# ФІЗИЧНА ГЕОГРАФІЯ

UDC 551.49

DOI: 10.18524/2303-9914.2020.1(36).205158

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# EUTROPHICATION AND POLLUTION DEVELOPMENT IN THE DANUBE RIVER AND COASTAL MARINE ZONE SYSTEM

Since the 1970s, the process of anthropogenic water euthrophication and the near bottom hypoxia linked with it, have caused widespread benthos fauna mortality. In addition to this negative phenomenon a lot of contaminations and pollutants are washed out from the fields and the coastal urban agglomerations by the river flow. In the process of sedimentation, the suspended matter is accumulated in the bottom sediments. It reinforces negative changes in benthic habitat conditions. One of the main modern problem is eutrophication and pollution (waste) in rivers, lakes and coastal marine systems. It illustrates the development of eutrophication and waste in a large, deep lake, together with the impacts on the lake and marine ecosystems. The Object of investigation is the Danube mouth area. The Subject of investigation is euthrophication processes and pollution input development in aquatic system. The Danube river extends almost all over Central Europe, which means that any waste from factories located directly near the Danube will inevitably get there. Therefore, the phenomenon of "water bloom" and periodic environmental disasters on the Danube are natural consequences of human activities. The level of pollution of the bottom sediments in the Northwest shelf of the Black Sea is examined. Modern data are compared with those of the late 20th century and their variability over 20 years. Substantial increase (by two orders) of copper, lead and nickel concentration has been marked. The diverse of contamination sources in larger catchment areas usually produce a mixture of pollutants, which is more difficult to treat than an industrial waste. For most sediments, there are more arguments in favor of disposal rather than treatment. Mechanical separation of the less contaminated fractions could be a useful step prior to the final storage of the residues. To improve the status of surface water bodies in the management area, it is necessary to take into account and reduce all existing factors and risks of deterioration of water quality. Environmental issues and the science behind them are of great public concern. Water management issues are also of critical importance. Human impacts within the river – delta –sea system are environmental contamination with nutrients, heavy metals, organic compounds, etc., degrading water and sediment

quality and leading to toxic impacts in biota, airborne pollution. Human impacts from outside of the wetland are lack of catchment scale management of land use upstream, leading to soil erosion and sedimentation.

**Keywords**: The Danube river, the Black sea coastal zone, euthrophication, pollution.

#### INTRODUCTION

The explosive growth of the human population during the past 50 years, added with the ever -increasing water demand per capita has resulted in a dramatic increase of human pressures on natural water supplies. These fast growing pressures led to general mismanagement of water resources, affecting all links of the water abstraction-distribution-use-collection-treatment-discharge management chain (even though in most cases worldwide this theoretical chain is never complete). Therefore, nowadays, water has become a very scarce natural resource as a result of human activities. Moreover, once impacted by human activities, the ability of water resources to recovery from pollution varies from days to years in rivers and lakes, and to centuries in groundwater. Water is a scarce natural resource, the quality of which must be protected, defended and managed. Water when impacted by human activities must be treated to ensure and protect the most sensitive uses of the water. Water is a renewable resource with a limited capacity to recover from the adverse impacts of human activities. Large scale water related science has a direct impact on the lives and livelihoods of people. They must be made aware of the ongoing results of such studies and ideally be directly involved as active participants.

In today's world, generation, storage, treatment, transport, recovery, transboundary movement, and disposal of wastes pose formidable problems for society and represent a serious threat for human health and the environment. Great concern exists for the future if this issue is not properly addressed [1].

Since the 1970s, the process of anthropogenic water euthrophication and the near bottom hypoxia linked with it, have caused widespread benthos fauna mortality. A lot of scientific publications were dedicated to the process of the anthropogenic euthrophication of the Black Sea shelf and its consequences [2–4].

In addition to this negative phenomenon a lot of contaminations and pollutants are washed out from the fields and the coastal urban agglomerations by the river flow. In the process of sedimentation the suspended matter is accumulated in the bottom sediments. It reinforces negative changes in benthic habitat conditions.

The main causes and effects of river – delta – sea system's degradation must be describe and analyze. Also must be describe the major aspects of climate change and their potential impacts on river – delta – sea system. And at least to describe and select appropriate methods for restoration or conservation. Set management (restoration/conservation) objectives, design the related monitoring programme and select appropriate measures in relation to various risk scenarios.

