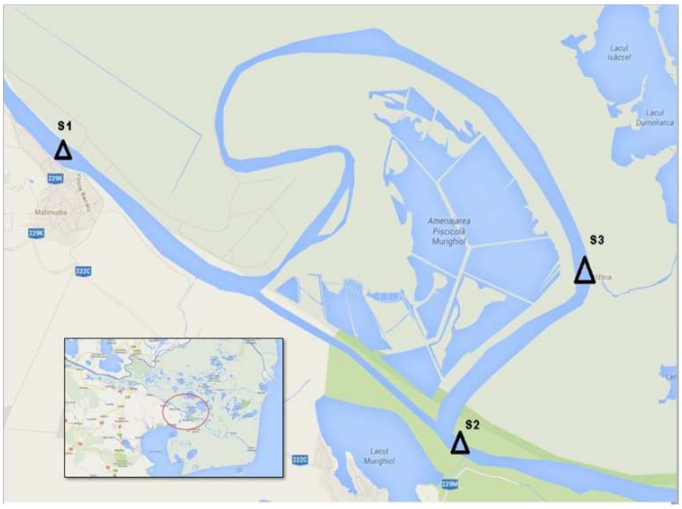

Fig.1. The Danube Delta map: sampling sites localization along St.Gheorghe Branch (*S1-Mahmudia, S2-Murighiol, S3-Uzlina*)

Sample collection

The samples were collected with a monthly frequency (from April 2003 to March 2013 in case of S2, S3 and August 2009 – March 2013 in case of S1) in order to determine the inherent variability of the monitored determinants and to obtain an adequate level of confidence and precision in the information.The sampling and preservation steps was done according with specific international standards (ISO 5667/ parts 1, 3, 6, 12; EN ISO 9391).

Water samples were collected and stored in adequate recipients. The sediment samples, both for physical-chemical analysis and biological were taken from the soft-bottom sediment using a Van Veen Sampler (Duncan & Associates, United Kingdom). All samples were kept in cooling boxes at 4^{o} C during transportation and the analyses were performed immediately after receiving the samples in the laboratory. For biological analysis, the samples were preserved with 4% formaldehyde solution.

Physical and chemical methods

The main chemical and physical elements determined in the water body were: thermal conditions, acidification status, oxygenation conditions, salinity, nutrient conditions, specific pollutants, pollution by all priority substances identified as being discharged into the water body, pollution by other substances identified as being discharged in significant quantities into the water body. Detailed data concerning analytical techniques, equipments used and physical chemicals detection were presented in Vosniakos et al., 2006, 2008, 2010, 2011, 2012.

Biological methods

The analysis of the biotic communities in the all sampling sites focused on the quantitative and qualitative components (dominant species, indicator species). The methods and equipments used for phytoplankton and macro invertebrates identification are described in Stoica et al., 2012, Stanescu et al., 2013.

Quality Assurance (QA) and Quality Control (QC) data

The samples were analyzed in NRDI ECOIND`s Pollution Control Departament which is accredited by RENAR (Association for Accreditation from Romania) and follows the requirements of ISO 17025/2005 standard. Also, the Department has certification with BVQI (Bureau Veritas Quality International) in accordance with ISO 9001 standard. For all the analyzed parameters, the laboratory uses standard methods (ISO, SR ISO, EN, SR EN, SR, STAS, EPA), reference materials and certified reference materials. All these standard methods were verified and the main performance parameters (limit of detection, limit of quantification, linearity, accuracy, precision, selectivity, the uncertainty of measurement) were established with the existing equipment from the laboratory.

Reference comparison values

The results were in accordance to the Water Law 107/1996 which transposed the Directive 2000/60/EC of the European Parliament and of the council establishing a framework for Community action in the field of water policy and to the Norm concerning the reference objectives for the surface water quality classification (Romanian Order MEWM no. 161/2006) in order to establish the ecological status of water bodies.