One of the main modern problem is eutrophication and pollution (waste) in riv-

ers, lakes and coastal marine systems. It illustrates the development of eutrophication and waste in a large, deep lake, together with the impacts on the lake and marine ecosystems. The purpose of the work is to assess current changes in the Danube mouth system under the influence of anthropogenic and natural factors.

*The object* is the Danube river mouth area. *The subject* of investigation is eutrophication processes and pollution input development in aquatic system.

### **DATA & METHODS**

In the Danube River Basin Management Plan which is the document developed and approved by 15 countries in the Danube Region in 2009 was marked that 6224 settlements are located in the river basin of which 2900 settlements have no sewage system and thousands of settlements have wastewater treatment plants that need reconstruction [5].

Samples were collected at various sites in the Kilia arm in summer time of the different years during 20 years long (from 1998 up to present) the (Fig. 1) and analyzed for selected trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn). All expeditions were done under the author management.

In marine part of investigations the average value of the studied parameters were processed by linear interpolation and given to the centers of squares, ranked by hydrological features.

According to estimates of the International Commission for the Protection of the Danube, the total amount of pollutants entering to the Danube from settlements is 1.5 million tons per year.

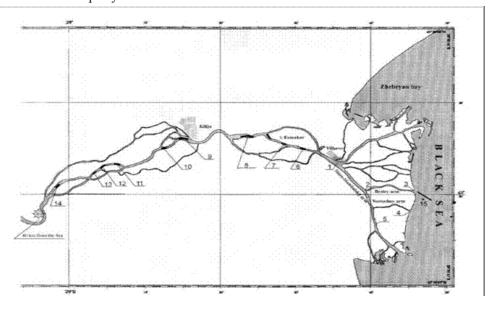


Fig. 1. Overview of the Ukrainian part of the Danube Delta (Kilia arm and secondary Staro-Stambulsky delta) and location of the sampling sites

From industrial sources of pollution entering to the river consists of 134 thousand tons including organic substances, mainly with wastewater from the chemical, paper and food industries. These materials were used in the paper. The statistical and illustrated analyses were done.

### **RESULTS**

Sources of nutrients. Many sources contribute to sediment contamination in a river catchment area: wet and dry fallout from air emissions, agricultural runoff from farms, solid and dissolved inputs from mines, discharges from landfills, industrial plants and sewage treatment plants and direct dumps into rivers, lakes and coastal seas. At present, it is hard to define the natural and anthropogenic sources of nutrients, because even natural sources of nutrients (river runoff, atmospheric deposition, bottom sediments) are influenced by anthropogenic activities. These sources can, however, be divided into point and non-point sources. Point sources (municipal and industrial wastewater discharges) are discharges of contaminants that come from a stationary or fixed facility, for example, from a pipe, ditch or drain. Point sources are regulated by laws that place limits on the types and amounts of contaminants released to water. Non-point source discharges are river runoff, atmospheric deposition, storm water runoff, groundwater and bottom sediments.

The Danube with its average runoff of 204 km<sup>3</sup> per year is the main source of nutrients into the Black Sea. During the last 50 years nutrients in river runoff have changed significantly. Nutrient values in the Danube delta runoff for the period 1948-2000 can be defined in the following periods:

Period I (1948–1960) – before regulated stream and eutrophication processes, Period II (1977–1985) – start of eutrophication processes, and Period III (1986–2000) – development of eutrophication processes. The Danube is the second major European river with a huge estuary located in two countries: Ukraine and Romania. The Danube watershed embraces 15 European highly industrialized countries that form a high level of anthropogenic press. During the last thirty years they influence the river, estuary and Black Sea. At present the Danube runoff is total regulated by dams. This factor changed the hydrological regime. Another factor that changed the hydrochemical regime is overcoming of nutrient first of all nitrogen and phosphorus. This reflected the environment of the river, estuary and Northwestern shelf of the Black Sea. Eutrophication, "water blooming" and near bottom hypoxia as a result of this process is development in the Northwestern part of the Black Sea. In estuary water quality and bottom sediments deteriorated, the fish catch and biodiversity decreased. At present new source of eutrophication is bottom sediment in the shore zone of the

Anthropogenic component in the nutrient's river runoff. Compounds of N and P are recognized as a main stimulator of the eutrophication process. It is a well known fact that their content in the basin increases as the cause of entering of the industrial, communal and agricultural discharge, since nitrogen and phosphorus are present in

composition of all types of discharges. It is impossible to divide these compounds into natural (entering water as the result of mechanical or chemical erosion, etc.) and anthropogenic by the existing analytical methods. Anthropogenic genesis nitrogen and phosphorus are involved into the natural cycles and later; it is impossible to define the origin of nitrogen and phosphorus [6]. Transformation of the riverine water starts in delta because the current velocity falls down in the branches. As a result of adsorption particles together with sorbed dissolved matter fall down fast. This matter can be in the compounds of as phosphorus (up to 50% from the total) and silicon (up to 30%) as well [7]. So, in the delta fresh water becomes cleaner and the delivering process from some chemical compounds takes place.

The dynamics of pollutants and eutrophication levels in the Danube River and local reservoirs. The Danube river extends almost all over Central Europe, which means that any waste from factories located directly near the Danube will inevitably get there. Therefore, the phenomenon of "water bloom" and periodic environmental disasters on the Danube are natural consequences of human activities.

As a basis have taken water bodies of lakes: Yalpug, Kugurlui, Kagul, Katlabukh, Kitai and of course the Danube River, which connects all these lakes with each other. The main problem of these water bodies is increased nutrient's concentrations (nitrogen and phosphorus compounds). These issues are critical for the Danube River itself and for all water bodies in the basin as well.

The total annual load near the Reni (Ukraine) was 453 thousand tones of total nitrogen, 14.3 thousand tones of total phosphorus. It is necessary to take into account that excessive the river water eutrophication begins under a content of nitrogen with the concentration of 0.2–03 mg/dm³, phosphorus – 0.01–0.02 mg/dm³. The average content of nitrogen in the Danube water in the Ukrainian part is 1.55 mg/dm³, phosphorus – 0.08 mg/dm³ was established (Fig. 2–5). The major cause of surface



Fig. 2. Ammonia nitrogen, (mg/dm3), the Danube, Reni

water contamination by nitrogen and phosphorus compounds is the insufficient level of wastewater treatment coming from municipal, industrial and agricultural point sources and surface runoff as well as organic pollution.

In conditions of non-flowing shallow Danube lakes and water warming the high concentrations of nutrient are the cause of intensive development of algae and higher forms of plant life (self-pollution of waters by organic substances) and provide the disturbance of the organisms existing in water, deterioration of water bodies, their siltation and natural aging. According to the level of pollution of water bodies: Katlabukh, Yalpug, Kugurlui and Kagul lakes are "moderately polluted", and Kitai lake belongs to the category "dirty". The main problem of these water bodies is excessive contamination with organic substances (exceeding water quality standards from 6 to 9 times), high level of water mineralization (exceeding the allowable value up to 6 times).



Fig. 3. Nitrate nitrogen, (mg/dm3), the Danube, Reni

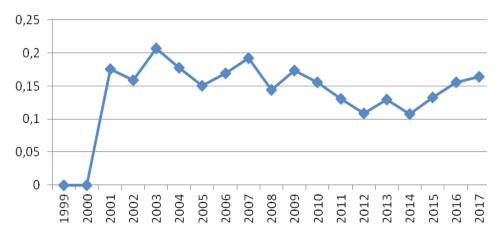


Fig. 4. Phosphates, (mg/dm3), the Danube, Reni

The main form of nitrogen in the Danube mouth coastal zone in a period eutrophication development is organic nitrogen. The mineral forms are 70-90 % from total except of flooding period – it is about 50 %. On the surface variability of concentration is very wide 0,020-15.946 mg L<sup>-1</sup>. Maximum was extremely high for the marine water. It was marked in a period of water blooming especially on the surface [3].

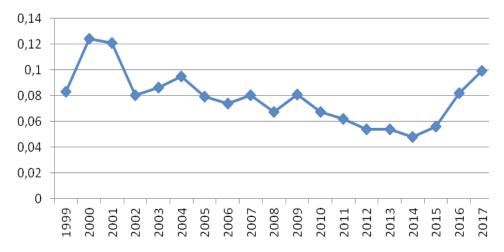


Fig. 5. Total phosphates, (mg/dm3), the Danube, Reni

Large scale measures to reduce phosphorus inputs from both point sources (wastewater) and diffuse sources (agriculture) have been effective, with the mean concentration in the lake being reduced.

In the upper and middle course of river systems, sediments are predominantly affected by contamination sources like wastewater, mine water from flooded mines and atmospheric deposition. Measures applied to the source of contamination are particularly important and may include improvement of traditional wastewater purification, but also approaches to the *in-situ* treatment of highly contaminated effluents such as introducing active barriers (fly ash, red mud, tree bark, etc.) to prevent heavy metal dispersion during flooding.