RESULTS AND DISCUSSION

The long-term changes induced on biotic communities alongside chemical parameters in Danube Delta systems was based on laboratory data, results of field experiments over ten-year period (2003-2013).

Surface water

The results of physical and chemical parameters determined in the studied area are presented in Table no.1.

Table 1. The main chemical quality indicators determined along Danube Delta in the monitored period

Quality parameters	S1 (Mahmudia) (2009-2013)				S2 (Murighiol) (2003-2013)				S3 (Uzlina) (2003-2013)			
	Min	*Max*	*Avg*	*SD*	*Min*	*Max*	*Avg*	*SD*	*Min*	*Max*	*Avg*	*SD*
Organic load												
COD (mgO2/l)	6.19	15	**10.5**	2.66	4.5	132	**31.7**	25.4	4	47.3	**15.2**	10.9
BOD (mgO2/l)	2.47	6.55	**3.62**	1.02	1.62	42.9	**11.05**	8.98	1.605	19	**5.78**	4.63
Salinity												
Conductivity (µS/cm)	359	559	**426**	62.9	268	679	**471.7**	99.2	265	536	**411**	52.2
Filtrable residue (mg/l)	177	259	**218**	23.6	184.8	416	**251**	58.7	175.3	278	**213**	21
Nutrients												
$N\text{-}NH_4$ (mgN/l)	0.06	0.79	**0.47**	0.24	<0.01	0.8	**0.38**	0.26	0.013	0.78	**0.34**	0.25
$N\text{-}NO_3$ (mgN/l)	0.12	2.93	**1.82**	0.97	0.48	3.38	**1.62**	0.83	0.68	3.92	**1.89**	0.83
$N\text{-}NO_2$ (mgN/l)	<0.006	0.31	**0.04**	0.08	<0.006	0.28	**0.03**	0.06	<0.006	0.03	**0.02**	0.01
N total (mgN/l)	2.14	7.07	**5.34**	2.14	1.085	16.7	**5.71**	3.6	1.91	7.07	**4.85**	1.97
$P\text{-}PO_4$ (mgP/l)	0.01	0.19	**0.11**	0.06	0.015	0.57	**0.13**	0.11	0.023	0.18	**0.11**	0.05
P total (mgP/l)	0.07	0.37	**0.21**	0.11	0.03	0.67	**0.24**	0.16	0.051	0.36	**0.19**	0.09
Toxic metals												
Ni (µg/l)	<1	24	**4.02**	5.79	<1	68.1	**12.4**	18.6	<1	10.3	**2.6**	2.85
Fe (mg/l)	<0.02	0.88	**0.3**	0.27	0.112	3.4	**0.71**	0.75	0.08	1.04	**0.35**	0.28
Mn (mg/l)	<0.002	0.03	**0.01**	0.01	0.003	0.29	**0.07**	0.08	0.005	0.05	**0.02**	0.01
Cd (µg/l)	0.4	0.4	**0.4**	0	<0.001	0.5	**0.36**	0.14	<0.001	0.5	**0.37**	0.13
Cr (µg/l)	<0.5	6	**2.09**	1.74	<0.5	21	**5.38**	6	<0.5	21	**3.52**	5.33
Cu (µg/l)	2.5	10.5	**5.74**	2.67	0.012	55.3	**12.9**	17.8	0.03	123	**14.5**	26.7
Pb (µg/l)	<2	3.2	**2.08**	0.31	<2	5	**2.15**	1.29	<2	5	**2.17**	1.27
As (µg/l)	<2	2.2	**2.01**	0.05	<2	3.9	**1.82**	0.88	<2	2.64	**1.73**	0.59
Hg (µg/l)	<0.1	0.24	**0.32**	0.061	<0.1	0. 77	**0.15**	0.2	<0.1	0.14	**0.22**	0.1
Zn (µg/l)	<2	24.7	**10.1**	7.07	<2	56	**9.58**	11.4	<2	57	**8.15**	11.7
Co(µg/l)	<0.5	1.3	**0.66**	0.33	<0.5	5	**1.17**	1.65	<0.5	5	**1.18**	1.65
Hazardous pollutants												
Petroleum products (µg/l)	<50	576	**164**	140	<50	457	**146.4**	131	<50	383	**105**	93.4
PCB (µg/l)	<0.01	0.01	**0.01**	0	<0.005	0.25	**0.020**	0.06	<0.005	0.03	**0.01**	0.004
Organochlorine pesticides (µg/l)	<0.01	0.06	**0.01**	0.02	<0.005	0.1	**0.011**	0.02	<0.005	0.03	**0.01**	0.01
γ – HCH (Lindane)µg/l	<0.01	0.01	**0.01**	0.003	<0.005	0.02	**0.005**	0.003	<0.005	0.03	**0.01**	0.01