During floods, sediment-bound pollutants can undergo large-scale dispersion in floodplains, dike foreshores and polder areas. The complex mixtures of toxic compounds and the scale of the pollution often preclude technical measures like chemical extraction or solidification of contaminated soil and sediment material. Instead, alternative measures have to be taken that consider different local factors such as soil, sediment and water quality, flow velocity, and the dynamics of the water level. The measures implemented should be flexible and easy to adjust to changing conditions. Any problem solution strategy for such sites, therefore, has to consider both the chemical stabilization, e.g. by processes of (enhanced) natural attenuation, and an increase of mechanical stability (reduced erodibility).

The river influences to the shallow water area. In some years the influence of the Danube can occupy 70 per cent of the Northwestern shelf of the Black Sea; in other years it is only 20-30 per cent. The total area of the Black Sea influenced by the Danube, according to the area of freshwater phytoplankton species recorded, is not less than 10<sup>5</sup> km<sup>2</sup>. Variability in the hydrochemistry depends mainly on river runoff, precipitation, seasonal temperature distribution, hydrobiological activity, especially phytoplankton, and anthropogenic factors such as pollution from industry and agriculture. Natural cycling of river runoff and regulated flow in the rivers is also very important. Intensive economic development and exhaustive environmental management has led to considerable ecological pressure on the Black Sea ecosystem. Development of the eutrophication process in the Black Sea occurred as a result of increasing amounts of nutrients in the river runoff associated with nutrient-enriched water coming from fertilized fields. When eutrophication due to river runoff was most intensive (1986-2000). The Northwestern shelf of the Black Sea is now showing a strong imbalance in the carbon cycle. Recent eutrophication is characterized by decreasing nutrients but increasing organic compounds in river runoff and in marine water, because of regulation of all the rivers entering the Northwestern shelf of the Black Sea and reduced use of mineral fertilizers in agriculture. In the summer, mineralization of organic compounds is rapid producing nutrients that provoke phytoplankton development, i.e. eutrophication.

Pollution in the river branches and shallow water system.

Trace elements and, where available, oil levels are roughly comparable among sediments from the three main branches of the Danube. As to chemical contamination, arsenic and mercury seem to be particularly problematic elements and deserve special attention in future investigations along with oil pollution and other ecotoxicologically important (but still overlooked) elements such as Ag, Sb and Se. At the opposite, Cr and Ni appear to have a natural origin in the delta and contribute little to the toxic potential of sediments in the Danube delta. Trace element concentration in Ukrainian branches (expressed as mean  $\pm$  1 standard deviation for all sampling points and sampling periods are  $0.382 \pm 0.203$  for Cd,  $34 \pm 16$  for Cu,  $26 \pm 8.3$  for Pb and  $105 \pm 37$  for Zn (all figures in mg kg<sup>-1</sup>) [8].

In the shallow water of the Danube estuary the comparison of Ukrainian's and Romanian's average pollutants concentration in the bottom sediments has been made.

The level of pollution of the bottom sediments in the Northwest shelf of the Black Sea is examined. Modern data are compared with those of the late 20th century and their variability over 30 years. Substantial increase (by two orders) of copper, lead and nickel concentration has been marked.

It is possible to mark, that in the Danube estuary the temporal dynamics of oil concentration in the bottom sediments reflects the technogenic press during the long period (30 years).

Mercury concentration both in Ukrainian and Romanian parts of the Danube region exceeds the natural geochemical condition for the open sea in 2 and 7 times, re-

spectively. The concentrations of arsenic, phenols, chromium and cobalt are roughly the same in the Romanian and the Ukrainian parts of the Danube. The results of the research can be indicators of anthropogenic impact [9].

### **CONCLUSIONS**

The diverse of contamination sources in larger catchment areas usually produce a mixture of pollutants, which is more difficult to treat than an industrial waste. For most sediments, there are more arguments in favor of disposal rather than treatment. Mechanical separation of the less contaminated fractions could be a useful step prior to the final storage of the residues. To improve the status of surface water bodies in the management area, it is necessary to take into account and reduce all existing factors and risks of deterioration of water quality. During the last 20 years period substantial increase (by two orders) of copper, lead and nickel concentration has been marked.