The pH regime ranged between 6.69 to 8.38 pH units, without significant changes. The oxygen indicators (dissolved oxygen, COD and BOD) showed moderate organic load, which classified the water body in III[rd] quality class. The dissolved oxygen concentrations varied seasonal. The lowest values were registered in summer (2.45 to 4.21 mgO_2/L) and the highest ones in winter (9.22 to 12.26 mgO_2/L) (Figure 2). The means value of nutrients ($N\text{-}NH_4$, $N\text{-}NO_3$, $N\text{-}NO_2$, total N, $P\text{-}PO_4$, total P) and chlorophyll ”a” in the last ten-years indicated good ecological status. In 2003-2009 were recorded high nutrients concentration as a result of fertilizes inputs (total nitrogen: 1.08 to 7.72 mg/L and total phosphorus: 0.03 to 0.48 mg/L) (Figure 3). Although, there were no differences between sampling sites.

Chlorophyll *a* was related to seasonal variation of the Danube’s flow over the whole study period (2012-2013). There was found a correlation between Chlorophyll *a* and the total inorganic nitrogen and no significant correlation between chlorophyll and phosphate, probably as a result of P consumption in the growth of diatoms, which prevail over the populations in the Danube Delta phytoplankton community (Stoica et al., in press).

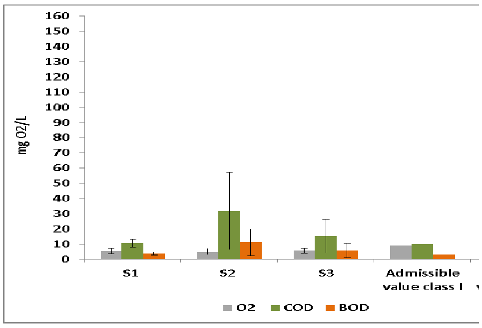

Fig. 2. Oxygen regime of water samples in 2003-2013 *(expressed as means values)*