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Environmental issues and the science behind them are of great public concern. Water management issues are also of critical importance.

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Надійшла 16. 04. 2020

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# РОЗВИТОК ЕВТРОФІКАЦІЇ І НАКОПИЧЕННЯ ЗАБРУДНЕНЬ У РІЧЦІ ДУНАЙ І ПРИБЕРЕЖНІЙ МОРСЬКІЙ ЗОНІ

#### Резюме

Починаючи з 1970-х років процес антропогенної евтрофікації води та пов'язана з нею гіпоксія на дні, спричинили широку смертність бентосних організмів. Окрім цього негативного явища, велика кількість забруднень та забруднювачів вимивається з полів та прибережних міських агломерацій річковим потоком. У процесі осадження зважена речовина накопичується в донних відкладах. Це підсилює негативні зміни умов донного середовища. Однією з головних сучасних проблем  $\epsilon$  евтрофікація та забруднення (відходи) у річках, озерах та прибережних морських системах. Це ілюструє розвиток евтрофікації та накопичення відходів у великих глибоких озерах разом з впливом на озерні та морські екосистеми. Метою роботи є оцінка сучасних змін якості умов гирлової області Дунаю під впливом антропогенних і природних факторів. Об'єктом дослідження є гирлова область річки Дунай. Предметом дослідження є процеси евтрофікації та збільшення відходів, що потрапляють у водну систему. Річка Дунай простягається майже по всій Центральній Європі, а це означає, що будь-які відходи з заводів, розташованих безпосередньо біля Дунаю, неминуче потраплять туди. Тому явище «водного цвітіння» та періодичні екологічні катастрофи на Дунаї є природними наслідками людської діяльності. В статті досліджено рівень забруднення донних відкладів у північно-західному шельфі Чорного моря. Сучасні дані порівнюються з даними кінця 20 століття та їх мінливістю протягом 20 років. Помічено значне збільшення (на два порядки) концентрації міді, свинцю та нікелю. Різноманітні джерела забруднення у більших районах водозбору зазвичай утворюють суміш забруднюючих речовин, обробляти яку складніше, ніж промислові відходи. Для поліпшення стану поверхневих вод у зоні управління необхідно враховувати та зменшувати всі існуючі фактори та ризики погіршення якості воли.

**Ключові слова**: річка Дунай, прибережна зона Чорного моря, евтрофікація, забруднення.

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# РАЗВИТИЕ ЭВРОФИКАЦИИ И НАКОПЛЕНИЕ ЗАГРЯЗНЕНИЙ В РЕКЕ ДУНАЙ И ПРИБРЕЖНОЙ МОРСКОЙ ЗОНЕ

#### Резюме

Начиная с 1970-х годов процесс антропогенной эвтрофикации и связанной с ней придонной гипоксией, вызвали высокую смертность бентосных организмов. Кроме этого негативного явления, большое количество загрязняющих веществ смывалось с полей и прибрежных городских агломераций речным стоком. В процессе осаждения взвешенное вещество накапливается в донных отложениях, что усиливает негативные условия обитания на донных биотопах. Одной из главных современных проблем является эвтрофикация и загрязнение (отходы) в реках, озерах и прибрежных морских системах. Целью исследования является оценка современных изменений качества условий устьевой области Дуная под влиянием антропогенных и природных факторов. Река Дунай простирается почти по всей Центральной Европе, следовательно, любые отходы с предприятий, расположенных непосредственно у Дуная, неизбежно попадут туда. Поэтому явление «цветения воды» и периодические экологические катастрофы на Дунае являются естественными последствиями человеческой деятельности. В статье исследован уровень загрязнения донных отложений в северо-западном шельфе Черного моря. Современные данные сравниваются с данными конца 20 века и их изменчивостью в течение 20 лет. Отмечено значительное увеличение (на два порядка) концентрации меди, свинца и никеля. Различные источники загрязнения в больших районах водосбора обычно образуют смесь загрязняющих веществ, обрабатывать которую сложнее, чем промышленные отходы. Для большинства донных осадков предпочтительнее их утилизация, а не восстановление первичных свойств. Механическое отделение менее загрязненных фракций может быть полезным этапом к окончательному хранению. Для улучшения состояния поверхностных вод в зоне менеджмента необходимо учитывать и уменьшать все существующие факторы и риски ухудшения качества воды.

**Ключевые слова**: река Дунай, прибрежная зона Черного моря, эвтрофикация, загрязнение.