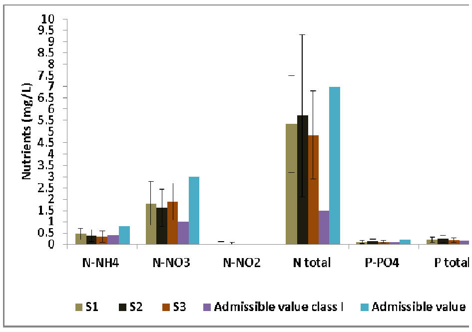

Fig.3. Nutrients in water samples in 2003-2013 *(expressed as means values)*

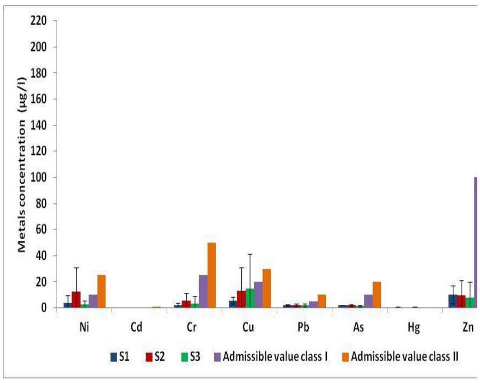

Fig. 4. Toxic metals in water samples in 2003-2013 *(expressed as means values)*

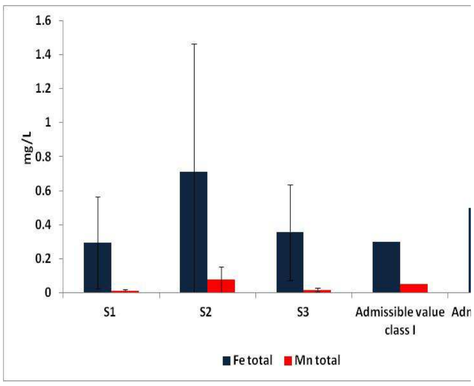

Fig. 5. Total Fe and Mn in water samples in 2003-2013 *(expressed as means values)*

The metals concentration in Danube Delta water was within the admissible value for I[st] class, except Hg at S1 (Mahmudia) which is in limit of II[nd] class in 2012 (Figure 4). The concentration of petroleum products, γ – HCH, organochlorine pesticides and PCB was also within standard quality admissible values. This may be due to the dispersion of pollutants in a short time and water self-purification capacity.

Due to heavy rains in 2005 which probably had led to alluvia with high iron content and due to anthropogenic activities (shipping and tourist activities) carried out in downstream Mahmudia, there is was an overcoming of the maximum permissible concentration (Figure 5) at S2 sampling site. It is estimated that the Tulcea county contribute less to the Danube Delta pollution, because large polluting industrial activities were closed or operating at low capacity.

In terms of phytoplankton, in all sampling sites was recorded the presence of oligo-betamezosaprobe diatoms species (*Navicula gracilis* (o-β), *Asterionella formosa* (o-β), *Cymbella ventricosa* (o-β), *Diatoma elongatum* (o-β)), betamesosaprobe species (*Amphipleura pellucida* (β), *Synedra acus* (β), *Nitzchia sigmoidea* (β) or Chlorophyta betamezosaprobe species (*Pediastrum boryanum* (β), *Scenedesmus acuminatus* (β)).

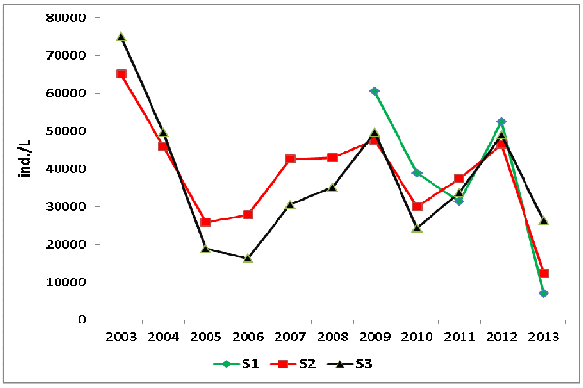

Fig. 6. Phytoplankton numerical density in 2003-2013 *(expressed as means values)*

Due to short life-cycles, phytoplankton organisms respond quickly to changes in the aquatic environment. In Figure 6, it is observed the variation of algae over ten-year period. The highest numerical density value of phytoplankton was recorded in 2003 at S3 (Uzlina) (75142 ind. /L) while still persisted the effect of eutrophication. In 2005, 2006 and 2010 due to strong floods the phytoplankton community was affected. However, the siliceous phytoplankton like diatoms dominated the entire community. The phytoplankton numerical density and biomass had an increasing trend observed in the summer of 2008, 2009 and 2012 in all sampling sites due to immobilization of nutrients and high temperature values associates with droughts.

Sediment

From all metals studied Cu and Ni represent a particular concern because of their significant total concentration levels found in the sediments.

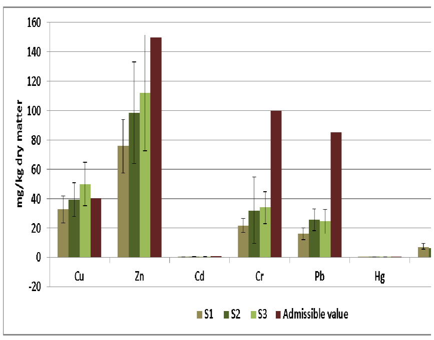

Fig.7. Metals in sediments (2003-2013) *(expressed as means values)*

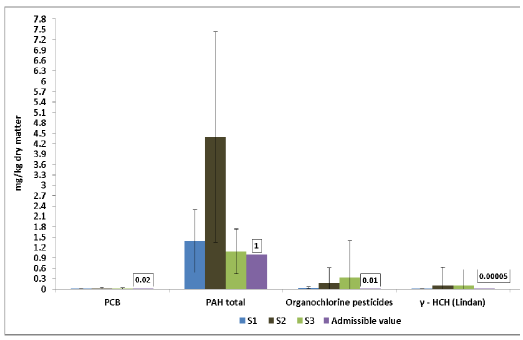

Fig. 8. Hazardous compounds in sediments (2003-2013) *(expressed as means values)*

Cd, Cr, Pb, Hg, As concentrations in sediment were within the standard quality admissible value, but often higher than in water samples due to their bioaccumulation capacity (Figure 7). The values ranged for Cd between 0.34 to 1.05 mg/kg d.m., for Cr between 7.5 to 127.3 mg/kg d.m., for Pb between 6.15 to 46 mg/kg d.m., for Hg between 0.1 to 1.11 mg/kg d.m., for Zn between 33.3 to 211 mg/kg d.m. and for As between 0.1 to 15.5 mg/kg d.m. The highest metals concentration was recorded predominantly at S3 (Uzlina). The Cu and Ni values were above admissible value. It supposes that is a historical pollution due to industrial discharges after 1970 coming from metallurgy, especially. Our results are in accordance with the metals values reported in other studies (Sakan et al., 2010, Esen et al., 2010, Xing and Liu, 2011). The total concentration of PCB`s was within the admissible value of standard quality.

In terms of hazardous compounds, a major ecological problem was the detection during all sampling periods of high PAH and organochlorine pesticides, especially γ-HCH and DDT/DDE/DDD. The PAH levels varied between 0.14-3.18 mg/kg d.m. in S1 (Mahmudia), 0.63-12.7 mg/kg d.m. in S2 (Murighiol) and 0.07-2.26 mg/kg d.m. in S3 (Uzlina). The total organochlorine pesticides and PCB were within the standard quality limit. In all monitored period, the γ-HCH exceeded the standard quality limit. The World Health Organization classified the γ-HCH as moderately hazardous.

The γ-HCH was used as insecticide, and after 2009 the production and agricultural use of γ-HCH was banned under the Stockholm Convention. This persistent organic pollutant recorded 0.11 mg/kg d.m. at S2 (Murighiol) and 0.09 mg/kg d.m. at S3 (Uzlina) during 2003-2013.

The DDT/DDE/DDD also used as organochlorine insecticide in agriculture, was detected in all sampling sites above de standard quality limit. After 2004 was outlawed by the Stockholm Convention. The presence of those persistent substances indicates historical sediment pollution with consequences on macro invertebrates' organisms.

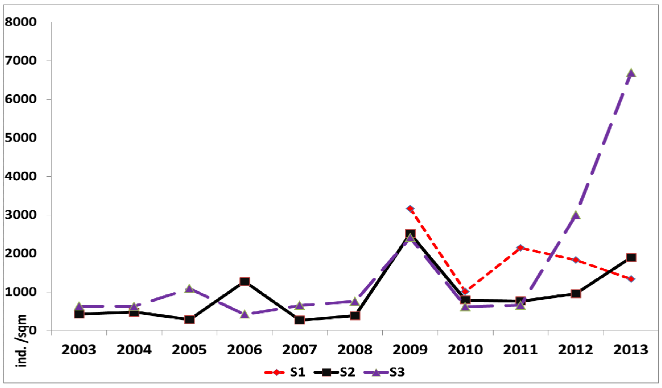

Fig. 9. Macro invertebrates numerical density in 2003-2013 *(expressed as means values)*

The macro invertebrates' analysis in the Danube Delta systems has aimed the quantitative component and qualitative determination. At temporal and spatial scale, the benthic fauna presented high distribution.

The spatial and temporal distribution of benthic macro invertebrates along Danube Delta aquatic systems during 2003-2013 is described in Table no.2.

For the entire study period, benthic macro invertebrates communities were better represented in S2 (Murighiol) and S3 (Uzlina) than in S1 (Mahmudia).

Gasteropods, Bivalves and Oligochaeta were predominant in all sampling sites.

The floods and changes in flow regime had also impact on the bed and bank structures, so the benthic macro invertebrates' diversity was reduced and loss of sensitive taxa.

The decomposition processes have replaced sensitive species with tolerant (Oligochaeta and Chironomidae), often foreign species (*Dreissena polymorpha*). Throughout the spatial and temporal variation of numerical density and biomass, changes in community composition were observed.

The maximum value of numerical density was recorded in 2013 at S3 (Uzlina) 6692.7 ind./sqm as represented in Figure 9. Oligochaeta species which are tolerant at persistent pollutants were present in increasing number in most locations. Compared with the last ten years, when the benthic fauna diversity was constant, nowadays it reveals a slight recovery.

Table 2. The main macro invertebrates organisms identified in Danube Delta sampling sites during 2003-2013

NO. CRT.	FAMILY	SPECIES
Oligochaeta		
1.	Tubificidae	*Tubifex tubifex*
2.		*Limnodrilus hoffmeisteri*
Hirudinoidea		
3.	Glossiphoniidae	*Helobdella stagnalis*
Gastropoda		
4.	Neritidae	*Theodoxus danubialis*
5.	Lymnaeidae	*Galba truncatula*
6.	Planorbidae	*Planorbis planorbis*
7.	Hydobiidae	*Lithoglyphus naticoides*
Bivalvia		
8.	Sphaeriidae	*Sphaerium corneum*
9.	Unionidae	*Unio pictorum*
10.		*Anodonta cygnea*
11.	Dreissenidae	*Dreissena polymorpha*
12.		*Cardium sp.*
13.		*Abra alba*
14.		*Mya arenaria*
Decapoda		
15.	Astacidae	*Astacus astacus*
Isopoda		
16.	Asellidae	*Asellus aquaticus*
Amphipoda		
17.		*Gammarus pulex*
Insecta – Diptera		
18.	Chironomidae	*Chironomus plumosus*
19.	Psychodidae	*Psycoda sp.*
20.	**Nematoda**	

CONCLUSIONS

The long- term biological changes along Danube and Danube Delta systems after industrialization period represented the research subject in this paper. The obtained results over ten-years Danube Delta monitoring indicated that the main driving forces (e.g. industrialization and urban development, extension and intensification of shipping, climate change, increasing agriculture production) had altered the phytoplankton and macro invertebrates' structure and composition. In 1981-1982 under the influence of the hydrological regime the modulatory effects exerted on the Danube brought changes in nutrient reserve. In the studied aquatic system, the uncontrolled domestic and industrial discharges, effluents loading, sequence of dry periods with heavy rainfall had led to significant levels of nutrients, organochlorine pesticides (DDD / DDT / DDE, γ – HCH), toxic metals and organic load which do not be neglected. The decomposition processes decreased dissolved oxygen and have replaced sensitive species with tolerant, often foreign species. The quality parameters (abiotic and biotic) presented both seasonal and annual variation during 2003-2013, but further studies will be needed to confirm and refine our results Nevertheless, according with WFD requirements, the achievement of "good ecological status" till 2015, in case of Danube Delta water body it is almost accomplished.

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